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ALUMINA CERAMICS

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THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared under USAF Contract No. AF 33 (657)-8741, Request No. ML-82. The work was administered under the direction of the Ceramics and Graphite Information Center, Materials Information Branch, Materials Applications Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio, 45433, with Mr. Barry R. Emrich serving as project engineer. The manuscript was edited and reviewed by Mr. W. B. Campbell, Department of Ceramic Engineering, The Ohio State University, Columbus, Ohio.

This report covers work conducted from August, 1964 to July, 1965. The manuscript was released by the author in September, 1965, for publication as a technical report.

This technical report has been reviewed and approved.

D. A. SHINN
Chief, Materials Information Branch
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ABSTRACT

This comprehensive survey has been compiled to provide a sourcebook for aluminum oxide ceramic technology. The features and characteristics of high-temperature, transition and hydrated aluminas are presented in detail and are adequate for both engineering and scientific reference. Subjects discussed include nomenclature, natural occurrence and associations, beneficiation and preparation techniques, crystallographic features and mineral-ogical properties. Mechanical, thermal, sonic, electrical, magnetic, optical, radiation (nuclear), chemical, and colloidal properties are critically reviewed. The aspects of grinding, forming and sintering pertinent to production of refractories, and applications including uses in cement, glass, cermets, electrical insulation, thermal coatings and airborne equipment are given. An extensive bibliography is provided.

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1 INTRODUCTION

The investigation of alumina as a ceramic material was undertaken to provide information under the following specifications, "This review shall deal with alumina both from a theoretical and practical point of view, and shall include information on the nomenclature, properties, and applications of alumina. Specifically, this review shall discuss, but not be limited to, the three major classifications: the high-temperature forms that are produced in general by calcination, the transition forms, and the hydrates. The following information shall be gathered for each form; occurrence in nature, methods of beneficiation or preparation, crystal structure, and optical, thermal, electrical, chemical, mechanical, and surface properties. Phase transformations shall be discussed, and a comprehensive review of ceramics made essentially from aluminas shall be provided. An extensive bibliography shall also be included. It is important that the information compiled be presented in a format which makes the data readily available to the user, showing relationships between properties and applications. The work will be unclassified."

Data on alumina in some or all of these categories have been collected within recent years. Among these, Oxide Ceramics (1960) by Ryshkewitch* provides a good account of the early work on sintered alumina, in large part representing his own research. Briefer coverage is given in Industrial Ceramics (1964) by F. Singer and S. Singer, in the English translation of Keramik (1958) by H. Salmang, in Introduction to Ceramics (1960) by Kingery and in Alumina Properties (1960) Alcoa Research Laboratories, edited by Newsome et al. Of these, only the last is devoted solely to alumina.

Ceramists are not in agreement as to what materials are included in the term "ceramics," nor do they seem to have devised simple, consistent definitions of the term that are entirely satisfactory. Kingery defined ceramics as "the art and science of making and using solid articles which have as their essential component, and are composed in large part of inorganic, nonmetallic materials." Mitchell defined ceramics as "all high temperature

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*References are tabulated in alphabetical order for the last name of the first author, or for the title when no author is given. Multiple references to the same author are identified by date or otherwise in text.

chemistry and physics of nonmetallic materials and the methods and techniques of forming products at high temperatures." The first definition allows inclusion of materials having melting points below room temperature; the second allows inclusion of liquid and gaseous products prepared at high temperature, as for example, carbon disulfide. Although materials of all kinds, including organic substances, are involved in the preparation of ceramic materials, it is believed that these definitions are too broad to cover the ceramic applications of alumina. Contrary to Ryshkewitch and the European practice, however, applications of alumina in glasses, glazes, and enamels are considered within the scope of this review.

The word "alumine" was suggested by de Morveau in 1786 as the proper name for the basic earth of alum. This was anglicized to alumina in England, while in Germany tonerde, meaning clay earth, is still used. The term "alumina" is presently used rather indefinitely in ceramic literature (1) to denote aluminous material of all types taken collectively, (2) to denote the hydrous and anhydrous aluminum oxides or hydroxides indiscriminately, and (3) to denote calcined or substantially water-free aluminum oxide, without necessarily distinguishing the phases present. It is occasionally used interchangeably with the molecular formula, Al_2O_3. The meaning is sometimes hard to determine from the context. In this review, as far as possible, the term is used mainly in the sense of the second definition.

More than 25 solid phases of alumina have been described in recent years, but it is doubtful whether some really exist. These phases, or forms, include amorphous, hydrous and anhydrous oxides, crystalline hydroxides and oxides, and aluminas containing small amounts of oxides of the alkalies or alkaline earths, designated as beta aluminas. The beta aluminas were initially thought to be pure oxide phases by Rankin and Merwin, later disproved by Ridgway, Klein, and O'Leary. The convention still persists, although these phases should be classified more logically as aluminates.

The phases found in nature, and a few of the artificial types, have common or mineralogical names. Most are also identified by Greek-letter formulas. Unfortunately, in the United States and other countries, investigators have not been in complete agreement on nomenclature, and there is confusion particularly in the Greek-letter formulas.

Corundum, emery, sapphire, and ruby are more or less pure forms found in nature and known from antiquity as abrasives and gem stones (Greville). All consist of the phase designated alpha alumina (α-Al_2O_3). Another native mineral, described by Haüy in 1801, was named "diaspore" by him, from the Greek for "scatter," because it flew apart upon heating. Vauquelin in 1802 gave its formula as $Al_2O_3 \cdot H_2O$. Dewey named a well crystallized mineral "gibbsite" for G. Gibbs an American mineralogist. It corresponded with the formula $Al(OH)_3$ or $Al_2O_3 \cdot 3H_2O$ (Torrey). This name is more acceptable than "hydrargillite," suggested by Rose in 1839 for an identical mineral found in the Urals. It is the principal phase of the "trihydrate" bauxites. Berthier examined a mineral

from Les Baux in southern France, containing about 52% Al_2O_3 and 20% bound water, from which it was supposed that the mineral was $Al_2O_3 \cdot 2H_2O$. The mineral was named "bauxite" by St. Clair-Deville.

When X-ray diffraction became generally available as an analytical tool, Böhm and Niclassen discovered a new diffraction pattern for an aluminum hydroxide precipitated from aluminum sulfate at 100°C. Böhm subsequently identified this pattern in pressure-digested aluminum hydroxide and in pure samples of the French bauxite, both having about 15% bound water ($Al_2O_3 \cdot H_2O$). He concluded that the phase was an isomer of diaspore. The name "boehmite" was suggested by de Lapparent for both the mineral and the artificial product. It is of historical interest that Mitscherlich had anticipated both the synthetic preparation by Böhm's method and its identity as an alumina monohydrate. No phase corresponding to $Al_2O_3 \cdot 2H_2O$ has been found in natural sources by X-ray analysis. L. Milligan was unable to show an arrest at this point in the heating curve of Bayer process alumina. The preparation of this phase has been claimed by Bulashevich and Tolkachev by reacting aluminum with sodium hydroxide solution at 95 to 97°C.

In America, the word "bauxite" has come to mean any highly aluminous ore composed mainly of one or more of the phases, gibbsite, boehmite, and diaspore. Bauxite was considered by Harder to have originated as a transported, weathered product. Laterite is a relatively untransported aluminum hydroxide of about the same mineral composition (Konta).

In 1925, Haber devised a system of nomenclature for the trivalent alumina phases then known. The "alpha" series included diaspore and corundum (alpha alumina); the "gamma" series included hydrargillite (gibbsite), bauxite (boehmite), and gamma alumina. The classification was obviously based on the end product of calcination, but this is somewhat arbitrary because gamma alumina also transforms to alpha alumina.

Böhm identified a new phase in aluminum hydroxide precipitates that had aged moist for several months at room temperature. The water content was about that of gibbsite, but the X-ray pattern was different, indicating an isomer of gibbsite. This phase was called "bayerite" by Fricke in 1928 on the erroneous supposition that it was the normal product from the Bayer process. L. Milligan had already shown in 1922 that the Bayer product is predominantly gibbsite. Bayerite was claimed to have been found in nature by Gedeon, and more recently (1963) by Gross and Heller.

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In the first instance, at least, this has been refuted by Sasvari and Zalai.

The failure of the Haber system to distinguish between bayerite and gibbsite prompted the devising of the Alcoa system of nomenclature (Frary). In this system, the choice of Greek letters was initially based on the relative abundance of the phase in nature. Gibbsite was called alpha alumina trihydrate; boehmite, alpha alumina monohydrate; bayerite, beta alumina trihydrate; and diaspore, beta alumina monohydrate. Gamma alumina and alpha alumina had the same significance as in the Haber system.

Coblentz in 1906, van Arkel and Fritzius, and Fricke and Severin found no water of hydration by infrared investigation of gibbsite, boehmite, or diaspore, but only the hydroxyl bands at 3 microns. These phases are hydroxides rather than hydrates. In present terminology, alumina trihydrate is used interchangeably with aluminum trihydroxide, and $Al_2O_3 \cdot 3H_2O$ with $Al(OH)_3$. Similarly, alumina monohydrate is used interchangeably with aluminum monohydroxide or aluminum oxide hydroxide, and $Al_2O_3 \cdot H_2O$ with $AlO \cdot OH$. In commercial usage the trihydrates are also designated as hydrated aluminas.

Moiseev claimed that fibrous alumina obtained by action of mercuric chloride solution on aluminum upon heating at 80 to 100°C produces $(AlO \cdot OH)H_2O$, which he called "bauxite dihydrate."

Weiser and W. O. Milligan in 1934 adopted the Haber series, and classified bayerite as alpha alumina trihydrate. Van Nordstrand et al. reported a third alumina trihydrate in 1956 for which the names bayerite II and randomite had been suggested. Nordstrandite has also been suggested, and this has been widely accepted. The phase is thought to be intermediate in lattice structure between bayerite and gibbsite.

Cliachite, zirlite, alumogel and other names were applied to supposedly amorphous bauxitic structures in some cases long before the availability of X-ray diffraction for appraisal of the extent of crystallinity. All fine-crystal bauxites exhibit characteristics of a colloidal state at one stage of their development. Aging converts the amorphous precipitates to crystalline forms, but colloidal properties may be retained.

Shishakov reported a third aluminum monohydroxide formed as hexagonal $AlO \cdot OH$ on aluminum surfaces, identical to the lattice attributed by Steinheil to a cubic form. Yamaguchi et al. prepared "tohdite," which they claimed had the formula $5Al_2O_3 \cdot H_2O$,

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by heating an aluminum hydroxide at 450-500°C for 20-100 hours with AlF_3 or $Ti(SO_4)_2$ as a mineralizer.

Frary in 1946 and Stumpf et al. in 1950 continued the Alcoa series by naming five anhydrous or nearly anhydrous phases: delta, eta, theta, kappa, and chi aluminas. Ulrich had named gamma alumina in 1925, and the term had been used rather vaguely for aluminas calcined in the low-temperature range, and in the oxidation of aluminum. Hägg and Soderhölm, and Verwey in 1935 had applied the name to the spinel structure of alumina. Jellinek and Fankuchen in 1949 computed new dimensions for the unit cell, which were not compatible with the dimensions derived earlier by Brill for a spinel-type lattice. They concluded that crystal growth affected the diffraction pattern. Stumpf restricted the limits of gamma alumina to the product whose X-ray pattern is like that in the alpha trihydrate and alpha monohydrate dehydration sequences at 500°C. New phases include rho alumina of Tertian and Papée, xi and xi aluminas of Cowley, and iota alumina of P. A. Foster in 1959. Some of these assigned transition phases, whose detection is based mainly on somewhat subtle X-ray diffraction differences, are of doubtful existence.

Standarization of the nomenclature for aluminas is very desirable particularly to avoid the confusion in the hydrous phases. Ginsberg reported the conclusions of a symposium held in 1957, in which an attempt was made to devise a universal standard nomenclature. Some features of the proposed system are improvements, as for example, the substitution of "hydroxide" instead of "hydrate," namely, aluminum trihydroxide for alumina trihydrate; aluminum oxide hydroxide for alumina monohydrate. Also, it was agreed to use the Alcoa nomenclature for the transition aluminas, but to designate some of them as "forms" rather than "phases," to imply the present uncertainty about them. The confusion in naming the hydroxide phases has not been resolved, however.

The designations alpha alumina ($a-Al_2O_3$) for corundum and beta alumina ($\beta-Al_2O_3$) assigned by Rankin and Merwin in 1916 to a supposedly monotropic form, have been retained in all systems. Following Ridgway's disclosure that beta alumina contains alkali or alkaline earth atoms, the foreign cation is now made part of the name, i.e., sodium beta alumina. Barlett called that form crystallizing from melts containing lithia, zeta alumina. Belyankin disputed its separate existence from gamma alumina radiographically as well as in refractive index and in density. Indeed, it matches eta alumina very closely, except in refractive index and, of course, composition.

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Two reduced oxide forms of alumina are known, Al_2O and AlO, but they have no special designations.

The Haber system of nomenclature is in general use in Europe, the Alcoa system in America. A comparison of the major nomenclature systems most frequently confused in the literature is shown in Table 1.

In the present compilation, the Alcoa assignment of Greek letters is used.

Table 1

Nomenclature of Crystalline Aluminas

| Mineralogical Name | Phase or Form Name | | | | | |
	Symposium (1)	Alcoa (2)	Haber (3)	British (4)	French (5)	Other
Hydroxides						
Gibbsite (6) Hydrargillite	$Al(OH)_3$	α-$Al_2O_3 \cdot 3H_2O$	γ-$Al(OH)_3$	γ-$Al_2O_3 \cdot 3H_2O$		
Bayerite (7)	$Al(OH)_3$	β-$Al_2O_3 \cdot 3H_2O$	α-$Al(OH)_3$	α-$Al_2O_3 \cdot 3H_2O$		
Nordstrandite (1) Randomite (8) Bayerite II (8)	$Al(OH)_3$					
Bauxite (9)						$Al(OH)_2$
Boehmite (10)	AlOOH	α-$Al_2O_3 \cdot H_2O$	γ-AlO_2H	γ-$Al_2O_3 \cdot H_2O$		
Diaspore	AlOOH	β-$Al_2O_3 \cdot H_2O$	α-AlO_2H			
Tohdite (11)						$5Al_2O_3 \cdot H_2O$ ϵ-Al_2O_3 (12)
Aluminas					Rho	
	Chi	Chi	–	Chi + Gamma	Chi + Gamma	
	Eta	Eta	–	Gamma	Eta	
	Gamma	Gamma	Gamma	Delta	Gamma	
	Delta	Delta	–	Delta + Theta	Delta	
						Xi^1, Xi^2 (13)
	Kappa	Kappa Iota (17)	–	Kappa + Theta	Kappa + Delta	
Corundum Sapphire	Alpha	Alpha	Alpha	Alpha	Alpha	
		AlO				
		Al_2O				
		$M_2O \cdot 11Al_2O_3$ (14)				
		$M_2O \cdot 6Al_2O_3$ (15)				
		$MO \cdot 6Al_2O_3$				
Zeta Alumina		$Li_2O \cdot 5Al_2O_3$ (16)				

Ref.: (1) Ginsberg, Hüttig, Strunk-Lichtenberg
(2) Edwards, Frary, Stumpf, et al.
(3) Haber, Weiser, & Milligan
(4) Rooksby, Day & Hill
(5) Thibon, Tertian, & Papée
(6) Dewey
(7) Fricke
(8) Teter, Gring, & Keith
(9) Böhm
(10) de Lapparent
(11) Yamaguchi
(12) Steinheil
(13) Cowley
(14) Rankin & Merwin
(15) Scholder
16. Barlett
17. P. A. Foster

3 PREPARATION OF ALUMINA PHASES

3-1 BAUXITE

The native aluminous minerals, corundum, emery, and the clays, have been associated with ceramic operations from antiquity. Exclusive of these raw materials, bauxite is the principal source of alumina for ceramic purposes. Bauxite mining began at Villeveyrac, France, in 1873. Since then, bauxite mining has spread around the world, particularly in the tropical areas, in southern United States, in the Guianas, in the Caribbean islands and Brazil, along the west coast of Africa, in the Mediterranean countries, in India, Malaya, Indonesia, and Australia, but also in Russia and China. Bauxite is generally believed to have been produced mainly by weathering, favored by abundant and intermittent rainfall. Moses and Michel conclude that a second step occurred in the case of Guiana bauxites, in which an uplift of the coastal plain, following weathering permitted bauxitization through leaching of kaolin by surface water.

Gibbsite is the most stable phase in bauxite at normal temperatures and pressures found in the tropics. As it is likely that temperatures above 100°C were involved in the genesis of bauxite, the formation of diaspore and boehmite probably resulted from high pressure.

In 1963, world production of bauxite was about 30 million long tons, of which over 11 million represents consumption of domestic and imported bauxite in the United States. Domestic ceramic uses as abrasives and refractories consumed about 408,000 tons. About 2.12 long dry tons of bauxite was required to produce one short ton of Bayer process alumina, and an average of 3.93 tons to produce one short ton of aluminum.

Even in the primitive era of ceramic operations, some preparation or beneficiation was required. The South American bauxites are subjected to hydraulic cleaning operations to remove overburden and sand contamination. The mined deposits are then blended on the basis of their chemical analysis into suitable grades for various uses. The principal impurities include SiO_2, Fe_2O_3 and TiO_2.

Bauxite is used directly in adsorbents, abrasives, and refractories, aside from its use in preparing metal. For these applications, specific grades must be sized, dried, and calcined, partially at about 980°C for fused abrasive use, and more completely at about 1540°C for refractory use.

Bauxites from British (Demerara) and Dutch Guiana (Suriname) are particularly suited to ceramic uses, because of their controlled low iron and low silica contents. Properties of typical ceramic grades from each source are shown in Table 2.

Table 2

Bauxite - Ceramic Grades

	(1) Suriname			(2) Demerara		
	Dried Chemical	Abrasive	Refractory	Abrasive AAC	Refractory RAC	Refractory RASC
Al_2O_3	61-62%	87.5%	89.0%	87.75%	87.75%	88.00%
Fe_2O_3	1.3-1.7%	5.4%	1.6%	1.50%	1.50%	1.50%
TiO_2	2.7-3.2%	3.5%	3.3%	3.25%	3.25%	3.25%
SiO_2	2.0-2.5%	2.9%	6.0%	7.00%	7.00%	7.00%
Loss on Ignition	31-32%	0.7%	0.1%	0.50%	0.50%	0.25%
Free Moisture	1.5-2.5%	nil	nil	nil	nil	nil
Size Range	-	-	-	1.5 in. lumps to fines		
Bulk Dens.	-	-	-	90	90	120

(1) Courtesy Suriname Aluminum Company

(2) Courtesy Aluminium Limited Sales Inc.

3-2 PREPARATION OF BAYER ALUMINA

The major application of pure alumina is in the production of metallic aluminum. Metallurgical-grade alumina is the cheapest source of pure alumina available. Over 5 million tons of 99% purity alumina was produced in the United States in 1963. In view of the influence of metallurgical-grade alumina on the economics of ceramic alumina applications, the preparation of this grade will be given first consideration.

The Bayer process is the principal production method in use today. Many other production methods have been proposed, however. The subject is too voluminous to cover more extensively than by a brief outline of the processes. Alumina and Aluminum, by Fulda and Ginsberg (1957) is probably the most complete discussion of the commercial production for the aluminum industry. A second edition (in German) was published in 1964. Extractive Metallurgy of Aluminum, Volume I, Alumina, edited by Gerard and Stroup (1963) contains excellent monographs on various phases of modern alumina production. The Aluminum Industry, Volume I, by Edwards, Frary, and Jeffries gives very complete information on the extractive processes prior to 1930. Most of the basic procedures had been proposed prior to that date.

The incentive for many of the proposed procedures has been to use more available and cheaper raw materials than bauxite. These include common clay, leucite, alunite, and andalusite, among others.

The general processes, exclusive of metallurgical processes for winning the metal directly, include the following:

1. Wet alkaline processes: (a) autoclave Bayer, (b) tower percolation.
2. Wet acid processes: H_2SO_4, HCl, HNO_3, H_2SO_3, acid salts.
3. Alkaline furnace processes (a) Na_2CO_3, $CaCO_3$, or mixtures, (b) sulfates, chlorides or other salts and reducing agents.
4. Carbothermic furnace processes.
5. Electrolytic processes.

3-2-1 Wet Alkaline Processes

The wet alkaline processes, in particular the Bayer process, are still the most economical of modern methods. The Bayer process is most suitable for low-silica bauxites containing gibbsite and boehmite.

Gibbsitic bauxites are easiest to digest. Porter has recently described the application of the Bayer process to aluminum phosphate ores, and Shakhtakhtinskii and Nasyrov its use on alunite. The Bayer process is optionally continuous or batchwise. The dried, ground bauxite is digested in an autoclave with a solution of sodium hydroxide and sodium carbonate, containing a flocculant (starch) and lime added to causticize the soda and to act as a filter aid. This requires a concentration of about 100 to 120 grams NaOH per liter and a pressure of 40 to 50 psi (at about 145°C) to dissolve the contained gibbsite and obtain a stable supersatrated sodium aluminate liquor. Liquors having a ratio of Al_2O_3: NaOH of about 0.8 by weight are stable against autoprecipitation at clarification temperatures around 105°C. This was the conventional American continuous process until the advent of bauxites containing appreciable amounts of boehmite.

Boehmitic European bauxites, and particularly some hard Greek bauxites, require more drastic digest conditions. Digestion at 280 to 700 psi and at above 300 grams NaOH per liter is usual practice. A continuous process requires operation at 285°C (1400 psi) to obtain good recovery of alumina. With the advent of bauxites containing appreciable boehmite in American practice, a compromise digestion at higher pressure, 400 to 450 psi (about 230°C) has been developed.

After digestion, the slurry is cooled by flash heat interchange to near boiling at atmospheric pressure and the waste solids (red mud) are separated by sedimentation and filtration. The red mud comprises mainly iron oxides, titania, carbonated lime, and desilication product. The lime represents makeup causticization of soda lost in previous cycles and in some cases, filter aid. The desilication product represents mainly soda and alumina lost by combination with reactive silica to form zeolitic compounds resembling sodalite. The clarified (green or pregnant) liquor is cooled by heat exchange with spent liquor to about 55°C, and a portion of the dissolved alumina is precipitated by introducing fine seed alumina trihydrate. Gibbsite is the normal precipitated phase, designated Bayer trihydrate, but Fricke showed that other phases are possible at different temperatures and with different seeding phases present, as long as the solution is supersaturated with respect to these phases. The precipitated trihydrate is separated from the spent liquor, washed, and for the most part, is calcined for ceramic applications. The spent liquor plus washings is evaporated and returned to process. Complete separation of the hydrate from the green liquor can be realized by gassing with carbon dioxide, but this then requires complete causticization as a separate external operation, as distinguished from

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the relatively lesser causticization required for makeup for losses in the seeding precipitation. Strokov observed that the properties of the product were markedly influenced by the temperature, duration, and speed of mixing during carbonation. At 80°C, the product contained from 0.5 to 0.6% alkali (in Al_2O_3). Tower leaching of partially calcined bauxite by sodium hydroxide under pressure is described by Fulda and Ginsberg, and by Zalar.

The conditions of seeding, temperature, agitation and time during precipitation are controlled to obtain the most economic separation of the Bayer trihydrate, and the most advantageous particle size distribution for subsequent operations. Factors which affect the purity and texture of the precipitated trihydrate also influence the quality of the calcined alumina, even though the product has passed through several transitions.

Typical properties and specifications of commercial grades of hydrated aluminas, prepared in a modern Bayer plant, are shown in Table 3.

Table 3

Typical Properties and Specifications of Hydrated Aluminas-Series
C-30

	C-31(1)	C-31 Coarse	C-33(1)	C-35(2)
Typical Properties:				
Al_2O_3 .... %	65.0	64.9	65.0	65.2
SiO_2 .... %	0.01	0.01	0.008	0.008
Fe_2O_3 .... %	0.003	0.004	0.002	0.004
Na_2O .... %	0.16	0.20	0.16	0.04
Moisture(110°C) .... %	0.04	0.04	0.04	0.04
Bulk density,loose,lb/ft^3	60-70	70-80	60-70	70-80
Bulk density, packed,lb/ft^3	75-85	90-100	75-85	85-95
Specific gravity	2.42	2.42	2.42	2.42
Sieve analysis(cumulative)				
On 100 mesh .... %	0-1	0-10	0-1	0-2
On 200 mesh .... %	5-10	40-80	5-10	5-20
On 325 mesh .... %	30-55	85-97	30-55	30-60
Through 325 mesh .... %	45-70	3-15	45-70	40-70

(1) Finer material is available
(2) Tentative properties

Courtesy Aluminum Company of America

3-2-2 Wet Acid Processes

Wet acid processes for ceramic aluminas have so far not approached the wet alkaline process in economy of operation. Difficulties have been mainly with corrosion of equipment, poor recovery of acid for reuse, and the high pickup of iron and other impurities in the product. The acid processes should be more adaptable to low-iron clays, kaolins, and high-silica bauxites, which give poor extraction or difficulty with desilication by the Bayer process. There is generally little contamination from silica in acid processes. Exhaustive references to acid processes prior to 1930 are given by Edwards, Frary and Jeffries. The following recent references (since 1958) show the continuing interest in potential methods for recovering metallurgical-grade alumina from clays and other alumina sources. Bakr preferred acid methods to alkaline or thermal reduction methods for clays. Peters et al. at the U. S. Bureau of Mines evaluated three sulfuric acid processes and one nitric acid process for calcined clay, and estimated capital and operating costs. Scott combined hydrolysis of sulfate liquor at 220°C and the use of bauxite to achieve partial neutralization of digestion liquors to recover a pure product from clays and bauxites. Kretzschmar roasted clay to make it more soluble in dilute sulfuric acid, and converted the silicic acid, that formed, to calcium hydrosilicate before separating the purified aluminum sulfate. Alternatively, the clay can be roasted with $(NH_4)_2SO_4$ and an addition of Na_2SO_4 at 400 to 550°C, and leached in 0.5% H_2SO_4 solution before hydrolyzing. By treating the pulp additionally with an alkaline solution, a yield of 94 to 96% Al_2O_3 was achieved (Skobeev). Loss of ammonia probably occurs above 400°C (Riedel). Mixed $H_2SO_4-(NH_4)_2SO_4$ has been used as the leaching solution and a yield of 68.4% alumina was obtained by hydrolysis with NH_3 (Bretznajder). Tucker extracted alumina from clay by dissolving it in nitric acid, and obtained an iron-free product by adding calcium chloride to the filtered solution, and by separating the iron in methyl isobutyl ketone.

In 1945, a development plant was built by Defense Plants Corporation at Salem, Oregon, using the acid ammonium sulfate (Kalunite) process (Libbey).

Anaconda Aluminum Company in May 1963 was operating a sulfuric acid process on Idaho clays on a pilot scale (6200 lb. of metal per day). The process has been claimed to cost about $40 per ton.

North American Coal Corporation also operated a sulfate process on coal processing wastes, to recover both alumina and sulfate values.

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Some recent references relating to improvements in Bayer plant operations are of interest. Kuznetsov et al. found that Bayer trihydrate, calcined at 250°C to boehmite structure, was the best nongibbsitic seed crystals for precipitating trihydrate, the grain size of which corresponds to industrial requirements. Lyapunov, Khodokova, and Galkina observed an increase in solubility of gibbsite in sodium aluminate solutions containing 6.9% added NaCl. Holder and Thome purified the filtered sodium aluminate liquor by treating with $KMnO_4$ and passing it through a bed of lime. Dunay et al. claimed advantages in two-fold washing, the use of hydrogen peroxide, and filtering through broken electrocorundum to reduce floating contaminants, Fe_2O_3, TiO_2, and SiO_2. Scott discussed the effects of seed and temperature on the particle size of Bayer hydrate. Reese and Cundiff described the continuous process production of alumina from Jamaican bauxite in detail. Scandrett and Porter discussed the continuous Bayer process for trihydrate bauxites containing significant amounts of boehmite.

3-2-3 Furnace Processes

Furnace processes have apparently had the most success in competing with the Bayer process in tonnage operations. Some furnacing methods require wet processing as a purification step. The ore is fused or sintered with an alkali or alkaline earth carbonate or oxide, or mixtures, to produce the corresponding aluminate. The product is then extracted and purified by wet alkaline procedures similar to the Bayer process. Sulfides, sulfates or chlorides may be substituted for the oxides. The Pedersen process is of this type. A mixture of iron ore, coke, lime, and bauxite, or other aluminous material is smelted to produce molten calcium aluminate slag containing 30 to 50% Al_2O_3 and only 5 to 10% SiO_2. Low-sulfur, high-grade iron is a by-product. Commercial operation of this process began in 1928 at Høyanger, Norway. Andalusite has been used as the aluminous material in a somewhat similar operation at Sundsvale, Sweden, producing at the rate of 4,000 tons per year during the war years.

3-2-4 Carbothermic Processes

In carbothermic furnace processes, the ore is fused under conditions to separate the impurities as molten metals, leaving the alumina in sufficient purity that wet separation methods can be evaded. The Hall and Haglund processes are of this type, primarily to produce metallurgical-grade alumina. The Haglund process

is economically operable when its ferrosilicon by-product is in demand. The Hall process is not presently in use.

Similar procedures have been developed for purification of fused alumina prepared from bauxite in the electric furnace for fused abrasives (Allen, Saunders, and Ridgway and Glaze). For abrasives, a mixture of bauxite, coke, and iron borings is fused in either a Higgins or a Hutchins furnace. Both comprise a water-cooled steel shell containing the charge, into which carbon electrodes are positioned. The shell of the Higgins furnace is a truncated cone, open at both ends, and with the smaller diameter up. The shell fits over a round carbon block. At the end of a furnacing cycle, the shell can be lifted off. The Hutchins furnace is crucible-shaped and closed at the bottom. The cooled product is massive and requires crushing to obtain the desired sizes.

Another type of grain is made with an addition of sulfides to the fusion. The product consists of single crystals of aluminum oxide in a water-soluble matrix.

White fused aluminum oxide is prepared from a special grade of Bayer process calcined alumina. No reduction to remove impurities is required. The fusing is mainly in Hutchins-type furnaces for batch production. Impure beta alumina migrates to the center of the pig, and can be separated later by visual inspection. White abrasive is also produced in a semi-continuous process in a pouring furnace. During pouring, micro and macro capillary pores form, which improves the crushing operation (Ridgway).

During the war years the Defense Plants Corporation built two pilot plants, one for treating clay by a lime-sinter process, and the other for treating anorthosite by a soda-lime-sinter process. The processes are not presently used. R. W. Brown developed a sintering process using a mixture of soda ash and limestone, applicable to high-silica aluminous ores. The combination of the standard Bayer process and this sintering process applied to the Bayer waste product (red mud), has made practical the utilization of large reserves of low-grade bauxite in the United States.

Much of the furnacing investigation has been applied to alunite, $K_2SO_4 \cdot Al_2(SO_4)_2 \cdot 4Al(OH)_3$. Gad and Barrett; Knizek and Fetter; Nekrich; Bretsznajder and Pysiak; Asahi; and Ponomarev et al. describe roasting operations involved either in direct removal of sulfate by volatilization or in opening up the material to wet purification processes.

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3-2-5 Electrolytic Processes

Roberts, and Schwerin proposed electrolytic methods of separating alumina from aluminate solutions. For many years no interest was shown in these processes. Recently, Guareschi has described a process of roasting aluminosilicas, dissolving in sulfuric acid, and electrolyzing the filtered and purified liquor. Reheis electrolyzes an aqueous solution of aluminum chloride in a 3-compartment cell. The center compartment is fed a slurry of aluminum hydroxide and dilute hydrochloric acid, which combines with any chlorine migrating from the cathode. A selective membrane prevents passage of chlorine to the anode.

3-3 AMORPHOUS AND GEL ALUMINAS

Gelatinous aluminum hydroxides are of interest because of their technical importance in preparing sorbents and catalysts. Surprisingly, they have seen only limited use elsewhere, as for example, as plasticizing additives in compositions for forming sintered alumina ware. Willstätter and Kraut and their co-workers investigated various types of gels, in most cases, precipitated from alum or aluminum sulfate solutions by ammonia, at temperatures below 60°C. They distinguished three types, which they designated α, β, and γ, and which have been the subject of continuing investigation to the present time. Unaged C_α is amorphous to X-rays, is readily soluble in 0.1% HCl, and dewaters to about 35% H_2O when treated with dried acetone and ether. C_α transforms within a few hours to C_β when aged in water, but loses almost one mole of bound water. C_β contains diffuse bands of boehmite, peptizes in dilute HCl and dissolves slowly. Kohlschütter and Beutler found that aging for several hundred hours in water, or for a few hours in dilute ammonia, converts C_β into C_γ, a mixture containing boehmite and crystalline trihydroxides, almost insoluble in dilute HCl. Geiling and Glocker showed that even when the initial product is maintained at low temperature (12°C) throughout the test (up to 48 hours), the product shows the boehmite pattern.

Gels can be prepared by neutralizing other aluminum salts (for example, the chloride or nitrate) in the alkaline direction with ammonium hydroxide or alkalies. They can also be prepared by neutralizing sodium aluminate solutions in the acid direction by adding carbon dioxide, sodium bicarbonate, or an acid. Havestadt and Fricke showed that rapid precipitations of sodium aluminate by CO_2 at 0° are initially amorphous, but eventually transform into bayerite. Precipitations at room temperature to about

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60°C form as bayerite. Gels can be formed by reacting water with "activated" surfaces of aluminum.

A gel in fibrous form is produced by action of mercury and moisture on aluminum (Cossa). At room temperature bayerite lines develop. This gel and the previously cited preparations are generally impure because of sorbed reactants. A method of producing gels of potentially much higher purity, with respect to ionic contaminants, consists of dropping distilled aluminum triethyl, $Al(C_2H_5)_3$ into water (Thiessen and Thater). Alternatively, the aluminum triethyl can be vaporized in a stream of nitrogen. Opalescent gels prepared by this method and stored for 2 months under water lost water of hydration at 17°C to an eventual composition of about $Al_2O_3 \cdot 3H_2O$, upon drying. They developed a faint bayerite pattern. Aluminum isopropylate, $Al(C_3H_7O)_3$, prepared by reacting aluminum and alcohol in the presence of an aluminum-mercury couple, has also been used to prepare very pure hydrolyzed gels. Torkar et al. hydrolyzed the aluminum alcoholate with 3 to 30% (by weight) hydrogen peroxide at 0 to 22°C.

Calvet et al.; and Imelik, Mathieu, Prettre, and Teichner found that amorphous gels precipitated from aluminum salts by a base at about pH 7 are impure and contain significant amounts of anions. Attempts to purify the gel convert it to crystalline products with a marked change in specific surface. Precipitations at a more alkaline pH (about 9) are purer, but are not strictly amorphous. Papée, Tertian, and Biais claimed to make a pure amorphous gel by precipitating aluminum nitrate at pH 8.0 with ammonium hydroxide or soda, followed by rapid washing and drying at 25°C. The product had excess hydration ($Al_2O_3 \cdot 3.45H_2O$), contained less than 0.1% NO_3^-, and was considered more amorphous than glass, resins, or liquids. It had a specific surface of 170 m^2/g, stable after a year. These products aged to "pseudoboehmite," having the same pattern as well-crystallized boehmite, but more diffuse (Imelik et al.).

The preparation method of the gels became influenced by the morphology. The amorphous gel is composed of small spherical particles about 30 A in diameter as seen under the electron microscope. Turkevich and Hillier observed that the spheres were combined into fibers in precipitates from aluminum nitrate by ammonia. On aging, these fibers arranged to form rectangular plates. The fibrous nature was retained on drying at 80°C and even on heating to 350°C. On further heating, particularly in steam, the granular fibers gradually disappeared to show lath-like surfaces. Similar results were shown for gels prepared by reaction of aluminum metal and acetic acid. Sawamura observed the fibrils in the C_α transition within two hours of aging. After 24 hours, most of the

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crystals were arranged in fibers of 200 to 500 A diameter and of indeterminate length. Souza Santos et al.; Watson et al.; Ohta and Kagami; Suzuki; and Moscou and van der Vlies investigated the gels in more detail. Souza Santos thought the fibers were boehmite, but Moscou claimed they were not pure and contained some bayerite. On further aging the fibers rearranged to form "somatoids," a name given by Kohlschütter to describe the characteristic particles in C_γ. The sequence is from spherical amorphous particles to fibers, to boehmite somatoids, to bayerite or other trihydroxide somatoids in hexagonal plates. Wislicenus in 1908 had described fibrous alumina formed on the surface of amalgamated aluminum. This material is composed of bundles of long, fragile fibers of aluminum hydroxide. It ages rapidly in water forming products that are morphologically analogous to those obtained from the C_α gel.

Kohlschütter had found that solid aluminum compounds react with ammoniacal solutions to yield products of easy filtration and washability. The reaction proceeds topochemically, that is, the external shape of the particles is retained. Moscou and van der Vlies state that sheet-like gelatinous boehmite forms directly without formation of amorphous hydroxide. Plate-shaped hydroxide particles are obtained from plate-shaped solid aluminum sulfate, while needle-shaped particles are obtained from solid aluminum chloride.

Cramer et al. prepared alumina gels for catalytic treatment of petroleum by reacting in aqueous solution basic aluminum chloride or nitrate, urea, and ammonium or alkali metal salts of acetic and glycolic acids to form a hydrosol at pH of about 3.5 to 7. The hydrosol was set in a water-immiscible liquid at about 52 to 100°C for about 10 hours to decompose the urea and raise the pH to about 8.

Hsu and Bates found that the molar ratio of NaOH to Al^{3+} is a significant factor in preparing gels from sulfate or chloride solutions. When the ratio was not over 2.75, the products were amorphous, and remained so for at least 6 months. When the ratio was 3.0 to 3.3, bayerite, nordstrandite, gibbsite, or mixtures were obtained within several hours.

Patrick prepared gels substantially free of water-soluble salts by mixing aluminum sulfide with water acidified with a volatile organic acid (acetic or formic) at from 0 to 80°C, and gelling the sol in dilute acid.

References to activators for accelerating the formation of

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aluminum hydroxide from metallic aluminum include the following: Hervert and Bloch used 100 to 10,000 parts per million by weight of the aluminum selected from the metals, tin, lead, and germanium; alkylamines, or arylalkylamines; or water-soluble alkanolamines reacting at freezing to 705°C; Evans used aniline at its boiling point; E. F. Smith claimed 0.1 to 0.2% gallium; Lefrancois any metal compound below aluminum in the electromotive series together with a strong acid having an ionization constant of at least 10^{-2}, but preferably from the group, mercury, zinc, and cadmium.

Bergman and Torkar subjected the aluminum to electrolytic attack in water containing only carbon dioxide or hydrogen peroxide. Welling applied an aqueous solution of hydrogen peroxide to amalgamated aluminum; Csordas exposed the amalgamated aluminum to a gas stream of oxygen and water vapor at 25 to 75°C.

Kandyakin states that the primary amorphous particles are oval, 0.01 to 0.05-micron in diameter, in agreement with size as determined from specific surface measurements. Papée, Tertian, and Biais found a small maximum in the X-ray pattern for pure amorphous gel between 1.5 and 3 A. Stumpf concluded that amorphous material is characterized by a band at 4.5 A, clearly distinguishable from crystalline material. Alumina pre- pared from aluminum isopropoxide hydrolysis was initially completely amorphous. Wilsdorf found that a model containing two Al_2O_3 molecules agrees with the electron diffraction rings of amorphous alumina produced by 75-hour air oxidation of aluminum. The structure consists of an octahedron of six closely packed oxygen ions with four aluminum ions in a tetrahedral arrangement and ionic distances of 2.80 and 3.95 A for O-O; 1.72 and 3.28 A for O-Al; and 2.80 A for Al-Al. Robson and Broussard applied radial distribution analysis to determine the most probable interatomic distances of amorphous silica-alumina compositions.

3-4 PREPARATION OF THE ALUMINUM TRIHYDROXIDES

3-4-1 Gibbsite, $a\text{-}Al_2O_3\cdot 3H_2O$, Alpha Alumina Trihydrate

Gibbsite is rare in nature in pure well-crystallized form, although it is the predominant phase of American bauxites.

As indicated in Sec. 3-3, the crystalline trihydroxides can be prepared by aging water suspensions of amorphous aluminum hydroxide. It is more expedient, however, to precipitate under

conditions of temperature, concentration, and rate that favor
direct formation of gibbsite. A suitable laboratory method for
gibbsite consists of partly neutralizing a sodium aluminate solu-
tion having a density of about 1.32 g/ml by rapid addition of
carbon dioxide at about 50 to 80°C (Fricke). The crystals vary
from pseudohexagonal plates to prisms having a diameter of about
0.3 to 3 microns.

Very pure, fine gibbsite is obtained directly by slow, spon-
taneous hydrolysis of alkali aluminate solution at room tempera-
ture (Fricke and Jucaitis). Single crystals can be grown to
large size if the precipitation continues for months.

Autoprecipitation from supersaturated sodium aluminate
liquors (80 g Al_2O_3/l, 120 g NaOH/l) at about 60 to 50°C in the
presence of fine seed trihydrate is the well-known Bayer pro-
cess. This process yields as much as two-thirds of the charge,
but the method is not very suitable for laboratory preparation.

Alkali-free gibbsite is claimed by Hauschild by hydrolysis
of aluminum triethylate, $Al(OC_2H_5)_3$ in the presence of from 1 to
20% ethanolamine, $NH_2C_2H_4OH$, at 20 to 60°C, and by slow aging of
the gel formed for several months. The product contains only
0.001% Na_2O, 0.001% CaO, 0.12 to 0.23% N, and only traces of or-
ganic matter.

Michel and Papée claim a high-purity gibbsite by precipita-
ting aluminum hydroxide, washing the precipitate to obtain a cake
containing about 35% by weight of Al_2O_3 and 0.1 mole of a univa-
lent acid ion per mole Al_2O_3. The suspension is aged for at least
2 days at 60°C. The cake is immersed in an alkaline medium con-
taining ammonium hydroxide or amines at 120°C for sufficient time
to allow crystal growth to about 100 to 200 A.

3-4-2 Bayerite, β-$Al_2O_3 \cdot 3H_2O$, Beta Alumina Trihydrate

Bayerite can be produced by moderately slow carbonation of
sodium aluminate solutions at 30 to 35°C. It is difficult to ob-
tain pure bayerite in this way because of the presence of boeh-
mite, gibbsite, and adsorbed alkali (Fricke, Fricke and Wever,
Fricke and Wulhorst). The method of aging amorphous gels precip-
itated from aluminum salts by ammonium hydroxide in the cold
(Kraut, Flake, Schmidt, and Volmer) usually does not give a uni-
form X-ray pattern. Kraut identified three types of bayerite,
designated A, B, and C.

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The treatment of aluminum or aluminum alcoholates with water at temperatures below 40°C (Fricke and Jockers) is favored for preparing bayerite. The modification of Schmäh involving the reaction of water with finely divided or amalgamated aluminum foil is well suited to laboratory-scale preparation. Lippens obtained patterns only for bayerite for this method, upon aging the product for one week at room temperature and pH 7.9. The product conformed to $Al_2O_3 \cdot 3.09 \, H_2O$.

Stewart claimed bayerite, 95% pure, in which a dilute aqueous solution of aluminum chloride or nitrate is added in increments to a sodium-free, 0.1- to 4-molar aqueous basic hydroxide having a nonmetallic volatile cation. The temperature is maintained between 0 to 49°C, and the pH is not reduced below 9.0.

Doelp disclosed a process for bayerite, 96% pure, by treating boehmite, gibbsite, or amorphous gelatinous alumina in an aqueous solution of 1 to 10 moles of tetramethyl ammonium hydroxide at below 40°C, and by precipitating with carbon dioxide below 40°C.

Hauschild and Nicolaus claimed a pure bayerite by treating aluminum cuttings with water containing 7 to 15% alkylamines at below 100°C. Monomethylamine at 80°C is preferred.

Harris and Sing investigated the surface properties of gels prepared from the aluminum alkoxides (alcohol salts) by interaction with sodium hydroxide solutions, and by hydrolysis. The latter gave a peak area of 1130 m²/g, and retained 300 m²/g. Bye and Robinson prepared gels by hydrolysis of aluminum s-butoxide dissolved in benzene using controlled mixtures of water and ethanol to provide only about twice the theoretical water for hydrolysis. The gels aged for 72 hours in the mother liquor had the composition $Al_2O_3 \cdot 1.8-1.9 \, H_2O$, and a surface area of about 410 m²/g. Pseudoboehmite appeared after 4 hours, and bayerite within 6 weeks. Aging in water was faster. Bayerite appeared within one week, and the surface area was reduced by 60 m²/g per day until the composition became $Al_2O_3 \cdot 3.04 \, H_2O$ at 22 m²/g. The maximum surface area was about 480 m²/g, obtained after aging for 3 hours, and represented the region of pseudoboehmite. They concluded that pseudoboehmite results from condensations of OH groups, but bayerite results from dissolution and recrystallization processes. Feitknecht stated that freshly precipitated hydroxides of trivalent metals can be amorphous, can possess one of two modifications of a partly ordered layer structure, a partly ordered double-layer structure, or a fully crystalline double-layer structure.

Kohlschütter observed that the bayerite somatoids appear as truncated pyramids or cones under magnification of about 2000. The electron micrographs of Watson and Moscou showed these forms to consist of plates generally layered perpendicularly to the long axis. Lippens found that this arrangement conforms with the trihydroxide double layer structure.

Tertian and Papee claimed that very pure bayerite can be produced by rehydration of rho alumina in water at about 25°C. The rho alumina is produced by dehydrating gibbsite in a vacuum at 200°C. The success of this rather complicated process depends on the original gibbsite being precipitated from sodium aluminate liquor on gelatinous aluminum hydroxide in a very fine size.

3-4-3 Nordstrandite, Bayerite II, Randomite

Kraut observed three X-ray diffraction modifications of bayerite; de Boer, Fortuin and Steggerda described two modifications, designated bayerite I and II. Van Nordstrand et al. identified a pattern in gels precipitated from aluminum chloride or nitrate in the presence of ammonium chloride, and aged at pH 7.5 to 9.0. They suggested that it conforms to a third phase of $Al(OH)_3$. Papée claimed to have obtained pure nordstrandite, presumably by long-time aging at pH 13 of a gel formed by the cited process.

Hauschild described a method for obtaining pure nordstrandite consisting of aging freshly prepared aluminum hydroxide gel in an aqueous solution of an alkylene diamine (preferably $NH_2CH:CHNH_2$ in concentrations below 35%) at 40 to 70°C. The gel is prepared by any of the usual neutralization methods, by reacting activated or finely powdered aluminum with water, or by precipitating the gel in the presence of the amine.

Keith prepares nordstrandite by precipitating a gel from aluminum chloride with ammonium hydroxide at 27 to 49°C and at pH 7 to 9. Upon washing and aging (2 to 5 days) at 43 to 49°C, nordstrandite is obtained; aging at 24 to 32°C gives gibbsite. Keith, Keith et al., and Teter et al. describe the preparation of commercial products for catalytic uses containing nordstrandite.

Ginsberg, Hüttig, and Stiehl state that conversion of bayerite to gibbsite begins with inclusion of alkali ions in the layer lattice, sodium being more effective than potassium at 20°C. Pseudoboehmite, the precursor of boehmite, is present in

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precipitates formed at 60°. Use of ammonium hydroxide as a precipitating agent gives distorted bayerite (nordstrandite), which, with sodium hydroxide, transforms to gibbsite.

3-5 PREPARATION OF THE ALUMINUM MONOHYDROXIDES

3-5-1 Boehmite, a-$Al_2O_3 \cdot H_2O$, Alpha Alumina Monohydrate

Boehmite occurs in nature in the European bauxites. It can be prepared by aging aluminum hydroxide gels, by thermal dehydration of gibbsite, bayerite, or amorphous aluminum hydroxide, and by rehydration of the higher oxides. Although the products from these different paths of transition may have substantially the same X-ray diffraction pattern, they differ markedly in properties. This is ascribed to the ease of preparation of boehmite in a wide range of surface area or activity, from about 15 m^2/g for the hydrothermal product to about 400 m^2/g for some of the aged gels.

As indicated in Sec. 3-3, the normal sequence of transition of amorphous aluminum hydroxide at atmospheric pressure, and above about 20°C is to gelatinous boehmite, to bayerite, to gibbsite. Tosterud, Ginsberg, and Oomes have found that gibbsite reverts to coarse-crystalline boehmite at 60 to 100°C in sodium hydroxide solutions.

Lippens favored the method of Schmäh for preparing the surface-active form of boehmite. Fibrous aluminum hydroxide was formed by room-temperature treatment of amalgamated aluminum foil (99.99% Al) with water vapor. After aging the amorphous material in twenty times its amount of water for about 300 hours, the product was dried in vacuum over P_2O_5 to a composition corresponding to $Al_2O_3 \cdot 1.6 \ H_2O$, and having a surface area of about 400 m^2/g. The diffuse X-ray pattern of pseudoboehmite was given, but when the aging time was extended to 290 hours, bayerite lines began to appear. About the same results were obtained by topochemical conversion of alum at pH 9.2 within 22 hours.

A very suitable method for preparing well-crystallized boehmite of low surface area is by hydrothermal conversion of Bayer alumina trihydrate in water (Hüttig and von Wittgenstein) or in dilute sodium hydroxide solution at 150 to 300°C. The charge of Bayer trihydrate may be as concentrated as 400 g/l. The Bayer trihydrate usually provides a small amount of alkalinity to aid the conversion. About 6 hours is required for conversion at

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180°C in water, but the product has excess water (about $Al_2O_3 \cdot 1.125\ H_2O$). Schwiersch obtained the theoretical water content by prolonging the digest time to 106 hours at 300°C. Hüttig, Peter, and von Wittgenstein obtained boehmite by heating dried alumina trihydrate in a bomb at 200°C, without a water medium. Massive Bayer alumina trihydrate (precipitor scale), cut to geometrical forms, converts to boehmite in place without disintegration under these conditions.

The conversion to boehmite is faster with increasing concentration of alkali within limits, and with increasing temperature, and increasing fineness of the charge. Ginsberg and Köster found that the conversion is about as fast for 0.6 g Na_2O/l as for 140 g/l at 180°C. They concluded, contrary to Bauermeister and Fulda, that boehmite forms by dehydration in place. Sato agreed with this. Present evidence indicates that while formation in place is the normal mode, it probably occurs by solution and reprecipitation. Precipitation can be induced on boehmite seed out of contact with the charge, and at an accelerated rate. Moreover, the rate of conversion is not the same as for dry dehydration. The equation for simple dehydration has the form: ln H = Kt, in which H is the molar concentration of combined water in the solid product at time t, and K is a constant. The equation for the hydrothermal conversion satisfies the form:

$$\frac{dM}{dt} = \frac{KnM^2}{3t^{K+1}}$$

, in which M is the molar amount of boehmite formed per mole Al_2O_3 at time t, and K and n are constants. The equation indicates that the rate is proportional to the amount of boehmite present.

Residual alkali may be reduced below 0.05% Na_2O in water digests by heating at 180 to 220°C (Sablé). Boehmite forms in well crystallized rhombs from alkaline solutions, but generally as ellipse-shaped plates, often as coarse as 5 microns, when formed in water. This process has been investigated to some extent as a potential source of alumina for ceramic purposes (Cera). It will probably receive more attention in the future.

Bloch claimed a boehmite process comprising heating finely divided metallic aluminum in water at 250 to 375°C. LePeintre obtained boehmite by electrolysis of a solution of aluminum sulfate and aluminum chloride at pH 4.0. Keith stabilized gel precipitates in the boehmite phase and prevented peptization by gassing the aqueous suspension with carbon dioxide.

Bugosh has developed a fibrous hydrothermal boehmite having discrete fibrils of average length, 0.1 to 0.7 micron, and

surface area of 50 to 450 m^2/g. Bugosh et al., and Bruce investigated the ceramic possibilities of this material in binders, coatings, and thickening, emulsifying, and suspension agents.

Boehmite forms as packets of fibers, oriented in preferential crystallographic directions on albite (Si_3AlO_3)Na, when the albite is subjected to hydrothermal treatment in water containing CO_2 at 200°C, according to Tchoubar and Oberlin.

Boehmite prepared by thermal dehydration of Bayer trihydrate and bayerite at about 170 to 500°C is likely to contain mixtures of other phases, depending upon the particle size, the rate of heating, the ambient pressure, and impurities present. This form has high surface area.

3-5-2   Diaspore, β-$Al_2O_3 \cdot H_2O$, Beta Alumina Monohydrate

Diaspore occurs rarely in well crystallized form in some Russian sources, but more abundantly mixed with flint clay in deposits in Missouri, and in high-iron nodular deposits in central Pennsylvania. Its main ceramic use has been in refractory brick. With gradual depletion of the refractory grades of diaspore, calcined bauxite is a replacement. Diaspore is of little use in the Bayer process of purification because of its poor solubility.

Laubengayer and Weisz were the first to prepare diaspore synthetically. The preparation required hydrothermal digestion of aluminum hydroxide in water at high pressure, and in the presence of seed diaspore upon which the diaspore was grown. Diaspore is the stable phase between 280 and 450°C, and at water pressures above 140 atmospheres, a rather formidable set of conditions for prospective commercial applications.

Krishner and Torkar prepared diaspore without seeding by reacting aluminum turnings with steam, and in a lower pressure region (about 100 atm.).

3-6   TRANSITION ALUMINAS

3-6-1   Dehydration Mechanism

The transition aluminas include the group of phases which fall between boehmite and corundum. The group originally had

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been designated loosely as gamma alumina. None has been found
in nature, but all have been prepared by thermal transformations,
and in some cases, by hydrothermal transformations of the alumi-
num hydroxides, and by oxidation of aluminum. Although designated
as oxides, some are probably hydrous. These structures have pre-
sent ceramic uses, particularly as adsorbents, catalysts, coat-
ings, and soft abrasives.

Stumpf, Russell, Newsome, and Tucker described the X-ray
patterns, transition sequences, and temperature ranges of seven
modifications, arbitrarily designated as chi, eta, gamma, delta,
kappa, theta, and alpha aluminas. They found that the sequence
of phases is influenced by the starting material. The transi-
tion temperatures are influenced by the amount of water vapor
in the atmosphere and by impurities. They found that Bayer
alumina trihydrate transforms successively to boehmite, to chi,
to gamma, to kappa, to alpha alumina. Bayerite transforms to
boehmite, to eta, to theta, to alpha alumina. Hydrothermal boehm-
ite transforms to gamma, to delta, to theta, to alpha alumina.
The designations were based primarily on differences in X-ray
diffraction patterns.

Other investigators have since discovered new phases, or
disagreed with the X-ray patterns or even the existence of the
present phases.

Before proceeding with the preparation methods for the transi-
tion phases, it seems desirable to review early investigations
of the dehydration process. Peculiarities in the dehydration
phenomena of the aluminum hydroxides have been revealed by static
and dynamic heating methods. These peculiarities are doubtless
related to the double layer structure found by Megaw in 1934 for
gibbsite, and which persists in other transition forms.

In 1932, Fricke and Severin determined the equilibrium water
contents versus temperature of the trihydroxides and mono-
hydroxides (Figure 1). Long periods (weeks) were required to es-
tablish equilibrium in some portions of the temperature range,
100 to 400°C, in others the time was relatively shorter. Gibbs-
ite dehydrated to about the water content of boehmite at 165°C,
and bayerite at 120°C, when both were held at a pressure of 100
mm Hg, but the actual transition points were vague. In the re-
gion of dehydration below residual water content corresponding to
$Al_2O_3 \cdot H_2O$, both gibbsite and bayerite dehydrated to lower water
levels than either hydrothermal boehmite or diaspore for the same
dehydration conditions.
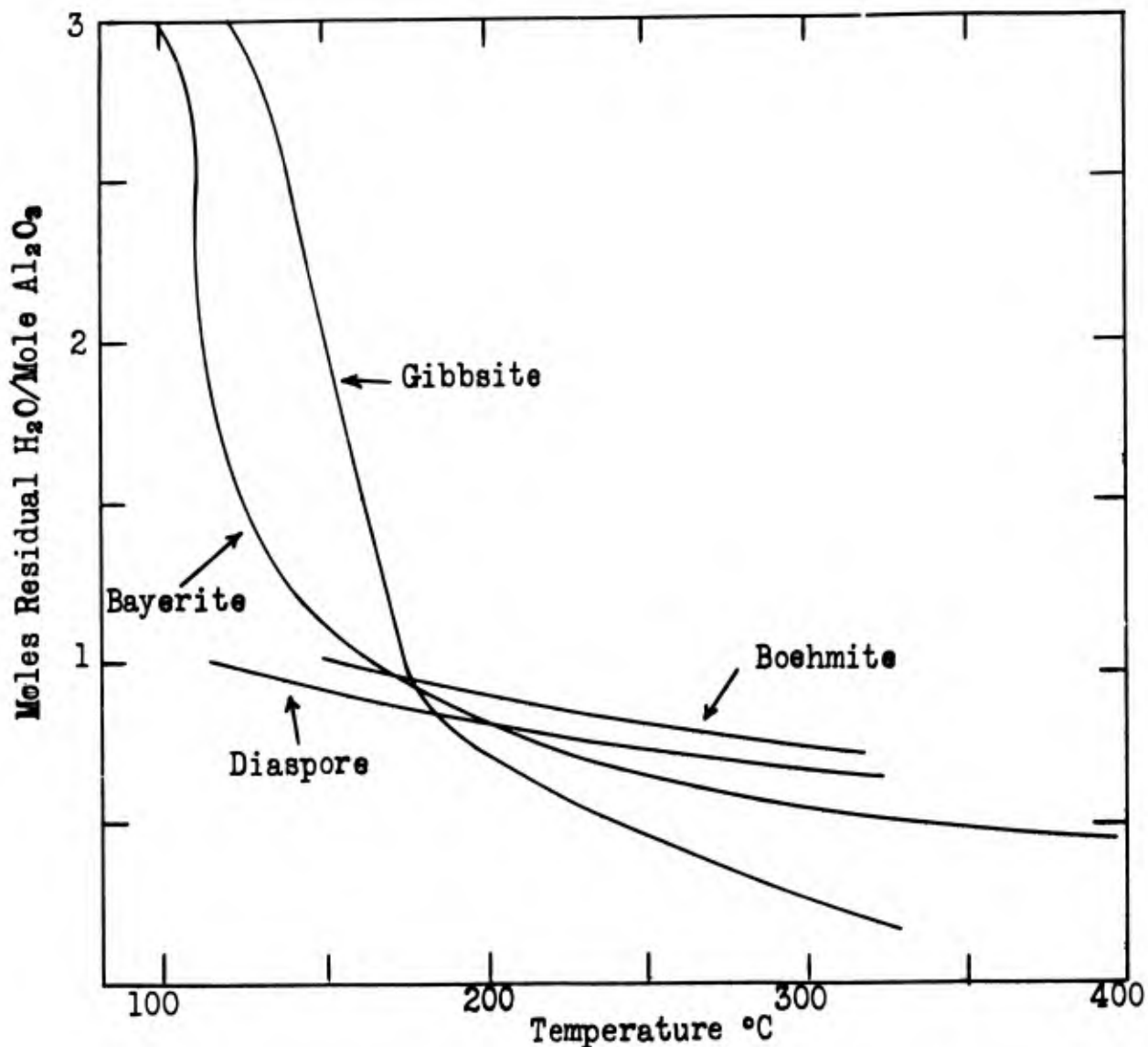
Figure 1. Dehydration Equilibria of Heated Alumina
Hydrate (After Fricke and Severin)

At atmospheric pressure, the course of dehydration of
gibbsite and bayerite (Figures 2 and 3) takes place in two
stages. The first stage dehydrates to a composition having a
water content below $Al_2O_3 \cdot H_2O$. The lower the heating tempera-
ture used to attain equilibrium, that is, the slower the dehy-
dration rate, the more nearly the structure approaches $Al_2O_3 \cdot H_2O$.
Even at 200°C, the rate of dehydration is very slow at atmos-
pheric pressure.
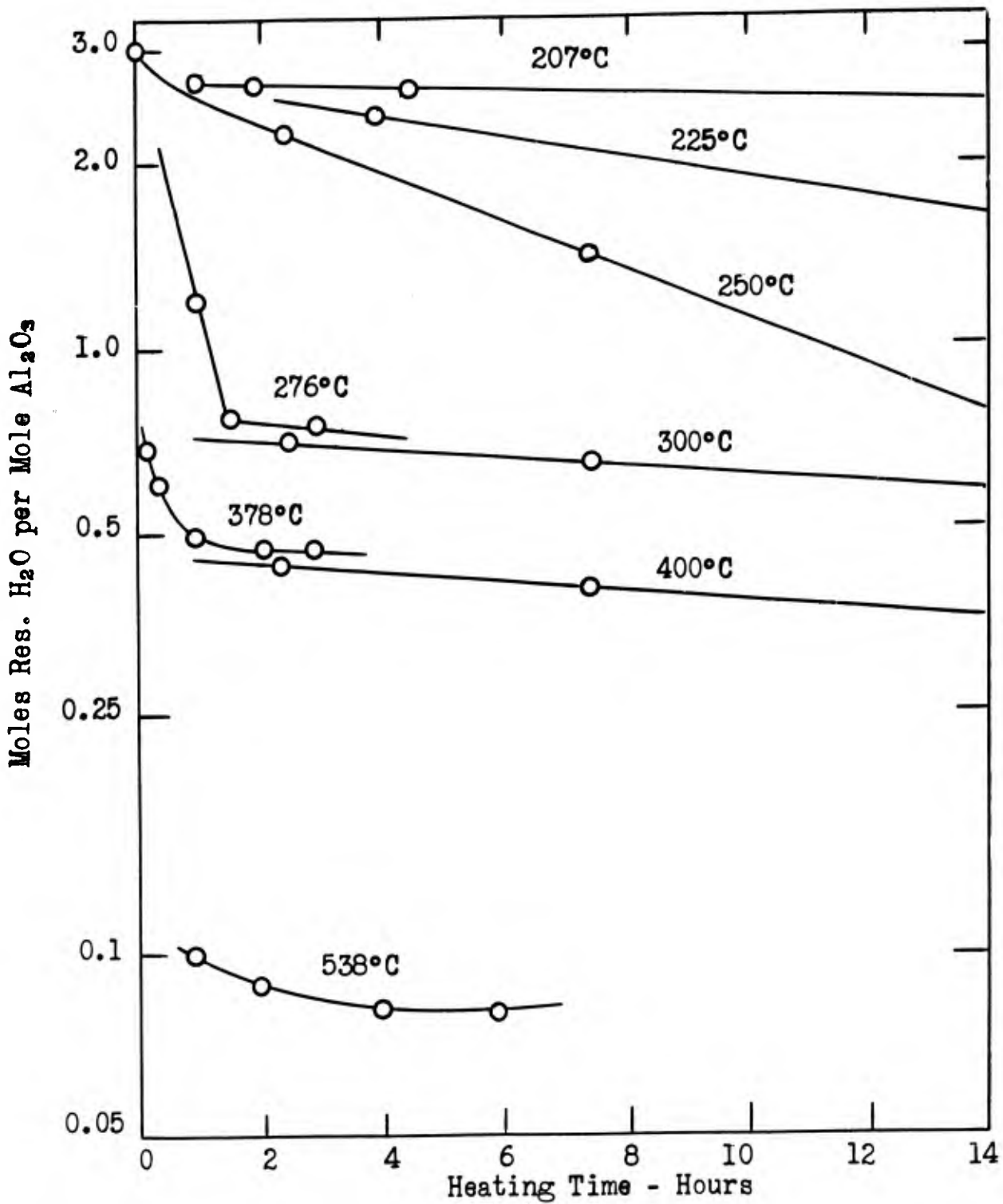
Figure 2. Dehydration of Bayer Gibbsite at Constant Temperature
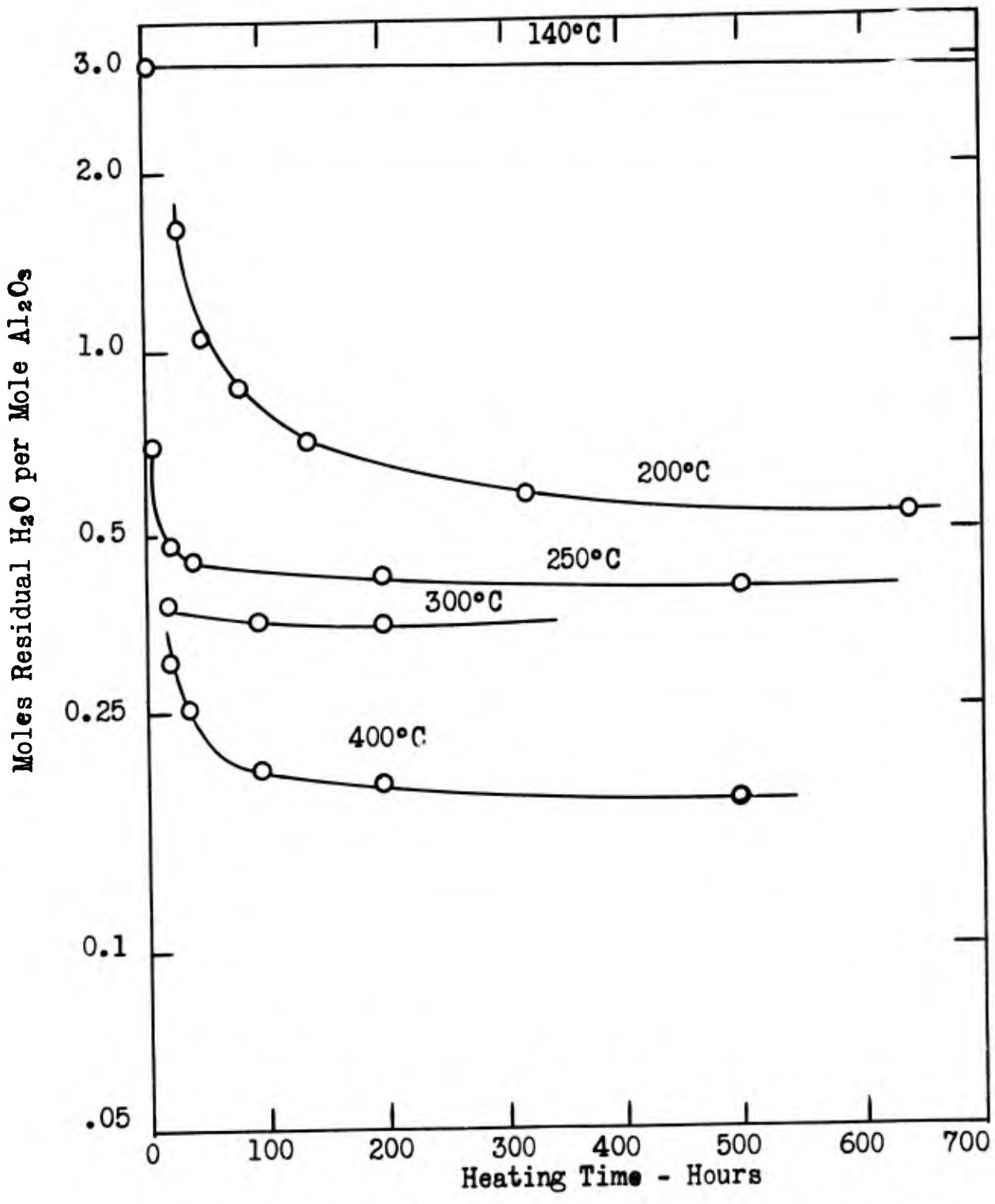
Figure 3. Dehydration of Bayerite (CO_2 Precipitated) at Constant Temperature

Blanchin decomposed alumina trihydrate at 100°C in vacuum. Blanchin, Imelik, and Prettre; and Tran-Huu et al. found that for an infinitely slow rise in temperature, the two stages of dehydration are separated by a temperature interval of about 100°C, during which the boehmite phase is stable, but very close to the composition $2Al_2O_3 \cdot H_2O$. Prettre et al. confirmed that for heating periods of 20 hours, the water content decreases uniformly in a 70°C interval from $Al_2O_3 \cdot 3H_2O$ at 100°C in vacuum (or 150°C at one atmosphere) to $2Al_2O_3 \cdot H_2O$, where an arrest for an 80° interval was observed before loss of water was again appreciable. Dehydration was essentially complete at 400°C in a vacuum, and at 500°C at atmospheric pressure. Chatelain found that gibbsite, when dehydrated in air or vacuum at about 230°C, becomes a mixture of boehmite and imperfectly crystalline Al_2O_3. Courtial and co-workers found that boehmite and a more or less amorphous solid are produced either simultaneously or successively at 230°C, and that the composition conforms to $Al_2O_3 \cdot 0.69\ H_2O$. Based on thermogravimetric (TGA), calorimetric, and chemical methods, the water contents were computed, and the relative amount of each phase present was determined.

Brown, Clark, and Elliott were the first to deduce that gibbsite decomposes by two mechanisms (1) to gamma alumina directly, and (2) to boehmite, which subsequently decomposes to gamma alumina. Day and Hill thought that gibbsite and bayerite decompose directly to anhydrous alumina, and that this subsequently rehydrates partially to form boehmite.

Papée and Tertian explained the two paths of transition as the result of buildup of steam pressure in the coarser particles to create a hydrothermal condition favoring boehmite formation. At about 200 to 220°C, the internal pressure causes fracturing of the crystals to terminate further formation of boehmite. Also, very fine particles might show less boehmite formation (Tertian and Papée).

Eyraud, Goton, and co-workers found that after a short induction period, the rate of decomposition was constant to about $Al_2O_3 \cdot H_2O$ at specific temperatures, beyond which the rate decreased (Figures 2 and 3). They investigated dehydration rates in the temperature range 206 to 243°C and in the pressure range 0.001 to 15 mm Hg water vapor pressure. They obtained activation energies ranging from 31 to 63 kcal/mole. Brindley and Nakahira obtained activation energies of 31 to 35 kcal/mole for the gibbsite to boehmite reaction, and 46.5 kcal/mole for the gibbsite to chi alumina reaction. They used a thermobalance to measure the weight loss, and applied an Arrhenius-type relation,

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ln K = ln A = 0.4343 E/RT, where T is the temperature in degree Kelvin, R the gas constant, and A a frequency constant.

Papée and Tertian, and de Boer derived differential heating curves from static thermal dehydration curves similar to Figure 1. The derived curves resemble actual curves obtained by differential thermal analysis (DTA).

Orcel; Jourdain; Norton; and Speil applied DTA to gibbsite and diaspore. Gibbsite heating curves reveal peaks of heat absorption (endothermic) at about 225, 300, and 550°C, and a peak of heat release (exothermic)at about 980°C. Diaspore has a single endothermic peak at about 500°C. Both gibbsitic bauxite and synthetic gibbsite reveal marked differences in intensity between the first and third peaks with respect to the second peak; in some cases, the first and third are absent. Steggerda demonstrated that these differences are related to particle size. DTA curves are shown in Figure 4 for gibbsite, bayerite, boehmite, and diaspore. Also shown are two curves for two fine commercial grades of gibbsite, Hydral 705 (0.4 micron) and Hydral 710 (0.9 micron), which show the marked reduction in intensity of the peaks involved. De Boer, Fortuin, and Steggerda concluded that the first peak represents boehmite formed by hydrothermal pressure within the crystals that are coarser than about one micron. The second peak represents the formation of an anhydrous phase (chi alumina) following crystal disruption at about 200 to 220°C. The third peak at about 550°C represents the dehydration of the boehmite formed under the first peak.

Boersma and de Jong discussed the quantitative aspects of DTA. Smothers et al., and Schmitter identified and classified various patterns. Alexanian applied DTA to the gibbsite dehydration in the range to 1400°C, and established the temperature stability for the following phases: gibbsite (to 220°C), boehmite (280°), a phase at 380° (chi?), gamma (400°), delta (560°), kappa (900°), alpha alumina (from 1300°). Calvet, Thibon, and Gambino obtained characteristic thermograms in a micro calorimeter for amorphous gel, pseudoboehmite, normal light boehmite, and a fine boehmite.

LeChatelier observed the sudden heat release at about 850°C during calcination of alumina prepared from nitrates and chlorides, but not for alumina from sodium aluminate. Heat evolution in this case can be induced by small amounts of fluorides. The method is used practically to increase mineralization of the alumina, and to conserve fuel by reducing the calcination temperature required to make the alumina nonhygroscopic (Pechiney).

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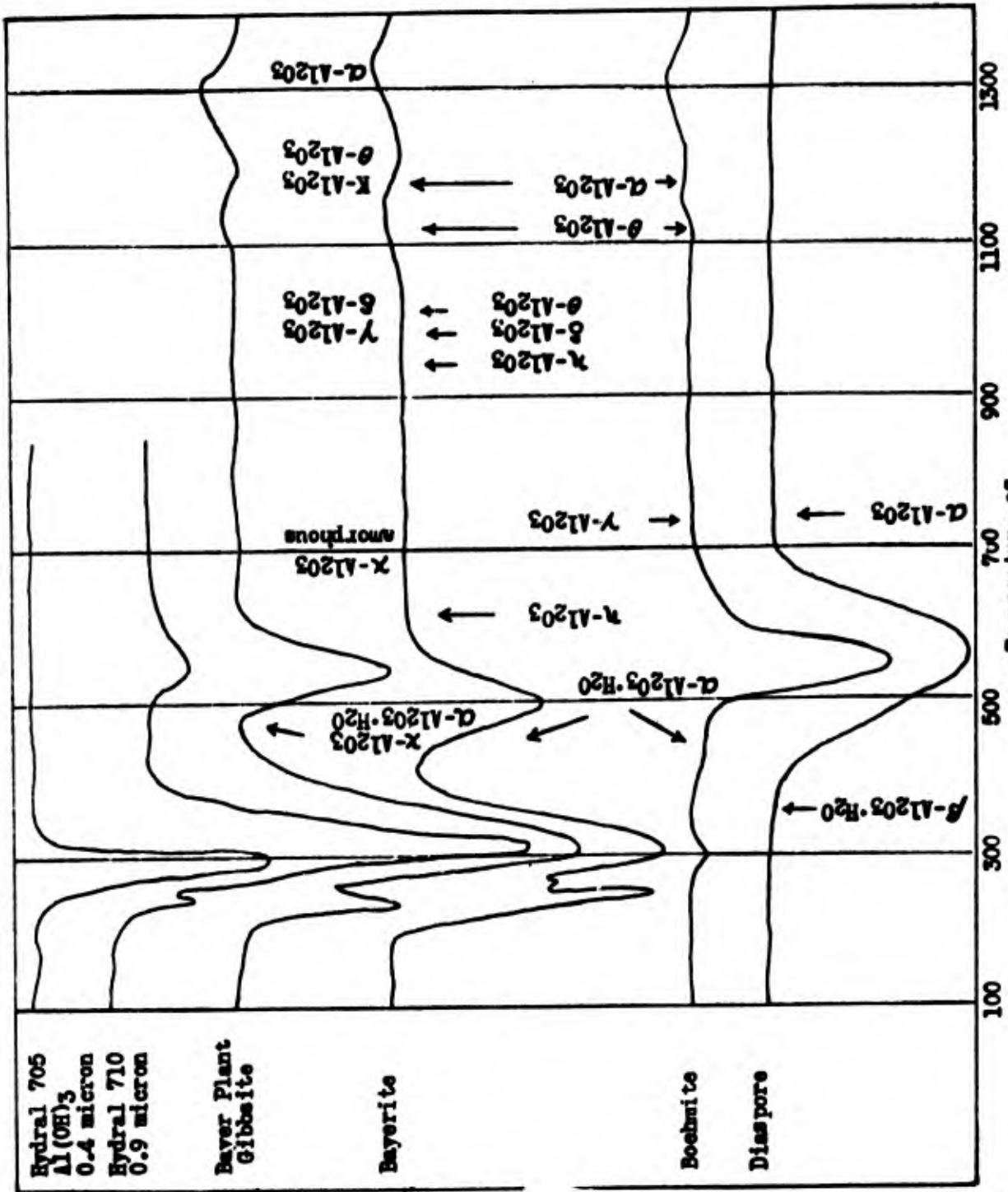
Figure 4. Differential Thermal Curves for the Hydrated Aluminas

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Maximum crystal size is attained for an aluminum fluoride concentration of about 1.4% (Lindsay).

Following the work on sequence of the transition phases of alumina by Stumpf et al., more or less complete surveys have been made by Rooksby; Day and Hill; Newsome et al.; Thibon, Charrier, and Tertian; Tertian and Papée; Ginsberg, Hüttig and Strunk-Lichtenberg; Stirland, Thomas, and Moore; de Boer and associates; and Sato. Of these, Tertian and Papée have furnished the most detailed description.

Lippens classified the transition aluminas into two groups: (a) low-temperature, dehydrated below 600°C and containing up to 0.6% H_2O, including the phases, rho, chi, eta, and gamma; (b) high-temperature, nearly anhydrous, obtained at 900 to 1000°C, and including the phases, kappa, theta, and delta. Several other phases have been proposed.

3-6-2 Sequence of Transition

The following sequences of transitions (shown graphically in Figure 5), mainly due to Stumpf et al. and Tertian and Papée, are generally accepted, although there is confusion about the X-ray identification of some phases and the existence of others. The sequences are affected not only by the starting materials but also by their coarseness of crystallinity, heating rates, and impurities. The approximate temperature ranges of stability of the phases are included.

Gibbsite Transitions

In vacuum, coarse or fine material: gibbsite transforms to rho (100 to 400°C), to eta 270 to 500°C), to theta (870 to 1150°C), to alpha alumina (1150°C).

Instantaneous dehydration at 800°C: gibbsite to eta, to theta, to alpha alumina.

In air, fine gibbsite: gibbsite to chi (300 to 500°C), to kappa (800 to 1150°C), to alpha alumina.

In air, coarse gibbsite: (1) gibbsite to chi, to kappa, to alpha alumina. (2) gibbsite to boehmite (60 to 300°C), to gamma (500 to 850°C), to delta (850 to 1050°C), to theta, to alpha alumina.

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Bayerite Transitions

The bayerite transitions are substantially of the same type as the gibbsite transitions except that fine bayerite in air transforms as follows: bayerite to eta (250 to 500°C), to theta (850 to 1150°C), to alpha alumina.

The difference between bayerite and gibbsite transitions is the substitution of eta for chi alumina, and the absence of kappa alumina in the bayerite transitions.

Boehmite Transitions

Fine boehmite (pseudoboehmite, 350 m²/g): boehmite to bayerite, to eta (100 to 350°C), to theta, to alpha alumina.

Coarse hydrothermal boehmite (less than 15 m²/g) prepared from gelatinous aluminum hydroxide, gibbsite, bayerite, or higher transition phases by digestion in H_2O at above 150°C: boehmite to gamma (360 to 860°C), to delta, to theta, to alpha alumina.

Diaspore Transitions

Deflandre in 1932 had shown that diaspore transforms to corundum by an ordered process, without intermediate products, at about 450 to 600°C. Herold and Dodd observed that diaspore clay forms corundum and gamma alumina at 400°C, but that between 400 and 750°C there is a gradual expansion in the size of the corundum unit cell, as determined by X-ray. Upon continued heat treatment at higher temperatures, the unit cell gradually reduces to the true dimensions.

Rho Alumina

Rho alumina is primarily a vacuum-produced phase. It is substantially amorphous, as its X-ray pattern shows only a few diffuse bands, the most pronounced having a spacing of about 1.40 A. It has a surface area of about 200 m²/g, and micropores not accessible to nitrogen. Rehydration of rho alumina by water at 25°C gives very pure bayerite (Tertian and Papée). It is therefore possible to prepare all the transitions from gibbsite, either by dehydration, or rehydration.

Chi Alumina

Chi alumina is distinguished by an X-ray spacing of 2.12 A, and is probably cubic, but not of the spinel type. Tertian and Papée claim that the Alcoa structure for chi alumina is a mixture of chi and gamma aluminas.

Gamma Alumina

Gamma alumina, according to Stumpf, is the cubic structure obtained by heating Bayer alumina trihydrate or hydrothermal boehmite at 500°C. Rooksby concurred with Hägg and Verway in designating gamma alumina as a spinel. This is probably the eta alumina of Stumpf. Gamma alumina (Stumpf's designation) is distinguished from eta alumina by differences in relative intensity and sharpness of the lines for eta, by the line at about 4.6 A for eta, and by splitting, for gamma, of a line appearing at 1.97 for eta. In other respects, the two patterns are closely related.

Kimberlin and Gladrow prepared eta alumina for use as a catalyst support by hydrolysis of an aluminum alcoholate at zero to 21°C, aging the water suspension for 20 to 65 hours to form beta trihydrate, and calcining at 345 to 650°C. Kirshenbaum and Hinlicky treat similarly, but heat finally at 200 to 800°C.

Hunter and Fowle obtained eta alumina by the oxidation of aluminum near its melting point, as well as by electrolytic oxidation. Caglioti and d'Agostino produced transition alumina by blowing air through molten aluminum. Filonenko, Lavrov, Andreeva, and Pevzner obtained an alumina spinel, $AlO \cdot Al_2O_3$, by intense reduction during fusion of alumina.

Houben and de Boer suggest that the crystalline structure of gamma alumina is probably due to the presence of about 3.4% water in the lattice (one mole H_2O per five moles Al_2O_3) to fill all open spaces in the spinel lattice. Additional water may react with the surface until the surface formula might be described as $AlO \cdot OH$, while the internal structure is HAl_5O_8.

MacIver et al. differentiated gamma from eta alumina by its higher water content. This was regarded as consisting of molecular water strongly adsorbed on the surface of the gamma alumina.

Yanagida and Yamaguchi prepared gamma alumina by

hydrothermal treatment at 500°C and 50 atmospheres pressure for 20 hours of boehmite previously dehydrated in air at 700°C. It contained 7.5% water upon drying at 150°C, and had a tetragonal axial ratio of 1.0357. An eta alumina specimen of lesser tetragonal deformation was obtained from dehydration in air of bayerite. It contained 3.8% water. Successive heat treatments at 400, 600, and 800°C, with cooling to room temperatures after each heat treatment, reduced the water contents of each alumina. The axial ratio and lattice dimensions of the gamma alumina were also reduced.

Cowley ascribed the extra spots and line segments, observed in electron diffraction patterns of gamma alumina on heated aluminum foil, to faults in the cubic close-packed stacking of the oxygen atoms, and arbitrarily designated the new phases xi, xi', nu, and mu. Alexanian claimed that these phases are merely mixtures of two real successive phases. He points out that traces of SiO_2, K_2O, Na_2O, and Li_2O combine with alumina above 600°C to give X-ray lines foreign to those of the actual phase.

Ando prepared gamma alumina by vaporization in an electric arc of an alumina-carbon electrode containing a mixture of alpha and gamma alumina bonded with low-ash carbonaceous material.

Delta Alumina

The initial patterns for delta alumina, of Stumpf et al., were obtained from low-soda hydrothermal boehmite that had been calcined in steam at 1000°C for one hour. Rooksby, and Rooksby and Rooymans suggested other preparation methods, some involving the presence of impurities to develop the structure. Improved structure was claimed for the delta phase by heating hydrothermal boehmite for 120 hours at 930 to 950°C. The phase is also obtained by rapidly calcining a mixture of 50 parts ammonium alum and 10 parts ammonium molybdate at 950°C, and holding for one hour at temperature. Delta is the form obtained by flame-spraying commercial-grade corundum on graphite substrate. The corundum should contain both lithium and sodium ions as prominent impurities. The product converts to delta alumina upon heating at 1000 to 1100°C. The necessity for so much impurity in these latter compositions is not very convincing for the method. Rooymans found Rooksby's product to be tetragonal. Tertian and Papée considered delta phase truly amorphous.

Plummer found that passage of gamma or alpha alumina through the oxyhydrogen flame forms well-developed crystals of delta and theta aluminas, providing the final particles are less than

15-micron spheres. Larger particles were alpha alumina. Juillet similarly hydrolyzed aluminum chloride vapors to obtain spherical globules only 150 A in diameter, mainly delta alumina, and with a specific area of 100 m²/g. Delta alumina has also been obtained by combustion of aluminum in air or oxygen, or in the presence of carbonaceous material, or by combustion of aluminum carbide in oxygen (Wartenberg 1952; Schneider and Gattow 1954; and Foster, Long, and Hunter 1956). Cuer and co-workers found that the flame reactor using an oxygen-hydrogen mixture is particularly suitable for preparing nonporous alumina chiefly in the delta phase and in spherical form.
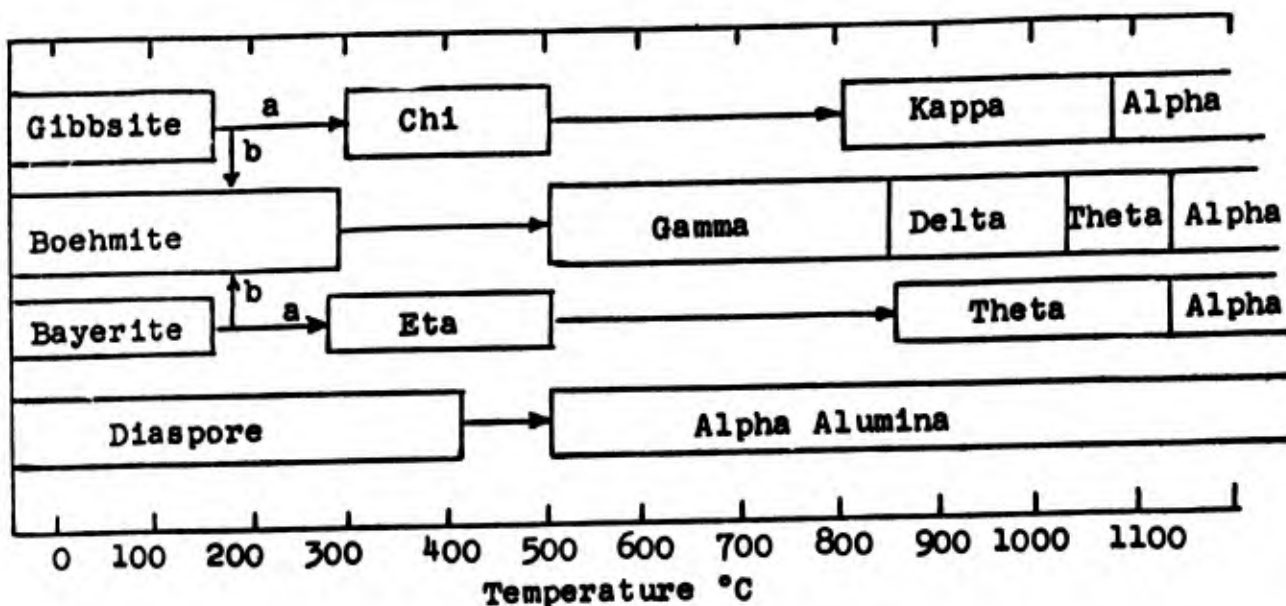
Figure 5. Dehydration Sequence of Alumina Hydrates in Air

Note: Enclosed area indicates range of stability. Open area indicates range of transition. Path b is favored by moisture, alkalinity, and coarse particle size (100 microns); path a by fine crystal size (below 10 microns).

Kappa and Theta Alumina

Kappa and theta aluminas, and some alpha alumina are the principal components of metallurgical-grade alumina. Kappa alumina has received some attention as a dental polish (Broge). Both structures are well crystallized and of markedly lower surface area than the lower transition phases. Kappa is orthorhombic

and theta is monoclinic. Kappa is the normal phase obtained by calcining fine-crystal gibbsite. It is prepared in fair purity from Bayer trihydrate by atmospheric dehydration in the narrow range, 1000 to 1050°C. Tertian and Papée claimed that the Alcoa structure for kappa is a mixture of true kappa' and delta aluminas.

Theta alumina is the normal product obtained by calcination of fine-crystal bayerite. It is prepared by heating bayerite for one hour at 1100°C in moving dry air.

Funaki and Shimizu (1959) determined that the thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$, and $Al(OAc)_3$ at 500 to 700°C is to amorphous alumina. On thermal decomposition, $Al_2(SO_4)_3 \cdot 18H_2O$ and $NH_4Al(SO_4)_2 \cdot 12H_2O$ yield gamma alumina at 850 to 900°C, but the product contains some amorphous alumina. All of the mentioned salts yield upon further calcination gamma, delta, theta and alpha aluminas, and in that order.

3-6-3 Phases Formed on Aluminum

An instantaneous amorphous film about 20 A thick forms on aluminum in air (Hass). Growth to about 90 A continues and stops in about one month. Heated films become crystalline at about 500°C. Aylmore, Gregg, and Jepson investigated the effects of exposures of 170 to 400 hours at atmospheric pressure and at 50°C intervals from 400 to 650°C. Oxidation at 400°C follows a parabolic-rate law. At higher temperatures the gain in weight rates consists of three distinct types in which the rate decreases, becomes constant, and again decreases.

Greenblatt found that the structure of oxide films formed on aluminum after exposure to water at 150 to 350°C consists of zones which increase in number as the exposure becomes more extreme and with ease of corrosion of the aluminum type. Columnar structures were observed joining the outer crystalline layer to the metal surface at the site of second-phase particles. Taylor, Tucker, and Edwards found that the oxide from electrolytic oxidation at less than 100 volts is amorphous, but is eta alumina at higher voltages. Lichtenberger noted that the oxidation of films at 20 to 80 volts originated as nuclei at the grain boundaries, then spread radially and coalesced until a barrier layer formed. Cass found that the film is anisotropic and biaxial, the bisector of the optical axes being always perpendicular to the surface. Koenig measured the lattice constant and found that it varies from 7.73 to 8.06 A, but is about 7.89 A at 800°C for all

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formation methods. Burnham and Robinson stated that electrolysis of aluminum at high voltages in boric, citric, and tartaric acids is nonporous, platelike, gamma-type alumina of hexagonal symmetry. Bergmann prepared bayerite by electrolyzing aluminum in dilute solutions of hydrogen peroxide, and mixed boehmite-bayerite in solutions containing carbon dioxide.

Steinheil prepared face-centered cubic "epsilon alumina" having a spacing constant of 5.33 A by oxidation of aluminum. Single crystals of beta-alumina were also obtained upon heating to melt off the metal.

Hannon patented the method of preparing aluminum oxide by grinding aluminum pellets, while maintaining the pellets free from contact with substances other than aluminum.

Continental Oil Company claims an epsilon alumina having a surface area of 300 m^2/g, prepared by hydrolysis of aluminum alcoholate at 80 to 100°C, and calcining to produce almost exclusively the phase.

3-6-4 Rehydration

Rehydration of the intermediate, rho alumina, was mentioned previously as a method for preparing pure bayerite. Rehydration is a factor of significance in connection with the formation of active aluminous sorbents, their continued cyclic use, and gradual changes in their sorptive capacity. Nieuwenberg and Pieters, and Hüttig and Kölbl investigated rehydration of activated alumina. The latter prepared curves of isobaric dehydration and hydration. Bentley and Feichem demonstrated the rehydration of anhydrous intermediate alumina to boehmite in steam. Day and Hill claimed that boehmite is formed in dehydrating both gibbsite and bayerite by secondary reactions between the original dehydration products and the water released.

Calvet and Thibon investigated the rehydration of activated aluminas prepared from gibbsite and bayerite sources in a microcalorimeter (Calvet). They found that alumina activated in a vacuum is more easily rehydrated than that activated at atmospheric pressure. Increase in the temperature of activation has an unfavorable effect on the tendency of the alumina to rehydrate. Alumina which has been activated at 180 to 200°C under vacuum and then heated in air at about 350 to 450°C does not rehydrate as readily as unheated alumina.

Tertian and Papee found that vacuum-dehydrated Bayer tri-hydrate (rho alumina) rehydrated to bayerite at 25°C, but any contained hydrothermal boehmite remained unchanged. Rho alumina prepared from bayerite was influenced by the conditions of water vapor release during the initial dehydration. Slow release and long contact of the water with the active surface greatly reduces the rate of rehydration. Rehydration to boehmite occurs at 100°C but requires days. Amorphous alumina produced by calcination of aluminum salts at 500 to 700°C rehydrates at room temperature to bayerite, and then gibbsite, independently of bayerite formation (Funaki and Shimizu 1959). These investigators in 1952 found no transformation of bayerite into gibbsite at room temperature during a 10-year aging period.

Ervin and Osborn found no rehydration for alpha alumina of low surface area. Krishner and Torkar prepared an active form of alpha alumina (pseudocorundum, by analogy with boehmite nomenclature), having a surface area of 40 to 70 m²/g, probably representing primary particles without micropores. The active alpha alumina hydrated to boehmite and diaspore, the latter in the form of small rods.

3-7 ALPHA ALUMINA

3-7-1 Preparation

The principal sources of alpha aluminum oxide are native corundum and manufactured production derived from bauxite. Mining of a corundum deposit in South Carolina was in operation during the war. Corundum from South Africa (Northern Transvaal) is still used, mainly for abrasives. Manufactured abrasives are, in general, superior. The South African product, according to Palmour, Waller et al., analyzes about 85% Al_2O_3, 4% TiO_2, 8% SiO_2, and 1% Fe_2O_3.

The principal methods for preparing alpha aluminum oxide are: calcination of the aluminum hydroxides, transition aluminas, and aluminum salts, and by solidification from melts. Less common methods are: hydrothermal synthesis at high pressure, vapor-phase transition, and burning aluminum in oxygen (Wartenberg 1952). Alpha alumina can be prepared in a wide range of properties insofar as they are affected by crystal size, crystal habit, and purity. Crystal size can be varied from about 0.03 micron to 30,000 microns or more.

The most important method for preparing alpha alumina for ceramic purposes, as well as for metal, is calcination of Bayer alumina trihydrate. Table 4 shows typical data for six commercial grades of ceramic alumina, designated "calcined aluminas." They are prepared at temperatures below the sintering level. They include variations in crystal size and in soda content. Also included in the table are four grades of tabular aluminas. The tabular aluminas are massive low-shrinkage forms that have been sintered without added permanent binders. The tabular aluminas are available in ball forms and in crushed and graded granular sizes from a top size of about one-half inch for dense forms (T-60 and T-61) to minus 325-mesh. A porous grade (T-71) having about 35 to 50% porosity is also available.

These aluminas are typical of the range of properties obtainable in Bayer process plants designed for the production of ceramic aluminas. With the exception of the grade designated A-1, all are substantially alpha aluminum oxide. The principal variations in these grades are crystal size, surface area and residual soda content. The grades, designated Calcined and Low-Soda Aluminas are soft-bonded and easily disrupted to ultimate crystallites.

The stated temperature of formation of alpha alumina from the transition phases varies from the range of 1100 to 1150°C (Stumpf et al.; Rooksby; and Tertian and Papée) to 1200 to 1300°C (Gorbuna and Vaganova, Arakelyan and Chistyakova). The transition is influenced by impurities and particle size. Dawihl and Kuhn prepared fine pure corundum containing less than 4 ppm Na_2O by calcining aluminum methylate, $AlO(C_2H_5)_3$, at 1200°C. Brundin and Palmqvist reacted a water-soluble aluminum salt and a water-soluble carbonate to obtain a microporous aluminum oxide.

Linde Company has furnished two commercial types of submicron aluminas prepared from ammonium alum. Type A is calcined in the alpha alumina range, is 99.9% pure, and is useful as an abrasive, a catalyst carrier, and a raw alumina for fine sintering. Type B has cubic structure and is suitable for the Verneuil process for making jewel alumina. Other references to processes involving decomposition of sulfates include Bretsznajder; Hegedüs and Fukker; Antonsen; Dingman et al.; and Stokes and Secord. Chirnside and Dauncey; Barnes; Burdick and Jones; Ikornekova and Popova; Nikitichev et al.; and Zemlicka discuss phases of the production of synthetic jewel corundum as a boule grown in the oxyhydrogen flame.

Ali specifies two ranges of hydrothermal transition as (1)

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Table 4

Typical Properties of Calcined and Low-Soda Aluminas

	A-1	A-2	A-3	A-5	A-10	A-14
Typical Properties						
Al$_2$O$_3$ .... %	98.9	99.2	99.0	99.2	99.5	99.6
SiO$_2$ .... %	0.02	0.02	0.02	0.02	0.08	0.12
Fe$_2$O$_3$ .... %	0.03	0.03	0.03	0.03	0.03	0.03
Na$_2$O .... %	0.45	0.45	0.45	0.50	0.10	0.04
Loss on ignition (1100°C) ...... %	0.6	0.4	0.4	0.2	0.2	0.2
Total H$_2$O (by Sorption-Ignition Test) .... %	1.	0.3	0.7	0.3	0.3	0.3
Bulk density, loose, lb/ft^3	55.	52.	55.	48.	60.	63.
Bulk density, packed, lb/ft^3	68.	68.	68.	63.	80.	83.
Specific gravity	3.6-3.8	3.7-3.9	3.6-3.8	3.7-3.9	3.8-3.9	3.8-3.9
Sieve analysis (cumulative)						
On 100 mesh ....%		4-15		2-10		4-15
On 200 mesh ....%		50-75		40-65		50-75
On 325 mesh ....%		88-98		75-95		88-98
Through 325 mesh ....%		2-12		5-25		2-12

Typical Properties of Tabular Alumina

	T-60	T-61	T-71	Balls 3/8 Inch
Typical Properties				
Al$_2$O$_3$ ....%	99.5+	99.5+	99.5+	99.5
SiO$_2$ ....%	0.06	0.06	0.04	0.04
Fe$_2$O$_3$ ....%	0.06	0.06	0.06	0.06
Na$_2$O ....%	0.05	0.02	0.01	0.05
Bulk density, packed lb/ft^3				
Converter discharge	125.	125.	85.	
Granular - Minus 14 mesh	135.	135.	.....	
Powder - Minus 325 mesh	140.	140.	.....	
Specific gravity	3.65-3.8	3.65-3.8	3.65-3.8	
Apparent porosity ....%	5.	5.	30.50	
Water absorption ....%	1.5	1.5	15.25	
74° to 212°F (Btu/lb/°F) ..				0.200
74° to 932°F (Btu/lb/°F) ..				0.233
74° to 1832°F (Btu/lb/°F) ..				0.244
Apparent porosity ....%				3.0
Water absorption ....%				0.9
Specific gravity				3.7-3.9
Balls per pound				202
Bulk density, lb/ft^3.......				135

Courtesy Aluminum Company of America

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The hydrothermal system Al_2O_3-H_2O has been investigated by Laubengayer and Weisz; Cooke and Haresnape; Ervin and Osborn; Roy and Osborn; Newsome; Druzhinina; Kennedy; and Krishner and Torkar. Ervin and Osborn used aluminum hydroxide gels in water to confirm and extend the phase diagrams of the earlier investigators. They delineated regions of stability for gibbsite, boehmite, diaspore, and corundum. Gibbsite transforms to boehmite at 140°C in room air or in water, at least up to 680 atm (10,000 psi).

Torkar and Krischner substituted formation reactions for dehydration reactions and extended the diagram to new fields (Fig. 6). At pressures above atmospheric the reaction of metallic aluminum of high surface with water was found sufficiently rapid and without the use of activators such as iodine or mercury. Besides forming diaspore at pressures of about 100 atm, other phases prepared included: metastable reactive alpha alumina ($a*$-Al_2O_3), formed between 320 and 400°C, and at steam pressures from 15 to 100 atm; "autoclave" gamma alumina, similar to eta or chi aluminas obtained by calcination; kappa-1-alumina, a new form that transforms into kappa alumina, and finally, stable alpha alumina. The temperature range found for hydrothermal alpha alumina agrees well with the range 400 to 550°C specified by Newsome. The reactive alpha alumina, of particle size only 300 to 800 A, had a lower density (3.7 g/cc) than for stable corundum (3.98). The thermodynamic relationship between the reactive form and corundum is analogous to that between pseudoboehmite and hydrothermal boehmite. The investigators considered the role of entropy and enthalpy in establishing reaction equilibrium and stability, a subject also discussed by Searcy. Krishner and Torkar determined the free enthalpy or "activity," assuming that the displacement of the equilibrium curve is due solely to the activity. Maximum attainable activity was taken as the disorder of the molten state. The excess of total enthalpy of the active alpha alumina was computed at 4 to 5 kcal/mole, and the entropy at 3.5 to 3.9 clausius higher than in stable alpha alumina. They concluded that reactions with active forms begin sooner and proceed faster than with stable substance. Sintering occurs sooner, and reactions can take place at lower temperatures, a desirable feature for ceramic applications.

Newsome obtained relatively large crystals of alpha alumina at 450°C and 300 atm steam pressure. Yanada et al. claim that the dimensions of the crystals depend on the grain size of the starting aluminum hydroxide. Kryukova and Nozdrina found that about 65% of the pressure-crystallized material is boehmite, 10% is diaspore, and only 20% is corundum. Yamaguchi et al. determined that the equilibrium solubility of corundum is independent of

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pressure. The gram equivalent ratio of dissolved corundum with respect to aqueous sodium hydroxide is 2.46 at 350°C, and 2.95 at 500°C. The activation energy is 3.8 kcal. Nucleation without seed starts at a supersaturation ratio of 0.12.

Ballman described a method for growing synthetic rubies on seed crystals in an aqueous medium containing corundum and a soluble chromium compound in contact with solid corundum held at 415 to 520°C, and not more than 20° higher than the seed temperature.
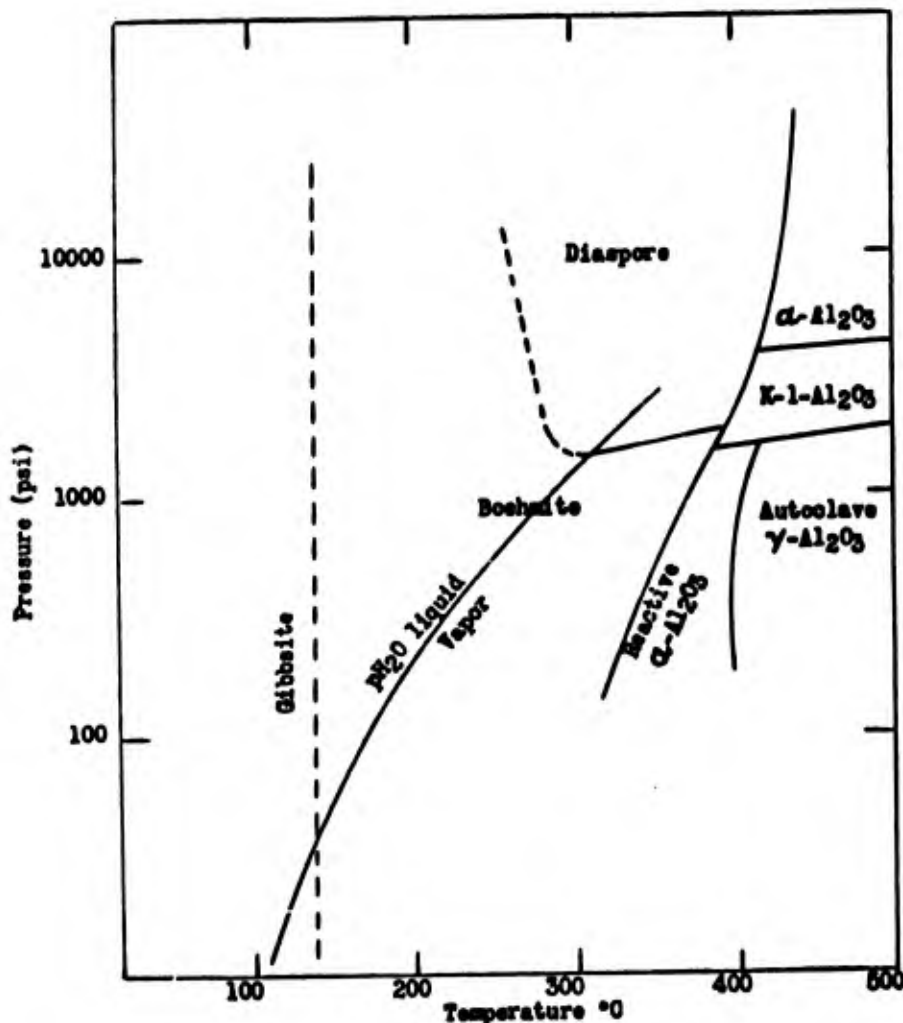
Figure 6. System Al_2O_3-H_2O
(After Ervin and Osborn, and Krishner and Torkar)

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The preparation of fused alumina from electric furnace melts has been mentioned in Section 3-2-4. The growth of single crystals from fusions other than alumina but saturated with respect to alumina has also been described. Remeika used mixtures of oxides of lead and boron. White crystallized from lead fluoride (PbF_2) at 1150 to 1300°C. Timafeeva and Voskanyan, and Giess found a marked increase in solubility of alumina in lead fluoride, between 900°C and 1250°C. Giess found the weight ratio of Al_2O_3 to PbF_2 was 0.093 at the lower temperature, and 0.151 at the higher. The principal faces of the corundum crystals grown from lead fluoride melts were (0001) and (10$\bar{1}$1) with minor (01$\bar{1}$2) and very small faces of (22$\bar{4}$3). Syosev and Obukhovskii used supersaturated melts of sodium, potassium, or lithium cryolite.

Spoerry prepared corundum from aluminum dross collected when aluminum scrap is melted. Wendell prepared the oxide by blowing an oxygen-rich flame against a pool of molten aluminum.

Coble prepared semi-transparent polycrystalline alumina having an in-line transmission of not less than 0.5%/mm thickness of the body in the wavelength range 0.3 to 6.6 microns, and not less than 10% at one wavelength. Increased transmission is attained by adding not more than 0.5% magnesia as spinel to reduce internal voids. St. Pierre and Gatti improved the transparency by firing the polycrystalline compact in a hydrogen atmosphere at 1650 to 1750°C for 50 to 300 minutes to remove gas-containing pores, and then firing at 1800 to 2000°C for not less than 15 minutes additional.

Worel and Torkar hydrolyze aluminum fluoride at 700 to 1000°C in air or oxygen containing from 10^{-16} to 3 mg H_2O/liter. Locsei hydrolyzes the fluoride in a fluidized reactor at 800 to 1000°C to obtain laminarly crystallizing alpha alumina.

May observed the growth of microcrystalline corundum platelets from vapor on objects heated in resistance furnaces with an aluminum oxide furnace tube and a hydrogen atmosphere. There was evidence for growth by the screw dislocation mechanism. Sears deposited nearly perfect single crystals from the vapor phase upon a suitable substrate. The degree of supersaturation of the vapor was adjusted by varying the temperature according to the equation

$$\log_n a = \frac{\pi a \, \theta^2 \, M}{\rho k T^2 R \log_n} \frac{B}{N}$$

in which a is the ratio of the partial pressure of the vapor to

the equilibrium partial pressure of the vapor at the deposition temperature, a is the interlayer spacing of the material, ρ is the density of the material, θ is the surface free energy of the material, M is the molecular weight, k is the Boltzmann's constant, R is the molar gas constant, B is equal to 10^{20} sec^{-1}, and T is the deposition temperature ($^{\circ}$K). Bauer, and Sears and DeVries investigated the growth process by the vapor-phase mechannism.

3-7-2 Factors Affecting Alumina Transitions

A few instances of factors affecting either the temperature of transition or the sequence of phases have already been cited. Some of these factors are: the starting material, particle size, the extent of disorder or activity, gases in the calcining atmosphere, impurities, and additives that either promote or suppress crystal growth or affect other properties. In general, the factors discussed here are those which affect loose powder transitions. Factors which affect sintering will be treated under that subject.

Ginsberg, Hüttig, and Strunk-Lichtenberg discussed the influence of the starting material on the transitions. They observed that Bayer alumina trihydrate, dried in air at 105°C, always contains a small amount of boehmite. Potassium and sodium ions in the lattice increase the temperature of transition of both gamma and delta aluminas to alpha alumina. The transition temperature is normally about 1150°C for Bayer alumina, but may be as low as 1050°C for reactive alumina containing less than 0.08% Na_2O (MacZura). The stability of boehmite is independent of the alkali content, however.

Layng; Huffman; and Bailey and Bittner prepared alumina catalyst supports containing as much as 12% silica, coprecipitated with the alumina to repress the transition to alpha alumina. Eliasson produced fine crystalline alumina by addition of 10% $(NH_4)_2PO_4$ to Bayer alumina trihydrate and by calcination for from one to five hours at 1000-1300°C. Pouillard found that trivalent iron reduces the transition temperature from gamma to alpha alumina.

Noda and Isihara found that fluorides, chlorides, and borax accelerate crystal growth of alpha alumina. Hüttig, and Hüttig and Markus showed that HCl atmospheres induce formation of alpha alumina at 850°C, while SO_3, HBr, Cl_2, NO_2, and SO_2 produce only gamma alumina. Murray and Rhodes converted amorphous alumina to alpha alumina by heating in an atmosphere containing oxides of nitrogen and a small amount of sodium nitrate at only 400°C. The addition of solid boric acid inhibited the formation of corundum. Edling et al. found that the low conversion temperature does not apply to crystalline alumina.

Hedvall and associates investigated the effect of different atmospheres on the chemical reactivity of gamma and alpha aluminas with lime. Oxygen, nitrogen, and sulfur dioxide were activators, but not sulfur trioxide.

Voltz and Weller patented the use of 0.5 to 1.5 cation percent of thoria, or 0.2 to 2.6 cation percent of hafnia to inhibit transformation to alpha alumina. Iler (1964) claimed that the addition of from 2.7 to 20% silica stabilized calcinations of fibrillar boehmite in the theta phase at 1150°C for at least 10 hours at the lower concentration, and in gamma phase for 24 hours at the higher concentration.

Wakao and Hibino found that the transition temperature from gamma to alpha alumina was reduced by additions of from one to 10% MgO, NiO, CuO, MnO_2, Fe_2O_3, TiO_2, or SiO_2. The maximum reduction was 250°C with 10% additions and 150° with 1%. The larger the metallic ion of the oxide and the higher the vapor pressure of the oxide at the transformation temperature of alumina, the larger the effect. Roberts and Jukkola used the Pechiney method of addition of a volatile fluoride to reduce the conversion temperature to alpha alumina during fluid calcination of finely divided alumina.

3-7-3 Special Ceramic Aluminas

When the German ceramic ware "Sinterkorund" was developed around 1930 (Kohl), the only types of pure alumina available in significant commercial amounts for ceramic purposes were a single grade of metallurgical-grade Bayer alumina (0.5% Na_2O) and fused white alumina fines. Small amounts of recrystallized ammonium alum were used in the Verneuil flame-fusion sapphire process (1902). The Bayer alumina was produced as a mixture of phases, approximately 60% alpha aluminum oxide and 40% higher transition alumina phases. The fused alumina fines was about of the same purity as that of the Bayer alumina from which it had been prepared, except for a lower free-soda content.

At that time slip casting appeared to be the most feasible forming method, particularly in the highly acid suspensions developed by Reichmann to improve the forming operation. The method had objectionable features in that the high acidity was corrosive on mold materials, and the slip-casting process was not well adapted to large-volume, commercial production of small items such as spark-plug porcelains. The slip-cast product was exceptionally good, however when prepared from Bayer-process alumina, partly because the free alkali was converted to a more volatile salt, and much of it had been withdrawn during the casting operation. The residual alkali in sintered ware was considered detrimental mainly to electrical properties, without, however, definite information on tolerable amounts.

Improvement in the quality of ceramic grades of alumina has developed along two different paths: (1) the reduction of impurities in normal Bayer alumina, and (2) the development of particle distributions having better technical properties.

Attempts to reduce the soda content of Bayer trihydrate by leaching in dilute mineral acids were not very rewarding because of the dispersion of the alkali within the crystal structure and the slow rate of diffusion (Stowe 1946). Upon calcination, the Bayer structure opens sufficiently to enable the practical release of about one-half the contained soda by dilute acid leaching (Gitzen, 1934, Yamauchi and Kondo). Leum et al. reduced the sodium oxide content to about 0.12% by mixing calcined alumina in water suspensions with Amberlite IR-120 ion-exchange resin.

Fessler (1937) reduced the soda to less than 0.05% by calcining in the presence of small amounts of boric acid. Thompson restricted crystal growth during this process by preventing the recycling of sodium tetraborate in the rotary kiln. Riesmeyer, and Riesmeyer and Gitzen leached with fluoboric acid or mixed acids to remove the soda effectually from alumina that had been precalcined without excessive crystal growth. Alternatively, fine crystal size and low soda content could be achieved by calcining Bayer trihydrate with boric oxide or with boric oxide and a fluoride, at a temperature below the effective volatilization temperature, and then leaching out the solubilized sodium salt (Gitzen, 1963). These methods leave a small amount of boron in the alumina, which acts as a fluxing agent in ceramic compositions. Lindsay and Gailey (1965) claimed the method of heating the alumina to above 1000°C with gaseous Cl and AlF_3.

Holder, Helmboldt and Vogt (to Giulini, 1963) claimed a process in which Bayer trihydrate is calcined in the presence of any of various silica-containing minerals of coarser particle size than the alumina. The soda in the alumina combines to form insoluble sodium aluminum silicates on the siliceous material, which can be separated substantially from the calcined alumina by sieving. Watson, Lippman, and Royce claimed by this process to reduce the sodium oxide content below 0.02%. The residual silica was as low as 0.07%, and the crystal size below 2 microns for alumina calcined at 1260 to 1540°C. Holder, Vogt, and Helmboldt also claimed that a soda content below 0.1% Na_2O can be attained merely by calcining Bayer hydrate at 1300°C for a sufficiently long period (determined by a dye test with alizarine red), and by removing by air separation the fraction substantially coarser than about 60 microns in diameter.

Fenerty calcined the alumina in the presence of sufficient aluminum fluoride (about 3%) at a temperature high enough to volatilize the sodium fluoride formed. Alternatively, unvolatilized soda could be leached out with dilute acid or alkaline solutions. Products containing less than 0.04% Na_2O were claimed, but the crystallinity of the calcined alumina was increased

into coarser size distributions. Nixon and Davis removed alkali to about 0.2% Na₂O by treating with sulfamic reagents.

The low-soda transition of Bayer trihydrate to boehmite by hydrothermal pressure digestion is also a feasible method for producing ceramic alumina containing less than 0.05% Na₂O (Barrett and Welling). The reactivity has so far not been quite as satisfactory as that obtained by calcining gibbsitic types.

Methods for producing ceramic alumina of a higher order of purity than is attainable in the normal Bayer process have already been mentioned. These are relatively high-cost procedures because they generally involve re-treatment of Bayer alumina by solution in acid or alkaline processes, or solution of high-purity aluminum (99.99%) in acids, alkalies, or anhydrous organic liquids. The calcination of recrystallized salts (sulfates, chlorides, acetates, nitrates) results in the formation of finely divided, high-surface transition aluminas, but small amounts of the anions may be retained under calcination conditions that produce reactive size distributions. The calcination of pure aluminum alcoholate, prepared from aluminum isopropylate has been shown to contain less than 4 ppm of sodium oxide (Dawihl and Kuhn). Residual alkali below 10 ppm is also claimed for a Solvay process involving the vaporization and oxidation of aluminum chloride. Silica, at 0.02%, is about in the range of Bayer alumina.

Residual soda can be avoided by precipitating the alumina from aluminum salt solutions by neutralization with ammonia. This involves the handling of gelatinous, slowly filterable precipitates that dry to hornlike masses rather than easily separable particles. Generally, a more favorable procedure is to decompose a purified aluminum salt by heat, as for example, by calcining aluminum chloride or aluminum sulfate. The Linde process in which an ammonium alum is decomposed by heat, involves a preliminary 3-stage, wet purification step. The calcined product may contain less than 200 ppm total impurities.

Iron-group impurities have been removed as carbonyls by treatment at 300 to 600°C with carbon monoxide and moisture (G. Free), or by heating at 600 to 800°C in carbon tetrachloride (Lehman), or by passing the acid aluminum salt solutions through a strongly basic anion-exchange resin column (Nagumo and Murakoshi).

Hayes removed calcium and magnesium salts from aluminum salt solutions prior to filtration by complexing with ethylene diamine tetraacetic acid (EDTA). Chromium was removed by oxidizing in sulfuric acid solutions and by separating in Amberlite LA-1 resin (Minamiie and Toshiro).

The analyses and, in some cases, attainable forming properties, are shown for some commercial high-purity reactive aluminas in Table 5.

Table 5
Typical Properties of Low-Soda Ceramic Aluminas

	Republic Foil Type 9902209	Cabot Alon	A-10	A-14	A-15	RC-152	A-16	Linde A	Gulton Alucer MC
Chemical Analysis(%)									
Na_2O	.02		.10	.04	.06	.05	.07	.02	.01
SiO_2	.05		.08	.12	.02	.07	.02	.01	<.01
Fe_2O_3	.003		.03	.03	.006	.03	.006	.002	<.003
TiO_2	<.001		.002	.002	<.001	.002	<.001	-	<.0008
CaO	.08		.04	.04	.04	.03	.04	-	.001
Ga_2O_3	.00		.02	.02	.004	.02	.003	-	-
B_2O_3	<.001		.1	.06	<.001	<.001	<.001	-	-
MnO	-		.0003	<.0003	.001	<.0001	.001	-	-
Cr_2O_3	.0005		.0002	.0002	.0002	<.0005	.0002	-	.007
MgO	.020		.001	.001	.001	.002	.05	-	-
ZnO	-		.003	.003	.001	.005	.002	-	<.001
CuO	-		.000	.000	.0002	<.0005	.0002	-	.0003
V_2O_5	-		.001	<.0001	.0003	<.0005	.0005	-	-
F	-		<.03	<.03	.01	<.03	<.01	-	-
Crystal Size (μ)									
Median	<0.1	.01-.02	7.0	4.0	2.5	2.0	0.7	0.1	1.5-2.0
Ceramic Properties[1]									
Density (g/cc)									
Pressed at 5000 psi	-	-	2.36	2.21	2.51	2.33	2.11	-	-
Fired	-	-	3.37	3.62	3.89	3.88	3.93[2]	-	-
Linear Shrinkage(%)	-	-	11.5	15.2	13.5	15.6	18.7	-	-

Cabot Alon column note: Alon C & R-13 are α and only Alon C contains Fe. 95% pure. Alon C(<1%), H2O(2-3%). (.2%), Cl(<1%), H2O residual. Alon R-13 has residual sulfate of 2%.

[1]Alumina ground to ultimate crystals,compacted at 5000 psi and fired 1 hr at 1700°C.
[2]A-16 fired 1 hr at 1550°C

The term "reactivity" is currently used to describe the new approach to improved pure-oxide ceramics. The minimum time-temperature conditions required to sinter or otherwise mature the ceramic body is stressed. An added criterion is optimum compaction or minimum fired shrinkage to mature. The phenomena involved in sintering are discussed to some extent in Section 16. The mechanism of sintering has been investigated mainly on the basis of uniformly sized spheres (Coble 1958), or available size distributions which do not necessarily satisfy the criterion for good compaction.

Ideality of size distribution has been considered from the standpoint of selecting size distributions so that the finer particles fill the voids created in packing the coarser particles (Furnas, 1931). The mathematical determination of the optimum size distribution in this manner has provided improved compaction and lower porosity in coarse size distributions in which it is possible to mechanically sieve the size increments. The treatment still requires some experimental determination of the best combinations because the particles themselves do not satisfy the assumed ideal shapes, or fail to settle into the necessary

combinations because the particles themselves do not satisfy the assumed ideal shapes, or fail to settle into the necessary compaction positions.

In the range of ceramic reactivity of present interest, about in the average particle size range from 0.05 to 5 microns, no mechanical separation methods of ground size distributions are presently feasible. Moreover, present calcination and grinding practice has not developed methods for altering the particle shape from platey crystals to equants or spherical shapes. The reactivity has been improved, however, so that fired densities of cold-pressed bodies (99.5% Al_2O_3) above 3.90 g/ml are attainable within one hour at 1500 to 1550°C. Former alumina types required about 4 hours at 1700°C to attain the equivalent fired properties. Densities as high as 3.93 g/ml have been achieved at shrinkages below 11% when fired for one hour at 1650°C. Shrinkages as high as 20 to 23% were obtained with former types having the same equivalent reactivity.

Increasing fineness in the submicron range has so far not been advantageous in sintering alumina. This is shown in low compaction densities by the usual forming methods, in excessive crystal growth, and in defective sintered ware.

3-8 BETA AND ZETA ALUMINAS

Beta alumina is the phase observed as an impurity in white fused alumina, representing the lower-melting fraction of the ingot. The soda in the Bayer alumina raw charge migrates to this fraction. The beta alumina fraction is usually separated from fused abrasive alumina because of its poorer hardness relative to alpha alumina. Its main ceramic usefulness at present is as fused cast refractories. Smith and Beeck prepared active beta-alumina catalysts by heating mixtures of gamma alumina with about 5% Na_2O as sodium nitrate at 1050°C for six hours. Fusion in the electric furnace is a suitable method for preparing well crystallized massive beta alumina.

Yamauchi and Kato found beta alumina in Bayer trihydrate (0.87% Na_2O) heated at 1300°C. By using the correct ratio of sodium carbonate to alumina, conversion can be initiated at 900°C and is completed at 1200°C. Excess Na_2O reacts to form normal $Na_2O \cdot Al_2O_3$ which melts at 1650°C. If no excess Na_2O is present, beta alumina transforms to alpha alumina at 1730°C. Sodium, magnesium, and calcium beta aluminas are stable at 1700°C if they have more than 5% of the corresponding oxides present (Funaki). According to Gallup, sodium beta alumina converts to alpha Al_2O_3 at 1300°C in vacuum or in hydrogen, but 1650°C is required for air or argon. Conversely, Saalfeld in 1956 found

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that alpha alumina converts to beta alumina at about 1000°C on treatment with hydrofluoric acid. Chiolite or cryolite are also effective. P. A. Foster in 1962 precipitated beta alumina from melts of sodium fluoride in the presence of solid sodium aluminate.

Ridgway, Klein, and O'Leary tentatively concluded that the formula for the alkali beta aluminas conforms to $Na_2O \cdot 12Al_2O_3$. Yamauchi and associates in 1943 prepared products having molar ratios conforming closely with this formula. Beevers and associates, by correlating the hexagonal structure with a revised value for density, 3.25, obtained the formula $Na_2O \cdot 11Al_2O_3$, rather than $NaAl_{23}O_{35}$, as suggested by Bragg, Gottfried, and West. DePablo-Galan and Foster confirmed the Beevers formula. In the belief that beta alumina is a stable phase, they revised the phase diagram, $Na_2O-Al_2O_3-SiO_2$, to indicate its field. Analogous compounds that have been described, include $K_2O \cdot 11Al_2O_3$, $Rb_2O \cdot 11Al_2O_3$, $Cs_2O \cdot 11Al_2O_3$, and $MgO \cdot 11Al_2O_3$. The related compounds in the alkaline earth series, however, have the formulas $CaO \cdot 6Al_2O_3$, $BaO \cdot 6Al_2O_3$, and $SrO \cdot 6Al_2O_3$. These also belong to the hexagonal crystal system. The lithium aluminate, zeta alumina, is cubic, and has the formula $Li_2O \cdot 5Al_2O_3$.

Brownmiller prepared potassium beta alumina at 1550°C. Kato and Yamauchi prepared potassium beta alumina at 1640 to 1700°C, and magnesium beta alumina at 1600 to 1800°C. Foster and Stumpf demonstrated the analogies between the alumina and gallia beta structures. Roth and Hasko claim a structure in the same crystal group for $La_2O_3 \cdot 11Al_2O_3$. Cirilli and Brisi prepared solid solutions of beta alumina and beta ferric oxide.

Scholder and Mansman reinvestigated the beta alumina structure in 1963 and concluded that the structure is $Na_2O \cdot 6Al_2O_3$. They claimed that all reaction products having a molar ratio of $Na_2O \cdot 11Al_2O_3$ are mixtures of $Na_2O \cdot 5Al_2O_3$ and Al_2O_3. They prepared isomorphous compositions of $Na_2O \cdot 6Al_2O_3$, $K_2O \cdot 6Al_2O_3$, $Rb_2O \cdot 6Al_2O_3$, and $Cs_2O \cdot 6Al_2O_3$. It is still indefinite whether the beta aluminas have fixed ratios of alkali to alumina.

Bor found that beta alumina recrystallizes in corroded glass tank firebrick in thin sharp-edged perfect hexagons embedded in glass. This is also the habit of crystallization from Bayer alumina.

Toropov and Stukalova found that sodium in beta alumina can be substituted by calcium, strontium, and barium by a double fusion with a 6-fold stoichiometric amount of the corresponding alkaline earth chloride. Filonenko and Lavrov prepared calcium beta alumina by prolonged heating of the oxide mixtures. Wisnyi synthesized $CaO \cdot 6Al_2O_3$ by flame fusion. Massazza prepared $SrO \cdot 6Al_2O_3$.

Barlett precipitated zeta alumina, $Li_2O \cdot 5Al_2O_3$, as octahedra from melts containing about 0.35% Li_2O. Akiyama added 2% lithium oxide to alumina and heated at 1700°C. Long and Foster in 1961 found that fused alumina containing 3.9% nitrogen, added as aluminum nitride, has an X-ray powder pattern identical with that of lithium zeta alumina, a spinel structure closely similar to eta alumina.

Kordes proposed the spinel structure for zeta alumina. Datta and Roy find that zeta alumina exists in many forms; it transforms at about 1295°C to a low-temperature cubic form. Hafner and Laves claimed intermediate forms between these two.

3-9 SUBOXIDES AND GASEOUS PHASES

Alpha aluminum oxide is one of the most stable compounds. Lanyi concluded that there was no reduction to metal in free hydrogen up to 900°C, and only slight formation with atomic hydrogen. In contact with carbon in the electric furnace at its melting point, alumina forms two oxycarbides, Al_4O_4C and Al_2OC with some metal (Foster, Long, and Hunter). Beletskii and Rapoport prepared the suboxide, Al_2O, by reduction with silica in a carbon monoxide atmosphere at 1800°C. The suboxide crystallized as needles from the vapor phase at a pressure of 1 mm Hg, and contained no carbide or nitride. The spinel form, $AlO \cdot Al_2O_3$, claimed by Filonenko, Lavrov, Andreeva, and Pevzner is a partially reduced form. Carnahan, Johnston, and Li found that the contact angle of liquid aluminum on alumina at about 1240°C and 10^{-6} mm Hg pressure decreased within 20 minutes to a steady value of 60 degrees. On sapphire at 1200°C, the drops spread and then suddenly contracted to a contact angle of 80 degrees. The spreading and contraction were repeated cyclicly. The behavior was ascribed to the formation of aluminum suboxide gas.

Arndt and Hornke observed that pure alumina that had been sintered at 1700°C volatilized appreciably at 1500°C. Zintl et al. claimed that alumina and boron react when heated to form the volatile monoxides, AlO and BO.

Bevan, Shelton, and Anderson; and Sandford and Ericsson showed that alumina loses oxygen when heated at 1400 to 1500°C in water vapor, but retains its weight unchanged in air or nitrogen. The loss amounted to as much as 0.2% in excess of possible Na_2O volatilization in 8 hours. Ordinary kiln gases are dissolved in mullitic material at 800 to 1200°C. Their solubility increases with increasing temperature. Rhodes found that alumina vapor diffuses in hydrogen or at low oxygen pressures to induce contamination of objects being furnaced at temperatures around 1200°C.

Brewer and Searcy concluded from vapor pressure measurements in Knudsen effusion cells that alumina volatilizes as AlO when heated alone, but as Al_2O when heated with aluminum. They found vapor pressures of 2×10^{-39} mm Hg at 1200°C and 5×10^{-19} mm Hg at 1830°C. The tests were made in tungsten cells with tantalum top shields. Von Wartenberg (1952) obtained higher values, around 8×10^{-4} mm Hg at 1950°C. The stable phases are Al and Al_2O_3 below 1000°C, Al_2O_3 between 1050 and 1600°C, and AlO above 1500°C (Hoch and Johnston). Both Al_2O and AlO are cubic.

Wartenberg and Moehl; Ackermann and Thorn; Navias; and Sears and Navias found that there is a reaction between alumina and the metals, tungsten and tantalum at high vacuum, even though not in contact. In tantalum equipment, aluminum is formed at 1600°C, and in tungsten equipment at 1900°C. The evaporation rate of alumina at 1900°C out of contact with possible reactants was less than 5.5×10^{-9} $g/cm^2/sec$, about three orders of magnitude less than the evaporation rate obtained by Brewer and Searcy in contact with a tungsten cell.

Walker, Efimenko, and Lofgren found that the calculated vapor pressures (assuming AlO to be the vapor species) in the temperature range 1493 to 1614°C were about five times as high as the least-squares extrapolation of the effusion-cell determinations of Brewer and Searcy. They found no reaction between sapphire crystals and water vapor up to 1600°C and a partial pressure of H_2O of 10 mm. There was severe reaction between water vapor and the platinum suspension. Vaporization was extensive, and not inconsistent with the possible formation of AlOH molecules in the vapor.

The seeming inconsistency in these rates of vaporization suggests the possibility of minor impurities, either present in the sapphire raw material or picked up during the formation of the boule, having an effect on the evaporated phase.

Burns, Jason, and Inghram found that the rate of evaporation of polycrystalline alumina, heated in vacuum in an arc-image furnace, increased by a factor of 3.3 as the phase changed from solid to liquid. A similar discontinuity was observed for mullite.

Juillet et al., Arghiropoulos et al., and Teichner et al., describe the preparation of oxygen-deficient aluminum oxide (approximately $Al_2O_{2.96}$) by heating alumina phases of high surface area or aluminum chloride in a vacuum at 500 to 1000°C. The alumina assumes a black color and becomes a semiconductor. The normal white color is restored when the nonstoichiometric form is reheated in air or oxygen.

The form of the alumina structure produced from vapor phase

transport has assumed significance for ceramic uses. Spherical platelet, and fibrous forms are obtained. Watson et al.; DeVries and Sears; Cunningham; and Sears and DeVries studied the growth and properties of fibers prepared both by rapid drying of colloidal suspensions that were subsequently heat-treated to develop strength, and by vapor deposition from aluminum. The vapor-phase method entails the presence of controlled amounts of moisture to facilitate formation of the volatile aluminum suboxide. Hegedüs and Kürthy obtained amorphous spherical alumina, deficient in oxygen, by calcining aluminum ethylate in hydrogen at 1600°C. Hargreaves, from thermodynamic considerations, concluded that the vapor-phase growth of whisker and platelet crystals of alpha alumina is by transport of Al_2O and not AlO. Spiral growth steps do not occur on the (0001) surface of these crystals. Lynch, Valdiek, and Robinson grew alumina whiskers in several distinct forms at 1700 to 1800°C in argon and helium atmospheres containing small amounts of hydrogen. Wainer and Cunningham produced fibrous anhydrous sapphire fibers by passing hydrogen with a dew point between -30 and -90°C over aluminum containing 25 mole percent Ti, Zr, Nb, Ta, or Si, and maintained at 1370 to 1510°C. Schmidt varied the size of the fibers and the plates by changing the degree of supersaturation and the temperature of the crystallizing zone.

Brisbin and Heffernan volatilized anhydrous aluminum chloride in a mixture of hydrogen and carbon dioxide at 1100 to 1200°C and 25 mm vacuum. Hexagonal fibers averaging 1 mm length and 0.05 mm diameter were obtained. Campbell investigated the feasibility of continuous formation of refractory fibers and whiskers by evaporating and oxidizing an aluminum halide on substrate powders carried in the gas stream. The supersaturation determines the growth morphology. In gaseous systems at constant volume, the degree of supersaturation is proportional to the partial pressures of the growth species. In this case, the partial pressures of gaseous H_2, CO_2, and $AlCl_3$ were controlled.

Kerrigan was successful in transporting and depositing whiskers of alpha alumina in HCl. A black, oxygen-rich species was formed. Papkov and Berezhkova obtained whisker alumina by heating corundum crystals in a graphite oven to 2000°C in argon or nitrogen or in vacuum. Timofeeva and Yamzin, and Shternberg and Kuznetsov grew corundum crystals on a seed from the gas phase by heating aluminum fluoride at 900 to 1250°C. DuPont de Nemours (British Patent 849,051) prepare corundum in ribbon-shaped fibers by heating aluminum in the presence of hydrogen and any inorganic silicon compound such as quartz, calcium silicate, or a silicate mineral at 1100 to 1450°C. The silicate mineral must be less than 4-mesh in size. After the charge has been heated to temperature, the pressure is raised to 860 mm Hg, whereupon the fibers form on the silicate.

Wainer and Mayer, and Beasley and Johns describe methods for preparing inorganic fibers in which the structure depends upon forming treatment and not by vapor deposition.

4 STRUCTURE AND MINERALOGICAL PROPERTIES

The industrial importance of the different phases of alumi-
na and its hydrates has induced much scientific investigation of
its crystal structure. Besides the ideal crystal structure, which
is a rarity in actual ceramic systems, defect crystal structure
and microstructure are significant. These are the structures be-
yong the crystal lattice and include such factors as surface area,
porosity, grain size, vitreous phases and crystalline mixtures of
phases that may be formed in a variety of ways, as for example, by
exsolution. The symposium, Microstructure of Ceramic Materials,
NBS Misc. Pub. No. 257, and Defect Solid State, Gray et al. dis-
cuss some of the factors involved.

4-1 STRUCTURE OF THE ALUMINA PHASES

The properties of the aluminas are determined mainly by the
crystal structure. In general, the phases of most significance
in alumina are those produced by pseudomorphic dehydration.

Powder X-ray methods for determining crystal structure are
not as suitable as single-crystal methods. In many cases, how-
ever, the lack of single crystals of the alumina phases as coarse
as one or two tenths of a millimeter has restricted the develop-
ment of exact information. Lack of exact information on the atom
parameters has thrown some doubt on the named structure or crys-
tal system for some phases.

The crystal structures of the alumina phases are shown in
Table 6. Mineralogical properties of the various phases are
shown in Table 7.

The crystalline modifications of alumina are, without excep-
tion, classed as ionic (Verhoogen). For the arrangement of ions
in the lattice, the coordination number of the cations is of
paramount importance. The relatively small Al^{3+} cation is usual-
ly 6-coordinated with respect to O^{2-} or $(OH)^-$ anions, and is
located in the interstices of octahedral anion groups. It may
appear at the center of tetrahedral groups of 4-coordination, as
in glass and in mullite. The Pauling principle of coordination
is generally satisfied within each octahedron, even with different
kinds of octahedral coupling, but in any case, neutralization is
obtained at least for each separate unit cell.

In the crystal lattices of the alumina phases, both cubic
and hexagonal close packing may take place. In cubic close-packing

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Table 6

Crystal Structure of the Aluminas

Phase	Formula	Crystal System	Space Group	Mole-cules	Angstroms a	Angstroms b	Angstroms c	Angle	Ref.
Hydrated Aluminas									
Gibbsite	α-Al$_2$O$_3$·3H$_2$O	Monoclinic	C$_{2h}^5$	4	8.641	5.070	9.720	85°26'	1
Bayerite	β-Al$_2$O$_3$·3H$_2$O	Monoclinic	C$_{2h}^5$	2	4.716	8.679	5.060	90°07'	3
Nordstrandite	Al$_2$O$_3$·3H$_2$O	Monoclinic		8	8.63	5.01	19.12	92°00'	4
Boehmite	α-Al$_2$O$_3$·H$_2$O	Orthorhombic	D$_{2h}^{17}$	2	2.868	12.227	3.700		5,12
Diaspore	β-Al$_2$O$_3$·H$_2$O	Orthorhombic	D$_{2h}^{16}$	2	4.396	9.426	2.844		5
Transition Aluminas									
Chi		Cubic		10	7.95				9
Eta		Cubic(spinel)	O$_h^7$	10	7.90				9,8
Gamma		Tetragonal			7.95	7.95	7.79		6,7
Delta		Tetragonal		32	7.967	7.967	23.47		10,11
Iota		Orthorhombic		4	7.73	7.78	2.92		9
Theta		Monoclinic	C$_2^3$	4	5.63	2.95	11.86	103°42'	13
Kappa		Orthorhombic		32	8.49	12.73	13.39		9
Corundum	α-Al$_2$O$_3$	Rhombohedral	D$_{3d}^6$	2	4.758		12.991		2
	Al$_2$O	Cubic			4.98(1100°C)				20
					5.67(1700°C)				
	AlO·Al$_2$O$_3$	Cubic(spinel)	O$_h^7$		7.915				22
Beta Aluminas (21)									
	Na$_2$O·11Al$_2$O$_3$	Hexagonal	D$_{6h}^4$	1	5.58		22.45		14
	K$_2$O·11Al$_2$O$_3$	Hexagonal	D$_{6h}^4$	1	5.58		22.67		14
	MgO·11Al$_2$O$_3$	Hexagonal	D$_{6h}^4$	1	5.56		22.55		16
	CaO·6Al$_2$O$_3$	Hexagonal	D$_{6h}^4$	2	5.54		21.83		15
	SrO·6Al$_2$O$_3$	Hexagonal	D$_{6h}^4$	2	5.56		21.95		15
	BaO·6Al$_2$O	Hexagonal	D$_{6h}^4$	2	5.58		22.67		17
Zeta Alumina	Li$_2$O·5Al$_2$O$_3$	Cubic	O$_h^7$	2	7.90				18,19

Ref.:
1. Megaw
2. Swanson, Cook, Isaacs, & Evans
3. Unmack
4. Lippens
5. Swanson & Fuyat
6. Saalfeld
7. Brindley & Nakahira
8. Verwey
9. Stumpf
10. Tertian & Papée
11. Rooymans

12. Reichertz & Yost
13. Kohn
14. Beevers & Brohult
15. Lägerqvist
16. Bragg
17. Adelsköld
18. Kordes
19. Braun
20. Hoch & Johnston
21. See Scholder & Mansmann for claimed structure Na$_2$O·6Al$_2$O$_3$
22. Filonenko, Lavrov, Andreeva & Pevzner

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Table 7

Mineralogical Properties of the Aluminas

Phase	Index of Refraction n_d			Cleav-age	Mohs Hard	Micro Hard kg/mm²	Dens. Measured g/ml	Ref.
	α	β	γ					
Hydrated Aluminas								
Gibbsite	1.568	1.568	1.587	(001)	2.5-3.5		2.42	1,2
Bayerite	1.583 (average)						2.53	3,2
Boehmite	1.649	1.659	1.665	(010)	3.5-4		3.01(14)	4,5,14
Diaspore	1.702	1.722	1.750	(010)	6.5-7		3.44	1
	ϵ	ω	Average					
Transition Aluminas								
Chi							3.0 (est)	19
Eta			1.59-1.65				2.5-3.6	6
Gamma							3.2 (est)	20
Delta							3.2 (est)	
Iota			1.604				3.71 (est)	7
Theta			1.66-1.67				3.56	6
Kappa			1.67-1.69				3.3 (est)	6
Corundum	1.7604	1.7686		none	9.0	2150	3.96-3.98	21,15
Al₂O								
Al0·Al₂O₃			1.77-1.80			2070	3.84	13
Beta Aluminas								
Sodium Beta	1.635-1.650	1.676					3.25-3.33	8,10,18
Potassium Beta	1.642	1.675						17,18
	1.640	1.668						
Magnesium Beta	1.629	1.665-1.680						16,8
Calcium Beta	1.752	1.759						11,12
	1.754	1.763					3.731	
Barium Beta	1.694	1.702					3.69	10
Lithium Zeta			1.735				3.61	9

Ref.
1. Dana
2. Roth
3. Montoro
4. Ervin & Osborn
5. Bonshtedt-Kupletskkaya
6. Thibon
7. Foster, P. A.
8. Rankin & Merwin
9. Kordes
10. Toropov
11. Filonenko & Lavrov
12. Wisnyi
13. Filonenko, Lavrov, Andreeva & Pevzner
14. Fricke & Severin
15. Coble
16. Bragg, Gottfried, & West
17. Kato & Yamauchi
18. Beevers & Brohult
19. Stumpf
20. Ginsberg, et al
21. Biltz & Lemke

of the densest arrangement, the ions of one plane occupy the
hollows formed by three ions of the next plane. Every fourth
plane of superposition in the crystal lattice repeats (ABC ABC)
to yield the face-centered cubic cell.

In hexagonal close packing, the sequence of close-packed
anionic planes recurs every third plane (ABAB). The linking
of octahedra and tetrahedra differs from that of cubic close-
packing. In the direction parallel to the hexagonal c-axis,
adjacent forms are linked through faces; in other directions
through edges. In both crystal structures, the ions situated
at octahedral corners belong to six adjacent octahedra. In
general, the octahedra and tetrahedra will be distorted by the
cations. Empty octahedra are larger, while those filled with
aluminum ions become smaller.

Gibbsite has been the most precisely determined of the
trihydroxide phases because of the availability of well crys-
tallized coarse specimens. Gibbsite is designated as monoclinic
by Dana. It usually occurs both native and in commercial pro-
duction as twinned, pseudohexagonal tablets. Saalfeld (1960)
observed triclinic crystals dispersed in the monoclinic structure
of the native form.

Megaw determined the structural arrangement of gibbsite to
consist of double layers of hydroxyl ions of closest packing
enclosing the aluminum atoms within their interstices. Each
aluminum atom is enclosed by three anions above and three be-
low to form an anionic octahedron. The double layers are stacked
in the direction of the c-axis. The aluminum atoms occupy only
two-thirds of the available interstices in their plane and are
arrayed in a pattern of hexagonal rings surrounding the vacant
sites. There are no aluminum ions in the plane between adjacent
double layers, and since the anions are superposed in these con-
tacts, rather than lying in depressions, this plane represents a
cleavage plane of weakness.

The stacking is deformed slightly in the direction of the
a-axis to give the monoclinic lattice. The triclinic form ob-
served by Saalfeld is obtained by a possible displacement in a
direction perpendicular to the (110)-plane (60° with the a-axis).
The open structure, in particular the hole through the centers
of the hexagonal rings, allows paths for ionic diffusion (Barrer
1941). Gibbsite crystals grow as pseudohexagonal prisms in the
presence of potassium ions, but often as platelet layers with
spiral growth or with distortions in the base layer in the

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presence of sodium ions (Wefers).

Bayerite was classified in the hexagonal system by Montoro and Yamaguchi and Sakamoto. The latter rejected X-ray reflections that could not be indexed in a hexagonal lattice. Also, a number of reflections that should coincide in a hexagonal lattice were found to be clearly separated (600, 330 and 601,331). Unmack classified bayerite in the monoclinic system. Wefers states that bayerite forms wedge-shaped somatoids composed of loosely packed Al(OH)$_3$ layers a few angstroms thick, and with their main axis perpendicular to the layers.

The interplanar spacings of nordstrandite have been furnished by Papée, Tertian, and Biais; and by Lippens. The latter found a monoclinic lattice most acceptable to explain the structure.

The three trihydroxides have substantially the same layer structure and the same dimensions except in the direction of the c-axis. The differences between the lattices in the length of the c-axis is about proportional to the number of Al(OH)$_3$ molecules per unit cell.

The two monohydrates, boehmite and diaspore, are closely related. Boehmite is characterized by cubic close-packing of the anions, which carries over into the transition aluminas. Diaspore is characterized by hexagonal close-packing, which accounts for its direct transition to corundum at relatively low temperature (Ewing, Hoppe, Ervin 1952).

Achenbach established the orthorhombic symmetry of boehmite, confirmed by Dana, who found rhombic lamellae in French bauxites. Reichertz and Yost, and Milligan and McAtee determined the structure, based on a comparison with the isomorphous iron hydroxide, lepidocrocite. Similarly, diaspore was correlated with its iron oxide counterpart, goethite. Van Oosterhout provided a schematic model that explains the structure of the aluminum hydroxides, consisting of an anti-parallel coupling having the form:

$$HO-Al-O$$
$$O-Al-OH$$
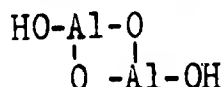
The couples can form chains with others in which it may be assumed that the hydrogen ions act as bonds uniting the oxygens in each of the octahedral layers with those in the adjacent octahedral layers. Molecular water is not present (Imelik, Glemser). In boehmite the couple is oriented with the longer

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axis parallel to the b-axis; in diaspore, the couple is oriented more compactly on the bias so that the aluminum ions are joined by lines parallel with the b-axis. The OH-directions form zig-zag chains between the planes of the oxygen ions in boehmite. (Kroon and Stolpe). The short unshared O-O distance is 2.70 Å.

Busing and Levy could determine by neutron diffraction that the positions of the hydrogen ions in diaspore are at an angle of 12.1° with the line of centers of the two different types of oxygen atoms, and are closest to the oxygens farthest from the aluminum ions.

Rho alumina, obtained by vacuum heating of gibbsite, is almost completely amorphous. Its X-ray powder pattern shows only a few diffuse bands, the most pronounced of them having a spacing of about 1.4 Å.

Chi alumina, the lowest transition phase from gibbsite in air (or nitrogen) also has a diffuse pattern, but is distinguishable from the other low-temperature aluminas by a line with spacing of 2.11 Å. Stumpf concluded that it is cubic, but not a spinel, with a unit cell dimension of 7.95 Å.

Both Saalfeld (1960) and Brindley and Choe ascribe to chi alumina a close packed-hexagonal structure with a = 5.57 Å, c = 13.44 or 8.64 Å, respectively.

Eta alumina is described as a cubic spinel. The unit cell of spinel, $MgAl_2O_4$, is formed by a cubic close stacking of 32 oxygen atoms, 16 aluminum atoms occupying one-half of the available interstices, and 8 magnesium atoms in tetrahedral holes. The formula is $Mg_8[Al_{16}]O_{32}$: the brackets are conventional for indicating octahedral sites. According to Verwey and Hägg and Söderholm, gamma alumina (eta alumina) is a spinel with 32 oxygen atoms and, consequently, only 21-1/3 aluminum atoms. The formula is $Al_8[Al_{40/3} \square_{8/3}]O_{32}$; the square indicating that vacancies are distributed in octahedral sites. Jagodinski claimed that the vacancies are exclusively in the octahedral sites, on the basis of Fourier analysis.

Gamma alumina, obtained by anodic oxidation of aluminum, supposedly has its vacant places distributed at random over all possible cation positions.

Stumpf's gamma alumina, conforming to a one-hour heat

treatment of Bayer trihydrate at 500°C, was thought to be cubic, but of too many interplanar spacings to conform with the spinel structure. Saalfeld (1958) found a tetragonal cell for the gamma alumina derived from gibbsite, confirmed by Brindley and Nakahira. A slow dehydration leads to the ordered tetragonal form, a fast, more drastic, heat treatment and less favorable starting material may give rise to a "statistically" cubic form (Tertian and Papée 1958). At about 430°C boehmite is no longer detectable in heated Bayer trihydrate. Glemser and Rieck observed that all gamma alumina has water strongly bound as hydroxyl ions. It was concluded by de Boer and Houben that gamma alumina (eta alumina) is a hydrogen spinel having the formula $5Al_2O_3 \cdot H_2O$ or HAl_5O_8, analogous to the zeta-alumina spinel $LiAl_5O_8$. There is little evidence for such a hydrate. Fortuin determined that all OH-groups are located at the surface.

It was concluded by Saalfeld (1960) that the dehydration scheme of the boehmite series is based on the cubic oxygen layer sequence ABC ABC, which is found in gamma alumina. In gamma alumina the aluminum atoms are all probably located in octahedral sites of the spinel.

Delta alumina, prepared by heating pure boehmite for only one to two hours at 1000°C, fits an orthorhombic structure, according to Stumpf. Rooksby obtained more sharply crystalline material by prolonged heating or by addition of mineralizers. Rooymans found a relationship between the interplanar spacings and those found by von Oosterhout and Rooymans for gamma ferric oxide, regarded as a defect spinel. The data fit a tetragonal cell having an axial ratio of $c/a = 2.946:1$. The cell contains three spinel cells, that is, a whole number of Al_2O_3 molecules (32). A fourfold screw axis parallel to the c-axis was also found (Lippens). Saalfeld, on the other hand, denied the existence of delta alumina.

Foster and Stumpf found that theta alumina and beta gallia are isomorphous. Indeed, all the gallia phases have exact counterparts in the alumina system. Roy, Hill, and Osborn (1953) established a series of solid solutions between theta alumina and a gallia isomorph. Kohn, Katz, and Broder obtained beta gallia in large single crystals by vapor phase deposition, and were able to establish the structure of theta alumina as a distinct form of alumina from the analogy in structure. Theta alumina is monoclinic. Saalfeld (1960) obtained substantially the same unit cell dimensions as Kohn et al. In contrast with the spinel lattice, the aluminum atoms preferentially occupy

tetrahedral positions. Theta alumina occupies an intermediate structural transition between the spinel lattice with the cubic oxygen arrangement and the corundum lattice with a dense hexagonal oxygen arrangement and the aluminum atoms exclusively in the octahedral positions.

Stumpf established the orthorhombic crystal structure for kappa alumina. According to Saalfeld (1960), kappa alumina has the layer sequence ABAB-BABA ...., with the aluminum atoms in octahedral and tetrahedral sites. In common with gamma, theta, and chi aluminas, the preferred orientations of its crystallites confirm the fact that the gibbsite lattice is not completely destroyed upon calcination, but that special directions are preserved. The strongest lattice direction is the a-axis of gibbsite.

Sasvari and Zalai explained the mechanism of lattice change during dehydration of gibbsite by assuming that the changes occur by collapse and disappearance of specific anionic plane' of the layers. The cations lying between the single planes so produced and the double layers realign into octahedral environment by cubic close packing. In going to boehmite, the original crystal layering arrangement AB BA AB BA... loses every third single layer to give the sequence A BA B B AB A A BA... before collapse, and B BA BA A ..... finally. If all the water is expelled at once, the disappearance of both planes from every second layer appeared to be the more likely method. Several different paths were conceivable for the dehydration of boehmite and diaspore.

The structure of corundum was approximately determined by X-ray methods by Bragg and Bragg. Pauling and Hendricks established the structure of rhombohedral alpha-aluminum oxide in 1925. The best present values for cell dimensions are probably the values of Swanson and Fuyat. Newnham and de Haan have recently investigated the crystal structure of Verneuil process specimens by zero-layer intensity data collected about the (100) face with a Weissenberg camera. The oxygen positions approximate hexagonal close packing, with the trivalent cations occupying two-thirds of the octahedral interstices. Hoch and Johnston claimed that the crystal structure of corundum at 2000°C is the same as that at room temperature. The theoretical density calculated from the unit cell constants is: 3.987 g/ml (Swanson and Fuyat), and 3.996 g/ml (Sedlacek, 1964). The measured theoretical density determined by Coble (1962) is 3.98 ± 0.01 on pure low-color sapphire. Biltz and Lemke (1930) found 3.96.

Alpha aluminum oxide crystals, as exemplified by Bayer process ceramic types have the shape of thin hexagonal, or more rarely, three-cornered plates. Small differences in habit are observed, mainly relating to the thickness of the plates, the edge faceting, and the size and degree of perfection of the crystals. Crystal habit is affected by several factors, among which are the kind and concentration of mineralizer present (fluorides, borates, phosphates, etc.) and the temperature of calcination. Crystal thickness may, for example, be altered by the choice of fluoride; cryolite produces thin, sharp-cornered plates in comparison with thick, rounded crystals produced by calcium fluoride.

Dana mentions and illustrates many examples of the crystal habit of native corundum, ranging from tabular to elongated hexagonal prisms and pyramids, and as rounded or tabular aggregates, as found in emery. The characteristic lamellar and striated structures showing rhombohedral and basal parting planes in hexagonal prisms are common (Schroder).
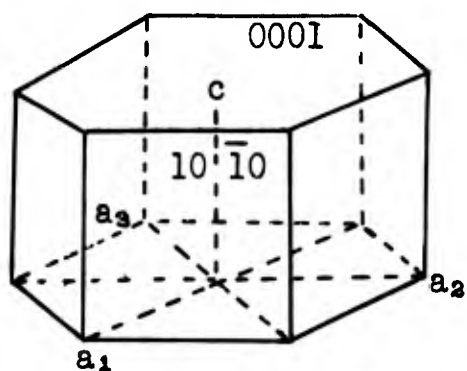
Alumina ceramic products are manufactured under conditions quite different than those under which the native form is produced, and their crystal habits are different, but there are analogies.

Baumann has described the crystal habit and microstructure of alpha alumina as it occurs in massive sintered and electrofused forms. In sintered alumina well developed crystal faces (euhedral to subhedral) having the tabular habit are usual. Spherical pores both within the crystals, often separated from the boundaries by a margin, and pores at the boundaries are numerous.

In fused melts from bauxite and Bayer alumina, the crystallization increases in size from the wall to the center of the ingot, depending upon the rate of cooling. Crystal size of several millimeters in diameter is attained from melts containing a small amount of titania. The crystallization is usually anhedral. In ingots prepared from Bayer alumina, occasionally alpha alumina crystals are free to grow in open spaces, forming well developed rhombohedra. On surfaces, particularly of shrinkage pipes or canals, skeletal needles and dendritic forms project, often growing along the direction of the c-axis.

Filonenko and Borovkova found that titanous compounds, in

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amount not over 4 to 6%, cause anomalous thermal expansion of fused alumina, with formation of a network of cracks on the surface. Other impurities have a marked effect on the structure and properties of fused alumina. Silica up to 3%, inhibits the development of beta alumina in white fusion alumina, but the rhombohedral crystallization persists (Schroeder and Logan).

Gaudin attempted to prepare synthetic corundum for jewel applications in 1837, by heating a mixture of powdered alumina and potassium sulfide in a crucible covered with charcoal. Only very small crystals (probably beta alumina) were obtained. Many investigators have since made the attempt. Fremy and Feil were the most successful until the advent of the Verneuil process in 1902. They fused alumina with lead oxide in a fireclay crucible; the lead aluminate was attacked by the fireclay, and the liberated alumina crystallized as small plates. The addition of 2 to 3% of chromium salts imparted a ruby color. Watch jewels were made from the crystals.

The Verneuil flame-fusion process for preparing artificial sapphires consists of dropping finely divided pure alumina onto a preoriented crystal of corundum, 2 to 3 mm in diameter, surrounded by an oxy-hydrogen flame furnace. The container for the alumina supply is equipped with a tapping device for feeding the powder uniformly to the area of impingement with the growing crystals (boule). The feed alumina is calcined ammonium alum. The boule is rotatable, and can be withdrawn from the heating zone in a slow continuous manner as the growth proceeds (Popov). Rods as slender as 1.5 mm may be grown to avoid excessive loss in cutting operations. Single crystals of 100 to 150 carats (20 to 30 grams) in 2 to 3 hours have been obtained as expanded boules.

The purest alumina is required for colorless sapphire. Metal oxides are added to the alum for colored crystals. Red (ruby) crystals contain about 1 to 7% chromic oxide; blue crystals a mixture of about 1% titania and 2% iron oxide; green crystals a mixture of vanadium and cobalt oxides; and alexandrites vanadium oxide only. Green crystals are also produced if the chromium content exceeds 8 mole %. At this concentration the lattice constants a and c begin to expand. The red color was believed to be due to isolated Cr^{3+} ions, whereas these ions are in contact at higher amounts. A solid solution containing 58% chromium which was green at room temperature became red at 90°K; a red solid solution containing 8% chromium became green at 460°K, and with 2% chromium became green at 650°K.

X-ray examination shows that no natural sapphires approach the perfection of structure of vapor grown synthetic sapphires. In the early days of production by the Verneuil process, defects in structure were observed, however, among which are strain and longitudinal splitting. Longitudinal splitting does not necessarily indicate twinning, but the release of strain, and is not generally in a principal crystallographic plane (Brown, Chirnside et al.), contrary to the opinion of Saucier. The optic axis and the plane of splitting lie close together, but both may be at any angle to the axis of the boule. Stofel and Conrad found that mechanical twins, both (0001) and (0$\bar{1}$11) types, were produced by compression in the range 1100 to 1300°C. Cracks propagated more readily along the twin boundaries than in the nontwinned crystal, suggesting a lower fracture strength than that of nontwinned crystals.

Conrad et al. observed twinning in 60 degree-oriented sapphire at temperatures as high as 1500°C. Gumilevskii observed surface grain markings indicating the crystal axes, and skeletal evidence in the form of particles at the grain boundaries and dendrites. Belova and Ikornikova reported that synthetic sapphires have a mosaic structure intermediate between the ideal monocrystal and polycrystalline growth. Amelinckx (1952) observed triangular growth spirals on the (0001) plane of synthetic rubies. This is the plane in which the aluminum atoms are located in the octahedral interstices of the oxygen atoms. Lima-de-Faria noted that intermediate stages in the dehydration process of diaspore are revealed by satellite X-ray reflections, which occur close to developed corundum spots at certain temperatures. The satellites may correspond to a sinusoidal structure-amplitude modulation along the c-axis of the corundum crystallite before dehydration is complete. The wavelength of the modulation was 39 A. Nonuniform line broadening was ascribed to stacking faults.

Webb and associates, and Dragsdorf and Webb grew sapphire whiskers and platelets by heating aluminum in moist hydrogen at 1300 to 1450°C for 2 to 24 hours. The whiskers were 3 to 50 microns in diameter and 1 to 30 mm long; they had hexagonal cross sections and [0001] axes. Evidence of screw dislocations were observed in the whiskers; none was found in the platelets. Many whiskers were hollow, the axial cavities having diameters of 0.5 to 3 microns. Axial twists, determined by X-ray and confirmed by optical observation, were ascribed to a screw dislocation Burgers vector equal to integral multiples of the c-axis, 12.97 A. Theories of Eshelby and some others require the presence of screw

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dislocations. Sears, DeVries, and Huffine have observed the Eshelby twists on the tapered tips of alumina whiskers. The twist and associated screw dislocation can be removed by nonuniform bending, occurring during the breakage of the whisker from its base. May (1959,a) found that the platelets grown in moist hydrogen atmosphere also show evidence of screw dislocation (Frank mechanism).

McCandless and Yenni; Smith and Yenni; and Hart, by applying heat and force, altered the shape of corundum unicrystals. Rod-shaped crystals were bent in a plane which makes an angle between zero and 45 degrees with the plane defined by the c-axis and the longitudinal axis of the rod. The stretched portion became opaque, while the body remained a unicrystal. Kronberg observed the arrangement of the tiny crystals that formed in the plastically bent regions, a phenomenon designated polygonization. The dislocations tend to line up in particular arrangements. Just above an edge dislocation where an extra plane of atoms is inserted, there is a compressive stress, and below the dislocation a tensile stress. Dislocations of the same sign (positive for those with the extra plane inserted above the slip plane) tend to repel one another if they are in the same slip plane. Dislocations of the same sign in different slip planes tend to line up above each other to form low-angle grain boundaries. A mosaic structure forms upon annealing. May investigated the kinetics of the process over the range 1750 to 1850°C, and found an activation energy of 140 kcal/mole.

Scheuplein and Gibbs found triangular etch pits corresponding to the intersection of individual edge dislocations with the surface, after immersing the corundum crystals in boiling phosphoric acid for about 5 minutes. Dislocations of both the (0001), $\langle 11\bar{2}0 \rangle$ and $\{1\bar{2}10\}$, $\langle \bar{1}010 \rangle$ slip system (where reference is made to the slip plane and slip direction, respectively) were detected. Crystals, bent while cooling, had about twice as many dislocations as are predicted by the Nye formula, and these were distributed randomly. A special method of deformation, which favored the participation of both the basal (0001), $\langle 11\bar{2}0 \rangle$ and the prismatic $\{1\bar{2}10\}$ $\langle \bar{1}010 \rangle$ slip systems, resulted in highly stressed crystals which fractured spontaneously, once the outside surface was scratched.

Palmour, Du Plessis, and Kriegel observed that basal-, prism-, and rhombohedral-plane specimens cut and polished from flame-grown sapphire boules developed fine surface textures during heat-treatment in the range 1700° to 1900°C. Microscopic

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examinations of such surfaces revealed low-angle grain boundaries, dislocations, and other crystal imperfections. Thermally etched textures apparently were generated by three overlapping processes; annealing, etching, and decoration. Annealing commenced at 1500 to 1700°C and was essentially complete at 1850°C. The cold-worked surface was progressively readjusted by surface and volume diffusion. At higher temperatures, the surface began to etch by evaporation. Surface decoration was indicated by a deposition of aluminous material on favorable sites in the form of low rounded bumps, occurring, presumably, during cooling. Thermal etching gave evidence of high-temperature relaxation of residual strain energy introduced at low temperature (analogous to cold work in metals) including that introduced by fracture, microindentation, and cutting and polishing during surface preparation. Voruz et al. observed dislocations in thin specimens of sapphire platelets directly by electron transmission techniques. The observations indicate the possibility that corundum has a high stacking fault energy and that slip may occur by the movement of perfect dislocations or that dissociation may occur over a distance of several Burgers vectors.

Fuchs claimed that even brittle corundum powders exhibit lattice distortion during milling on the basis of measurement of X-ray line broadening. Stephens and Alford found that the average density of edge dislocations lying in prism planes was 3.0×10^5 per cm^2, which could be changed only slightly by additions of chromium and by annealing at 2000°C. An average basal dislocation density of 2×10^6 per cm^2 decreased by 35 to 80% upon annealing. Crystal orientation (the angle between the c-axis and the axis of growth) showed no effect on dislocation density but a pronounced effect on the subboundary arrangement and density. The substructure of 60-degree crystals is intermediate between that of 0-degree and 90-degree crystals. Prismatic and basal slip were observed on all as-grown crystals; profuse basal slip polygonized readily upon annealing; the densities of dislocations in flux-grown crystals were lower than those of Verneuil crystals; and basal twinning on the plane {10$\bar{1}$0} was observed on all flux crystals. Lommel and Kronberg, using a high-resolution Berg-Barrett X-ray technique, compared dislocation data with etch patterns. Thermal etching data were in good agreement with the chemical etching data of Scheuplein and Gibbs. Correlation between X-ray data and etch figures was good for sapphire but not for a light ruby containing 0.75% Cr_2O_3.

Paladino and Reuter grew sapphire single crystals of

moderate size by the Czochralski method of continuous pulling
from the melt. A pickup of less than 0.01% W from the containing
tungsten crucible and 0.0001% Ni was observed from melts of Linde
alumina. Impurities that became less or disappeared by spectro-
graphic analysis include: B, Na, Mn, Fe, Ga, In, and Pb. Impuri-
ties that remained the same include: Mg, Si, Cr, Cu, and Ag.
The defect structure by this method was decidedly less than that
of the Verneuil process.

Laudise and Ballman hydrothermally synthesized even more
perfectly crystalline corundum by seeding in dilute sodium car-
bonate solution at 395 to 520°C and 12,000 to 55,000 psi. The
crystal growth was about 0.006 in/day. Kryukov found that
boehmite and gibbsite are by-products from the hydrothermal
synthesis of corundum.

4-2 PSEUDOMORPHOSIS

Achenbach in 1931, Damerell, and Tertian in 1950, observed
that the dehydration of gibbsite crystals is pseudomorphic,
that is, the external shape of the crystals is retained and
there is an orientation relationship of the crystal axes of the
new phase to those of the original. The crystals lose trans-
parency and smoothness upon heating, and fine-grained fibers
develop parallel to the hexagonal surface. The gross form of
the Bayer agglomerate is retained even to 1200°C substantially
unchanged. Void space resulting from the loss of water from the
gibbsite and increasing density of the transition phases is dis-
tributed in microporosity of very high surface area in the po-
rous skeleton (Weitbrecht and Fricke). Pseudomorphosis is of
considerable importance because of its effect on surface area
of the intermediate phase structures, and on crystal size and
size distribution of the fully calcined aluminas for ceramic
forming processes.

Hüttig and Ginsberg concluded from micrographs of the heated
Bayer trihydrate, that dehydration takes place in a continuous
process preceding lattice change. The transition phases are
fragments in the crystal structure. During boehmite formation,
the retention of form was best when the transformation was in
alkali; next best in water; and poorest when in air. Trans-
parency was lost from the interior of the crystal, at least in
dry dehydration. Nahin and Huffman prepared electronmicrographs
of heated aluminum hydroxides. Voids, apparently generated by
dehydration are shown in theta alumina and other high-temperature

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phases. Bayer trihydrate calcined at 1040°C was sharply micro-crystalline in the cubic system. A diffuse X-ray pattern was shown for crystals ranging in size from less than 100 to 250 Å. The pore size was about 40 to 60 Å. Stirland, Thomas, and Moore concluded from electronmicrographs of thermal decomposition of hydrated aluminum chloride, that at about 300°C, striated flakes 0.5 to 5 microns form, containing a few holes, 400 to 500 Å in diameter. The holes generally are partially occupied by dense inclusions. The holes and inclusions increase in number with increasing temperature. At 1000°C the inclusions appear as hexagonal or rectangular forms. At 1100°C, the inclusions loose sharpness, and coalesce, apparently by engulfing the striated structure, to form relatively large open pores.

Thibon, Charrier, and Tertian; de Boer, Fortuin, and Steggerda; Steggerda; Saalfeld; Ervin; and Lippens and de Boer were also interested in pseudomorphic changes. Ervin observed that the X-ray powder diffraction patterns of all of the transition aluminas have in common the strong line at 1.39 Å. This reflection belongs to the (440) plane for the spinel structure. It passes through all the oxygen ion centers and the possible aluminum ion centers, whether tetrahedral or octahedral. The less intense (400) plane of spinel at about 1.99 Å passes through every anionic and octahedral cationic position. On this basis, all the transition aluminas have oxygen ions in approximately cubic close packing. The differences in their patterns represent changes in intensities of reflections resulting from differences in distribution of the aluminum ions. The initial cationic disorder of the low-temperature phases depends upon the source of the alumina. The transitions become more ordered with increasing heat treatment.

4-3 SURFACE AREA OF ALUMINA

Gelatinous alumina pastes, prepared by the methods described in Section 3-3, especially the methods of Kraut and Schmäh, exhibit high surface area and high sorptive capacity for water vapor and other gaseous phases merely upon drying at about 120°C. Harris and Sing obtained initial surface areas as high as 1100 m^2/g for gels formed by hydrolysis of aluminum isopropoxide. Storage of these unstable gels in the presence of water vapor caused a loss in surface area to about 500 m^2/g. The adsorption isotherms of nitrogen, determined at -196°C on the outgassed products were of the reversible S-type, characteristic of physical adsorption on nonporous solids. Gels that had been

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dehydrated at room temperature approximately to the formula $Al_2O_3 \cdot 3H_2O$ showed no X-ray evidence of crystalline hydrate structure.

The initial gel loses water to about $Al_2O_3 \cdot 1.1-1.9H_2O$ upon drying at room temperature. Bye and Robinson (1961) obtained peak surface areas of about 480 m²/g for samples aged about three hours in water at room temperature into the pseudo-boehmite structure. Upon continued aging, the development of crystalline bayerite caused a reduction in surface area to about 250 m²/g within 18 hours, and to as low as 50 m²/g within 96 hours in the presence of a crystal-growth accelerator, NH_4OH (Lippens).

Tertian and Papée (1958) showed that the reactive pseudo-boehmite can be recrystallized in various stages of microcrystal growth to normal boehmite having a surface area of only 40 m²/g, by hydrothermal digestion at 300°C for about 18 hours. Calvet and Thibon observed that the surface of well crystallized hydrothermal boehmite may be less than 10 m²/g. Pseudoboehmite is not merely finely divided or poorly crystallized boehmite similar to hydrothermal boehmite (Papée, Tertian, and Biais). Differences in structure were shown by variations in the interplanar spacings, 6.11 Å for well crystallized boehmite, but 6.6 to 6.7 Å for the pseudoboehmite. The water in excess of the theoretical amount in well crystallized hydrothermal boehmite may be more than 0.25 mole, and in pseudoboehmite more than 0.6 mole. Goton considered this to be a trihydrate phase located around the surface of the crystallites because of the heating conditions required to decompose it. Tertian and Papée rejected this view, and pointed out that the amount, if present as trihydrate, could be detected by X-ray. Also, the loss of up to 12% water at about 300°C is followed by neither a significant increase in surface area (from 3 to only 3.5 m²/g) nor a structural change. The excess represented by $Al_2O_3 \cdot 1.6H_2O$, if present as a monolayer, would cover about 265 m²/g, essentially the total active surface of the pseudoboehmite.

Russell and Cochran measured the change in surface area of the hydrated aluminas with the dehydration temperature for heating periods of one hour at temperature. The surface area was measured by adsorption of n-butane. Gelatinous boehmite (dried at 140°) having an initial surface area of 340 m²/g, commenced to lose surface area at about 400°C, but retained about 70 m²/g at 1200°C. Coarsely crystalline hydrothermal boehmite, having an initial surface area of about 2.5 m²/g,

developed only 120 m²/g, peaking at about 500°C, pointing up the relatively poorer surface properties of this type. The surface area of the heated gibbsite did not reach as much as 2 m²/g until the weight loss was 8%, that is, a product equivalent to $Al_2O_3 \cdot 2.5H_2O$. The relatively low value for surface area at this point implies that the new surface was largely concealed in the interior of the particles, or, more probably, that it represented the formation of low-surface hydrothermal boehmite. The maximum surface area attained was about 340 m²/g, peaking at 400°C in dry air, and thereafter falling to less than 25 m²/g at 1200°C. Fine-crystal gibbsite and bayerite developed 425 and 380 m²/g, respectively, the higher values reflecting less susceptibility to coarse boehmite formation. The bayerite peaks of area occurred at about 300°C.

Blanchin found a substantial decrease in the surface area of gibbsite held for twenty hours at 400°C. Fricke and Jockers, and Fricke and Eberspächer confirmed the losses in surface area for bayerite and boehmite above 400°C. Emolenko and Efros determined the loss for activated aluminas produced by calcination of aluminum oxychloride. For 2-hr calcinations at 500, 600, 700, and 800°C, the specific surfaces were about 255, 174, 160, and 127 m²/g, respectively.

Gregory and Moorbath obtained curves for variation in surface area with temperature resembling those of Russell and Cochran, but by another technique, the emanation of thoron from the specimens. The method, devised by Hahn, has been improved in sensitivity by the techniques of electronic counting and recording. Upon heating gibbsite, impregnated with thorium salt during precipitation, a large increase in emanation occurred at 300 to 450°C. Minor changes were found at 850, 890, 1020, 1070, and 1090°C. A large decrease occurred at 1130°C. The changes did not correlate very well with structural changes observed photographically (Moorbath).

Carruthers and Gill investigated the surface area and structural changes occurring in an industrial trihydrate and a monohydrate in the heating range from 1200 to 1720°C. The surface areas for heating periods of two hours at 1200, 1400, 1600, and 1700°C were 5, 3, 1, and 0.3 m²/g, respectively. The surface area of alpha aluminum oxide obtained by calcination of the lower phases is usually less than 1 m²/g. Russell and Cochran obtained a surface of 85 m²/g for Missouri diaspore clay upon heating at 600°C. Only alpha alumina was shown by X-ray analysis. A strained, high-surface structure might account for

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the peculiarities observed by Herold and Dodd in this calcined product. Krishner and Torkar obtained 40 to 70 m²/g for hydrothermally produced alpha alumina having a particle size range of 300 to 800 Å, and a pore distribution of 100 to 50 Å.

4-4 POROSITY

Porosity, and its special case, permeability significantly affect the properties of alumina ceramics, and in a wide range of magnitude. Porosity is generated in sintered alumina structures for various reasons, some of which are: to improve permeability to gases and liquids for porous diaphragms and diffuser plates, to increase the thermal insulation of refractories, and to improve the fuel combustion in radiant heaters. Volatile or combustible burn-outs (sawdust, naphthalene) have been used to generate pores. Gas generators include: hydrogen peroxide (Ryshkewitch 1953), and aluminum powder with acids or alkalies.

Gross porosity beyond 50% by volume can be developed by calcining mixtures of ground and unground Bayer alumina at high temperatures. Uniformly distributed porosity is attained by "bisque" firing fine-ground alumina in the undersintered range 1000 to 1400°C.

Torkar (1954) pointed out that the property relationship of a porous or mixed body to those of its components applies to magnetic permeability, the dielectric constant, gaseous and liquid diffusion, the velocity of sound, the refractive index, elasticity, and thermal and electrical conductivity. The application of the mixed body theory to the "conductivity properties" of a porous material, that is, a solid-air system, leads to the expression: $y/y_1 = Kx_1/[K + (1 - x_1)]$, in which y and y_1 are the values for the mixed body and for the solid component; x_1 is the volume proportion of the solid component; $1-x_1$ is the porosity, p; and K is the "structure factor." The value of K varies from infinity for parallel orientation to zero for series orientation. It has the same value for all properties. The ratio y/y_1 is known as the β value of the property. When β is less than 0.7, the curves deviate markedly from the constant value.

Among the applications for sintered alumina in which porosity is undesirable are vacuum tube envelopes and ceramic lathe tools. Before firing such a compacted form, the porosity is

almost entirely open or permeable. Upon sintering, the open pores are gone when the total porosity has decreased to 5%. At 95% of theoretical density, the structure is gas-tight (O'Neil, Hey, and Livey).

Hayes, Budworth, and Roberts; Fryer et al.; and Budworth investigated the permeability of extruded sintered alumina tubes (total porosity 4 to 9%, purity 99.3 to 99.8% Al_2O_3). These tubes were impermeable to oxygen, nitrogen, and argon at temperatures below 1500°C. At 1500 to 1750°C, the specimens showed appreciable permeation to oxygen, presumably by a surface diffusion process. The diffusion coefficient was about $100\mu^2$/sec. Very slight or no permeation was found for nitrogen, and none for argon. After continued exposure for 100 hours at 1700°C, permeation by normal channel-flow developed suddenly and swamped the earlier phenomena. The permeation of nitrogen through hot-pressed sintered alumina (4 to 14% total porosity) was predominantly by Knudsen flow.

The effect of porosity on the mechanical strength and other properties of sintered alumina is discussed in those sections.

Surface area alone is not sufficient to qualify a porous desiccant or catalyst. De Boer, Heuvel, and Linsen; de Boer and Lippens; Barrer, McKenzie and Reay; Cranston and Inkley; Innes; and others have attempted to determine the shape and distribution of the pores from the shapes of the hysteresis curves obtained in sorption and desorption of the activated aluminas, and by application of the Kelvin equation for vapor pressure. The vapor pressure over a liquid with a curved surface is given by the equation:

$$\ln x = \ln p/p_0 = \frac{-2\sigma V \cos \psi}{RT\ r_k}$$, in which x is the rela-

tive vapor pressure over the liquid, σ is the surface tension of the liquid, ψ is the contact angle between the liquid surface and the solid, V is the molecular volume of liquid, and r_k is the Kelvin radius. In empty pores the sorbed liquid may condense at a higher relative pressure than it evaporates from the fully filled pores. This is the phenomenon called hysteresis.

Barrett, Joyner, and Hallenda gave a method for cylindrically shaped pores, Steggerda and Innes for slit-shaped pores.

Five general types of hysteresis loops have been distinguished, from which fifteen capillary shapes could be deduced. The adsorption isotherms of the activated forms of alumina fit the three main types, A, B, and E, all of which have steep desorption curves. Type A has a steep sorption branch, type B a gradual sorption branch, with a broad hysteresis range, and type E a gradual sorption branch with a narrow hysteresis range. The pore shapes are mainly open and closed tubular capillaries, ink bottle shapes, and slit shapes.

Sheet-like gelatinous boehmite shows a hysteresis loop intermediate between types A and E. The crystalline hydroxides give type B loop upon heating. Many of the narrow pores formed in activated gibbsite do not allow capillary condensation to occur. Two types of pores are believed to form in succession: platelike pores having a width of about 30 Å, lying in the cleavage plane of the gibbsite crystals; and pores having a width of about 10 Å, which divide the alumina structure into parallel rod-shaped crystals. Hydrothermal boehmite, upon heating develops slit-shaped pores, generally with type-B characteristics, with openings of about 25 Å.

Fricke and Jockers (1951), and Fricke and Eberspächer found that the pore diameter of dried gelatinous boehmite was about 60 Å at room temperature for a surface area of about 200 m²/g. The pore diameter began to increase above 400°C, reaching a value of 140 Å at 1100°C, for a surface area of only 37 m²/g. Fine bayerite, having a pore diameter of 14 Å at room temperature to 400°C, increased in pore size to 144 Å at 1100°C with an accompanying drop in surface area from 431 m²/g to only 33 m²/g. Boreskov et al. found that the porosity as determined by sorption and mercury porosimeter methods was unaffected by heating up to 600°C. On heating to 1200°C, the surface area decreased by a factor of 60, but the pore volume decreased by less than a factor of 2. Several investigators have provided electron micrographs showing that the pores become fewer and larger with increased heating.

A. G. Foster determined a Gaussian distribution for heated alpha trihydrate with a maximum at 26 Å, by applying the Kelvin equation to water sorption results. Drake and Ritter measured the size distribution of the coarser porosity by compressing mercury into the pores. The total pore volume was 0.388 ml/g, of which over 0.082 ml/g represented porosity coarser than 1000 Å in diameter. Some gross permeability is essential, however, to enable easy access of the sorbate to the micropore

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structure.

Chrétien and Papee determined the relative amounts of micro and macroporosity from the difference between total volume by immersion and the sorption of water and some organic liquids. Wosniczek showed that the conditions under which the alumina gels were produced determine to a large extend the internal structure and particularly the volume and size distribution of the pores. Sanlaville found two distinct maxima in pore size distribution of transition alumina: (1) 7 to 18 Å, having a surface area of 235 m²/g; and (2) 18 to 300 Å, having a surface area of 36 m²/g.

Bielanski and Burk found that water vapor is adsorbed in three stages at 25 and 50°C on alumina that has been activated at 450°C. Diffusion in oxide micropores is one mechanism. At pressures above 4.6 mm Hg, surface diffusion probably predominates. Water-vapor adsorption was measured at 40°C on samples of alumina that had been activated at temperatures from 250 to 1000°C. Isotherms were obtained from which the specific surface of the samples (180 m²/g at 450°C, falling to 46 m²/g at 1000°C) and pore structure could be determined. The smaller the diameter of the pores, the lower the activation temperature for reaching a maximum surface area.

As examples of the importance of control of pore size in sorptive and catalytic operations, the preparation of molecular sieves is cited. Basmadjian et al. control the pore volume and size distribution in alumina by the addition of water-soluble organic polymers (polyethylene glycols and oxides, methyl cellulose, and polyvinyl alcohols) to suspensions of the alumina prior to or during precipitation. Konoval'chikov et al. adjusted the pore structure of a precipitated Al_2O_3-Cr_2O_3 catalyst by displacement of intramicellar water from the initial gel with isoamyl alcohol. Kimberlin and Gladrow subjected dried hydrous aluminum oxide to an elevated pressure in the range of 15 to 1000 psi and a temperature in the range of 212° to 550°F, and dried the product by releasing steam from the reaction zone while maintaining the elevated pressure. A catalyst of increased pore volume and diameter was obtained.

4-5 SORPTIVE CAPACITY

Adsorption is the phenomenon of attraction and fixing of gaseous and liquid molecules to the surface of a solid, a property possessed by all solids to some degree. Adsorption results

from unbalanced surface forces or unsatisfied valences of the surface molecules. The amount of adsorption depends upon the attractive force of the adsorbent and the amount of surface area available. Although all molecules are adsorbed to a certain extent, molecules having high polarity, such as water, methyl-chloride, and some olefins, are likely to be more strongly held. Adsorption is accompanied by the liberation of heat and, conversely, desorption requires the application of heat. In physical adsorption, the heat released equals the heat of condensation of the adsorbed material plus the heat of wetting.

The strong desiccating action of moderately heated aluminum hydroxide, activated alumina, has been known at least since 1879 (Cross). The properties that make the activated aluminas particularly suitable for desiccant use are: the ability to develop high surface area during formation or dehydration; a high degree of chemical inertness; resistance to softening, swelling, and disintegration when immersed in water or other liquids; high resistance to shock and abrasion; and the ability to return to the original highly adsorptive form by a suitable thermal regenerative treatment.

The activated bauxites provide similar properties, but, in general, to a lesser degree and in frailer structures, subject to deterioration in moist condition (Heinemann). Ramaswamy et al. used activated bauxite in drying wet chlorine gas, and reactivated without impairing its efficiency. Bell nodulized flame-activated, ground bauxite. The nodules were cured to firm, spherical shapes upon aging until rehydration took place.

Commercial types of activated alumina are prepared: (1) by partially dehydrating massive alumina trihydrate, a by-product of the Bayer process, designated F-1*; (2) by forming amorphous gels according to the methods described in Section 3-3, type H-151. A special type, F-6, that indicates visually when the adsorbent is spent (at about 20% relative humidity) contains cobaltous chloride. This grade is used in breather-equipment on tank cars, in transformers and storage tanks, on pneumatic and electrical control equipment, in laboratory desiccators, between multiple-glazed windows, and like applications where a visual indication of the degree of adsorption is desirable. A second type, F-5, is impregnated with calcium chloride, which about

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* Aluminum Company of America designations

doubles the sorptive capacity or "one-shot" rapid desiccating applications at somewhat higher dewpoints. Reactivation above about 180°C causes progressive decomposition of the calcium chloride. Another type for controlling atmospheres in heat-treating furnaces contains about 2.5% nickel formate, F-7. Many other types, in which silica or metal oxides or salts are co-precipitated with or impregnated on the activated alumina, have catalytic applications. Some types of activated alumina are shown in Table 8. Sorptive capacities of two grades are shown in Figure 7.

Table 8
Typical Properties of Desiccant, Chromatographic, and Catalytic Aluminas

	F-1	H-151	F-20	T-71	F-110	F-7
Typical Properties						
Al_2O_3 .... %	92.	90.	92.	99.5+	92-94	84.0
Na_2O .... %	0.90	1.6	0.90	0.01	0.08	0.90
Fe_2O_3 .... %	0.08	0.13	0.08	0.06	0.03	0.08
SiO_2 .... %	0.09	2.2	0.09	0.04	0.01	0.09
Loss on ignition(1100°C) %	6.5	6.0	6.2	0.0	6.0-8.0	12.1
SO_3 .... %				0.09		
CaO .... %				0.06		
Nickel formate .... %						2.5
Form	Granular	Ball	Granular	Granular	Balls	Granular
Surface area, m^2/g	210	390	210	0.5	180-280	
Bulk density,loose, lb/ft^3	52	51	58	76	50	52
Bulk density,packed,lb/ft^3	55	53	68	85	55	55
Specific gravity	3.3	3.1-3.3	3.3			
Static sorption at 60% RH	14-16	22-25				
Crushing strength	55	75				
Pore volume, ml/gm					0.15-0.20	0.38
pH			9.0			
Sieve analysis						
on 80 mesh ....%			2 max.			
Through 270 mesh ....%			5 max.			

Courtesy of Aluminum Co. of America
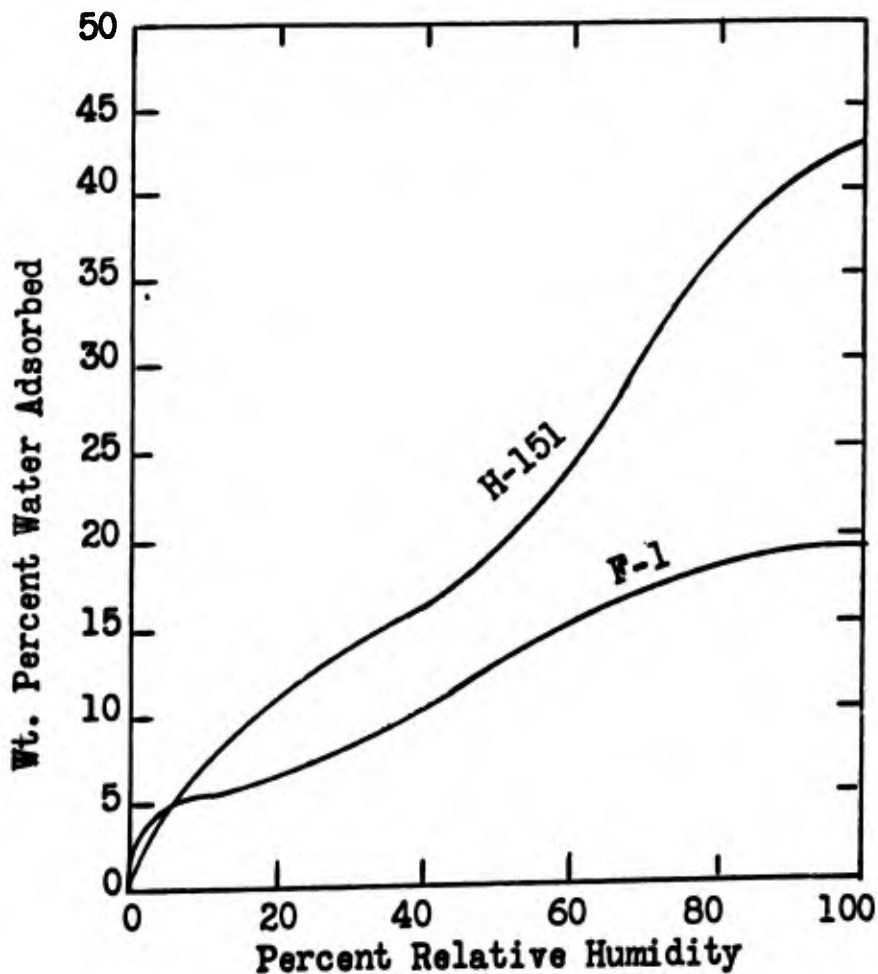
Figure 7. Equilibrium Curves for Water
After Normal Activation at 400°F

Ehman prevented dusting of granular activated alumina in refrigeration systems by coating the particles with 0.05 to 5% by weight of phosphoric anhydride. Smirnov et al. prepared mechanically strong activated alumina by decomposing the aluminum carbonates $(Na,K)_2O \cdot Al_2O_3 \cdot 2CO_2 \cdot nH_2O$ at about 100°C.

A partial list of gases and liquids which can be dried by activated alumina (Alcoa brochure, February 1, 1963) includes the following:

Gases

Acetylene, air, ammonia, argon, carbon dioxide, chlorine, cracked gas, ethane, ethylene, Freon, furnace gas, helium, hydrogen, hydrogen chloride, hydrogen sulfide, methane, natural gas, nitrogen, oxygen, propane, propylene, and sulfur dioxide.

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Liquids

Benzene, butadiene, butane, butene, butyl acetate, carbon tetrachloride, chlorobenzene, cyclohexane, ethyl acetate, Freon, gasolines, heptane, hexane, jet fuel, kerosene, lubricating oils, naphtha, nitrobenzene, pentane, pipe-line products, propane, propylene, styrene, toluene, transformer oils, vegetable oils, and xylene.

Activated alumina, produced from massive Bayer trihydrate (F-1 type), adsorbs moisture to 14 to 16 percent of its dry weight at 60 percent relative humidity. Dew points of minus 75°C are attainable. Activated alumina (H-151 type) is especially suited for the drying of foods and drugs. Its static sorptive capacity at 60 percent relative humidity is 22 to 25 percent of the dry weight.

Kipling and Peakall observed that the adsorption of vapors by solid oxides was only partially reversible. Water vapor and the vapors of the lower aliphatic alcohols are held by chemisorption if oxide ions are present in the surface. Physical adsorption can take place on the chemisorbed material. De Boer, Fortuin, Lippens and Meijs stated that the chemisorbed water is proportional to the specific surface area, amounting to about 24.8 mg $H_2O/100$ m^2. This suggests a binding of one water molecule to two oxygen atoms in the surface. The surface covered with chemisorbed water adsorbs more water by physical sorption. The monolayer capacity is also approximately proportional to the specific surface area, and is about 33 mg $H_2O/100$ m^2. Lauric acid can be adsorbed on the water layer adsorbed on the alumina surface, and can displace water beyond a critical water content of about 50 mg $H_2O/100$ m^2. Actually, alumina that has been calcined at 800 to 1200°C picks up and retains a significant amount of water which resists expulsion at temperatures as high as 500°C.

The decrease in effective surface area by chemisorption is a factor in the cyclic use of activated alumina in service as sorbents. Applications of adsorption generally take place under dynamic conditions, that is, under conditions of gas flow in which the desiccant is not allowed to come to equilibrium as it becomes spent and its efficiency decreases. There may be an initial loss of as much as 30 percent of the original dynamic sorptive capacity depending upon the conditions selected, after which the loss becomes exceedingly slow. The service can be

carried through hundreds of cycles; an original charge (F-1) in a unit for drying annealing-furnace atmosphere performed satisfactorily for more than 25 years.

This stability against loss of activity is possible only if there is no chemical reactivity between the active surface and the sorbed substances. Activated alumina reacts chemically with some fluorides, hence cannot dry them. Advantage has been taken of this, however, to diminish the level of fluorine in municipal water treatment to useful concentrations for dental protection. Activated alumina also provides practically complete removal of fluorine from the product of the hydrogen fluoride alkylation process. Savinelli investigated the fluoride-ion exchange capacity of activated alumina regenerated by dilute alum solutions. Satisfactory exchange of fluorides was obtained from waters of high carbonate hardness, but not from waters of high sodium or potassium bicarbonate alkalinity.

Some liquids react with activated alumina; for example, acetone is catalytically oxidized to mesityl compounds upon heating. Some components may be deposited as solids or viscous liquids on the active surface, as for example, sulfur. Miller and Weir claimed improved drying of paraffinic hydrocarbons containing sulfur compounds by treating the activated alumina with dilute mineral acid. Bienstock et al. removed sulfur oxides from flue gas by absorption at 330°C in alkalized alumina. The absorbent was then regenerated by heating with hydrogen or steam-reformed natural gas.

Unsaturated organic compounds sometimes polymerize to high-boiling compounds which may foul the desiccant. Carbonaceous deposits form from natural gas and unsaturated hydrocarbons, which act to reduce the active surface. High-temperature regeneration (500 to 600°C) of H-151 type of activated alumina under oxidizing conditions restores almost the original sorptive capacity. Krieger and Heinemann purged with steam at 370°C and finally reactivated at 400 to 700°C.

Common methods for determining the sorptive capacity of desiccants involve the isothermal pickup of water at controlled humidities and temperatures, either under static or dynamic conditions of flow. In many commercial operations, however, the adsorption is to a large extent adiabatic. Bower compared the efficiency of several desiccants (barium oxide, lime, anhydrous calcium chloride, and calcium sulfate, and silica gel) with that of activated alumina under dynamic flow of moist air

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at 30°C. The activated alumina reduced the moisture content of the air to only 0.0018 mg/l, and was exceeded in efficiency of removal only by barium oxide on the weight basis.

Stowe determined that about 18.0 cal/g of activated alumina represents the heat release when activated alumina (F-1) is immersed in liquid water. About 24.4 cal/g is released for activated gelatinous, amorphous alumina (H-51). Robert found that the heat of wetting of 15 organic liquids on activated alumina is proportional to their degree of adsorbability. The heat of adsorption varied from 10 kcal/mole water adsorbed when the level of water adsorbed was 3% by weight to over 105 kcal/mole when the level was about 0.1% (Cornelius et al.). Sanlaville found that the differential heat of adsorption is 6 to 7 kcal/mole for 0 to 30 mg H_2O/g Al_2O_3 (the first layer), 0.9 kcal/mole for 130 mg H_2O/g Al_2O_3 (the second layer), and only 0.25 kcal/mole for more than 150 mg H_2O/g Al_2O_3.

Freymann concluded that the water adsorbed on alumina is in the liquid state, inasmuch as it has a microwave absorption at 3.15 cm. Liquid water has an absorption in this region, but not hydrated alumina.

Getty, Lamb, and Montgomery; Miller and Roberts; and Getty and Armstrong investigated the dynamic sorption of water vapor from gases, to improve the understanding of industrial dynamic drying conditions. In drying gases under pressure, the heat of adsorption is dissipated easily because of the high heat capacity of the gas. Under certain conditions, a temperature wave precedes the sorption wave. The adiabatic operating capacity of the desiccant bed is much less than that calculated from isothermal equilibrium data. Equations for adiabatic capacity were determined for use in the design of large industrial gas dryers which operate without internal cooling. Fleming, Getty, and Townsend applied these principles to the design of a 4-tower natural gas dehydration section in a helium extraction facility at Liberal, Kansas. It uses about 350,000 lb of granular activated alumina to dry over 840,000,000 scf of natural gas daily.

Winter followed the exchange between an oxygen atmosphere containing 1.2% ^{18}O and transition alumina by means of a mass spectrograph. At 500°C, an initially fast first-order exchange had a heat of activation of 37 kcal/mole. A slow reaction followed. A similar exchange was observed for heavy-oxygen water vapor (Whalley and Winter). The exchange between water vapor and alumina attained 20, 30, and 50% equilibrium at 200, 400, and

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600°C, respectively (Karpacheva and Rozen). The initial first-order exchange was independent of the oxygen pressure, and was considered to result from surface oxygen ions. The rate constant increased from 0.0067 min^{-1} at 485°C to 0.0146 min^{-1} at 592°C. The subsequent slow exchange was ascribed to diffusion of oxygen ions from an interior layer to the surface. After exchange of O^{18} from water vapor, further exchange could be effected with ethyl alcohol vapor at 200 and 400°C, probably by the same mechanism. Dontsova observed a similar exchange in CO_2 at 1100°C. Rozen et al. concluded that the mechanisms involved are the heterogeneity of the surface, polydispersion, and a combination of adsorption and solution.

Greaves and Linnett determined the coefficients of recombination for the removal of oxygen atoms at the surface of alumina. The decay of atom concentration was exponential (first order), but the activity could not be related to any single parameter associated with the surface material.

Holm and Blue found that pure alumina of high surface area has high activity for hydrogen-deuterium exchange. This is greatly increased by raising the calcination temperature from 400°C to 800°C. Silica in the catalyst decreased the exchange but increased the rate of hydrogen transfer reactions from naphthenes to olefines. Bernstein observed that the rate of exchange of O^{18} was appreciably less than that of deuterons from D_2O^{18} to boehmite powder (12.2 m^2/g surface area) from 100 to 230°C. This suggested that the diffusion of oxygen-bearing carriers (such as OH^-, H_2O or O^{2-}) is independent of the protons (deuterons) through the lattice. Apparently only one-half the oxygen atoms in the boehmite are exchangeable. The activation energy for the proton (deuteron) diffusion coefficient is approximately 12 kcal/mole. The deuteron exchange between D_2O and bayerite at 25°C was more rapid than with the smaller particles of boehmite at the same temperature. The proton mobility in bayerite appears to be an order of magnitude greater.

The active surface of the alumina spinel may be assumed to contain covalent bonds locally between incompletely coordinated aluminum atoms and the surrounding oxygen atoms. These aluminum atoms are associated with acid sites on the surface. They behave as electron pair acceptors (Lewis acids) and will strongly bind water molecules with the formation of protonic acids (Brönsted acids), as is shown by the two structures:

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600°C, respectively (Karpacheva and Rozen). The initial first-order exchange was independent of the oxygen pressure, and was considered to result from surface oxygen ions. The rate constant increased from 0.0067 min^{-1} at 485°C to 0.0146 min^{-1} at 592°C. The subsequent slow exchange was ascribed to diffusion of oxygen ions from an interior layer to the surface. After exchange of o^{18} from water vapor, further exchange could be effected with ethyl alcohol vapor at 200 and 400°C, probably by the same mechanism. Dontsova observed a similar exchange in CO_2 at 1100°C. Rozen et al. concluded that the mechanisms involved are the heterogeneity of the surface, polydispersion, and a combination of adsorption and solution.

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```
  ..     ..
: O : Al : O :           H  H⁺        Alumina-silica cracking catalysts
     ..                  : O :        owe their activity to such acid
     O                   ..           sites (Trambouze and Perrin).
                    O : Al⁻ O         Mixtures of neutral silica sols
Lewis acid              ..            with neutral alumina sols develop
                      : O :           strong acid.  One equivalent of
```

acid is produced for each atom of aluminum consumed in this re-
action. The reaction becomes less effective with aging of the
gels (Tamele).

De Rossett, Finstrom, and Adams claimed that the adsorption
of hydrogen sulfide from mixtures of hydrogen sulfide and hy-
drogen at 260 to 560°C was like that of water and ammonia in re-
acting as a base at Lewis acid sites formed by stripping oxygen
anions from the spinel surface. Over a range of H_2S partial
pressure from one micron to 4.4 mm, 39 to 107 micromoles H_2S/g
Al_2O_3 were observed. Heats of adsorption ranged from -25 to
-38 kcal/mole, depending on the degree of predrying of the alumi-
na.

Statistical calculations made by Clark and Holm for the ad-
sorption of NH_3 in the region of fixed adsorption indicate a
broad distribution of adsorption energies. The adsorption data
fit the integral form of the Langmuir equation. Entropies were
several times smaller than those for uniform sites. Below a
coverage of 0.36×10^{14} moles/cm², the adsorbed NH_3 molecules
have lost all translation and rotation. Above this value one
degree of rotational freedom may have been regained.

Smith and Metzner developed a molecular model of the sur-
face transport rate process, containing only one arbitrary pa-
rameter. Experimental measurements of the migration rates of
propane, butane, propylene, perfluoropropane, and Br_2CF_2 over a
wide range of pressures and a moderate range of temperatures on
an alumina catalyst surface support the theoretical model.

Mizutani, Sakaguchi, and Iizuka used the adsorption of
alcohol and aromatic compounds as a measure of adsorbent activ-
ity for use in petroleum refining. Topchieva et al. found that
during the dehydration of ethyl alcohol with activated alumina,
the surface of the alumina became hydrated, and this increased
its catalytic activity. It was possible to adsorb methyl alco-
hol both on hydrated and dehydrated surfaces.

Roach and Himmelblau investigated the adsorption of calcium,
strontium, and thallium ions from molten mixtures of zinc and

potassium chlorides by both activated alumina and silica. No adsorption for any of the cations could be obtained on the silica. Thallium was not adsorbed on alumina, but strontium and calcium were adsorbed, the rate being twice as fast for strontium. The calcium isotherm at 250°C fitted the Freundlich and Langmuir equations. No effective method was found to elute the cations from the alumina column.

Aleixandre-Ferrandis determined the quantitative sorption on activated alumina of many organic acids dissolved in common organic solvents. He preferred activated alumina prepared by the method given in German Patent 561,713. Fridman claimed that activated alumina having a surface area of about 180 to 370 m²/g and a pore radius of 25 to 55 Å has a higher sorptive capacity for the acidic compounds in oxidized transformer and turbine oils than silica gel. This is particularly true for acids of low molecular weight. For a period of 370 days, 0.15% of activated alumina in the oil sorbed the same amount of acids as is sorbed by 2% of silica gel. Fairly stable oils with an acid number as high as 0.10 mg KOH were regenerated within two weeks to the specifications of fresh oil. Aluminum Company of America offered instructions in a manual "Activated Alumina Maintenance Program: Power System Oils" (1955) for preventing deterioration of oils used in transformers, oil circuit breakers, and hydro-electric powerhouse equipment by continuous circulation of the oil through bypass filters in which the alumina adsorbs moisture and acids and prevents sludging and corrosion of metal parts. Sargent and Kipp, and Sawyer, Keefer, Kipp, and Shaw demonstrated the excellent service of activated alumina in maintaining lubricants in gas burning in-line internal combustion engines and in large radial gas engines.

Engel and Krijger impregnated a porous alumina with an aqueous solution of an aluminum salt in an amount sufficient to fill the pores without causing agglomeration, and heated at above 200°C in order to obtain an active contact decolorizer of hydrocarbon oils.

Czaplinski and Zielinski claimed that it is more effective to separate helium, neon, and hydrogen by adsorption in alumina under pressure of a few atmospheres at the temperature of liquefied nitrogen. Hydrogen is the most strongly adsorbed, followed by neon; helium is the least adsorbed. At pressures of about 30 atmospheres, helium and neon are about equally adsorbed.

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4-6 CHROMATOGRAPHIC ALUMINA

Chromatography is the special case of adsorption in which the identification and separation of adsorbed ions are based on color, fluorescence, or other induced visual effects. Chromatographic separations are often made in columns of uniformly sized (80 to 200 mesh) high-purity activated alumina. The substance to be separated is dissolved in water or other suitable liquid. The adsorbed components of the substance separate into layers in the column at positions determined by the firmness of adsorption. The adsorption is by displacement of ions of equal sign (Schwab; Shuvaeva and Gapon). Both anionic and cationic adsorption can occur, depending upon the surface treatment (Sacconi; Grasshof; Plank), but alumina gel is primarily an anion sorber.

The chromatographic method has been applied to the detection, isolation and purification of alkaloids, biological solutions of hormones, toxins and other complex structures, drugs, enzymes, fats, food products, inorganic salts, dyestuffs, alcohols, vegetable oils, liquors, gases and vapors, etc. (Strain; Zechmeister and Cholnoky; E. and M. Lederer). Applications of ceramic interest appear to be quite limited in scope.

The gel aluminas of Willstätter and Kraut were prepared under closely regulated conditions for use in enzyme separations. Brockmann standardized the activity of Merck's technical alumina trihydroxide by heating it to a strong red heat and then partly deactivating to various degrees by contacting it with moist air for different periods. Six classes of adsorbents were distinguished by means of their adsorption of the following dyes, which have increasing sorptive activity; methoxyazobenzene, azobenzene, Sudan yellow, Sudan red, aminoazobenzene, and hydroxyazobenzene. Interferences in the chromatographic separations arise because the water on the alumina is distributed between the surface and the eluant. With changed activity of the alumina, some separations are not possible. Adjustment of the water content of the eluant prevents the interference (Hesse and Roscher). Nikolic and Velasevic prepared oxides having the same activity as Brockmann's alumina by heating the following salts at $600°C$ for 6 to 7 hours: $Al_2(SO_4)_3 \cdot 18H_2O$, $AlCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $NH_4Al(SO_4)_2$.

For many column separations, the single size distribution, 80 to 200 mesh, of chromatographic alumina (F-20) is satisfactory. Solutions of barium, calcium, strontium, cadmium,

magnesium, manganese, zinc, and tungsten salts have been freed from trace impurities of iron, copper, lead, and silver by passage through activated alumina (Lister). Fricke (1953), and Venturello and Burdese found that copper chloride solutions precipitate as $Cu_2(OH)_3Cl$ in an immediate reaction through the surface hydroxyl groups and in a secondary reaction continuing with time resulting from rehydration of the oxide. Quantitative separations were obtained; the chemically adsorbed copper ion was replaced by aluminum in solution.

The order of decreasing cation adsorption found by Sacconi is: (Th, Al, U^4), (Zr, Cr, Ce^4), Fe^3, Ti^4, Ce^3), Hg^2, UO_2^2, Pb, Cu, Ag, Zn, (Fe^2, Co), (Ni, Cd), Tl, Mn. Shibata showed the following order: Bi^2, Fe^3, Hg^2, Pb^2, Cu^2, Zn, Co^2, Cd, Ni^2, Fe^2, and Mn^2. He claimed that calculation of the potential energy for adsorption employing the radius of the hydrated ion also showed this order. The order of decreasing anion adsorption found by Kubli is: OH^-, PO_4^{3-}, $C_2O_4^{2-}$, F^-, (SO_3^{2-}, $[Fe\ CN]_6^{4-}$, CrO_4^{2-}), $S_2O_3^{2-}$, SO_4^{2-}, ($Fe[CN]_4^{3-}$, $Cr_2O_7^{2-}$, (NO_2^-, CNS^-), I^-, Br^-, Cl^-, NO_3^-, MnO_4^-, ClO_4^-, Ac^-, and S^2. Neugebauer; Schafer; and Cetini and Ricca applied the chromatographic technique to many inorganic ion separations on basic and neutral activated alumina columns; the OH ions of the alumina surface were first removed or blocked before applying chromatographic adsorption.

Tewari, Dey, and Ghosh measured the decrease in sorptive capacity with aging of gels precipitated from aluminum chloride solution with 110, 100, and 90% of the equivalent alkali hydroxide solution. Aging had more influence on the sorption of cations and basic dyes when the gel was precipitated with a deficiency of alkali. The influence of aging was greatest on the sorption of anions and acid dyes when the gel was precipitated with excess alkali. Brierly and Smith (1964) investigated the changes occurring in the surface of dry alumina held in storage when strongly hydrophilic solvents were used. The activity was found to be independent of the age of the dried activated alumina.

4-7 CATALYTIC ALUMINAS

The catalytic aluminas act either by themselves or in combination with other chemical agents to perform certain reactions at accelerated rates or to enable the reactions to take place at lower temperature or pressure than otherwise would be required. The catalyst itself is not changed during the

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operation. The alumina may serve as a support for catalytically active metals (Pt, Cr, Mo, Ag, Pd), metal oxides (Co, Ni, Mn, Fe, Cr, V, Mo, etc.), and salts (fluorides, chlorides, etc.), impregnated on the active surface. It may also be co-precipitated from mixed solution, often to modify pore size, as in mixtures of alumina and silica gel (Belon).

Bayer plant production provides large tonnages of economical catalytic aluminas. The direct use of Bayer-process activated alumina having high surface area in the destructive dehydration of alcohols, and the use of massive tabular alumina of low surface area for oxidation reactions are typical applications. The latter is available in high purity and in rugged granular and spherical forms having excellent resistance to thermal and mechanical shock in fixed-bed applications. Powder forms of tabular alumina have high attrition resistance in fluid-bed applications. High-surface catalysts are also produced by precipitation from alkali aluminate or aluminum salt solutions by methods described in previous sections. The surface areas range from less than 0.1 m^2/g to about 300 m^2/g.

Pelletized and extruded catalyst shapes may be prepared by common ceramic methods. For example, Schulze and Hillyer (1948) prepared a pelletized catalyst of alumina containing barium, magnesium, and potassium oxides (1) by dry mixing and pelleting the ingredients, followed by heating to about 650°C to activate and bond; (2) by impregnating the prebonded alumina pellets with solutions of the other components, followed by a heat-treatment; or (3) by wet mixing of the ingredients followed by extrusion, drying and activation. Reimpregnation of porous pelletized forms with an aqueous solution of an aluminum salt ($Al_2(NO_3)_3$ or $AlCl_3$), precipitation by ammonium hydroxide, and recalcination improves the physical strength (Brennan et al. 1959). Owen added an organic binder during pelletization, which upon partial burning out of the binder at 200 to 600°C, produced a pellet with a porous shell. This enabled a depth-controlled impregnation with aqueous solutions of desired catalysts which were subsequently converted to the oxide by heating.

Much attention has been given to producing spherical or spheroidal shapes in micro and macrosizes for catalytic operations. Tongue and Baral prepared microspheres by mixing an acidified silica gel containing aluminum sulfate with ammonium hydroxide to precipitate aluminum hydroxide, by partially dewatering the gel suspension, and by spray drying. The residual soluble salts were removed by washing, and the salt-free spheres

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were then calcined to attain enhanced attrition resistance.
Strecker and Callahan applied a similar method to the production
of a chromia-alumina catalyst. Gladrow and Kimberlin prepared
both micro and macrospheres by spray-drying hydrolyzed aluminum
alcoholate hydrosols, followed by calcination for from one to
six hours at 900 to 1300°C. Innes (1964) prepared alumina
microspheroidal particles having good attrition resistance by
alkalizing an acidic alumina sol to a pH of 8.5 to 10.5, to
convert it to a gel slurry, and spray-drying the slurry. Fisher
and Ueltz prepared approximately spherical particles by spraying
a creamy mixture of alumina and aluminum chloride into ammonia
water, and subsequently collecting and drying the particles.

An ingenious method for producing macrospheres consists of
suspending droplets of alumina hydrogels or hydrosols in water-
immiscible liquids (hydrocarbon oils) under conditions to induce
set (Universal Oil Products Company 1948; Archibald; Messenger;
Hoekstra). Murray and Moehl added an organic basic gelling agent
to induce set at 50 to 104°C. Michalko added hexamethylene
tetramine to the suspension before passing it to the oil bath to
form droplets. Cramer and Schwartz prepared the hydrogels by
mixing a solution of sodium aluminate, a hydroxy-carboxylic acid
(citric acid), and a water-soluble aluminum salt (aluminum sul-
fate). The hydrosol is set at 57°C in less than three seconds,
and may be aged in petroleum oil. Nixon prepared the alumina
hydrosol by reacting hydrogen peroxide with aluminum bromide.
Richardson and Schexnailder passed droplets of silica hydrosol
downwards through a solution of anhydrous aluminum alcoholate
in excess alcohol. The water in the silica sol hydrolyzed the
aluminum alcoholate, causing gelation of the silica and deposi-
tion of alumina on the hydrogel.

The catalytic activity of alumina depends on its mode of
preparation, and changes in character with the calcination
temperature. At temperatures around 350°C, the action is de-
hydrating; at higher temperatures, a dehydrogenating action
develops.

A list enumerating over 180 representative applications of
catalytic processes using alumina directly or as a support for
other catalysts is given in Alcoa Product Data Brochure "Acti-
vated and Catalytic Aluminas" February 1, 1963. The catalytic
procedures include the general processes: reforming (con-
version of lower-boiling gasolines and naphthas to products of
higher antiknock rating), cyclization(aromatization and other
ring closures), dehydrogenation, hydrogenation, cracking,

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isomerization, synthesis, destructive dehydration, reaction with water, reactions of sulfur compounds, oxidation, and halogenation (chlorine, fluorine, etc.). Only a few examples can be mentioned here.

The most extensive commercial application of alumina in catalysis is as a support for platinum and the oxides of molybdenum and chromium. Reforming processes include such organic conversions as hydroforming, platforming, and the general refining of hydrocarbon distillates. Patents on reforming alumina catalysts impregnated with platinum have been issued to Haensel (1949, 1957, 1958); Hunter and Kimberlin; Dinwiddie and Mosesman; Brennan et al.; Hinlicky and Serniuk; Feller; Connor and Shipley; Teter and Keith (1959); and Kimberlin and Buchmann. Hall and Kutinski (1963) have determined the number of exposed platinum atoms (the surface area of the platinum) and also the number of hydroxyl groups on the alumina by exchange with deuterium gas as the temperature was raised. H/Pt ratios of 0.7 to 0.9 confirmed previous work, indicating that most of the metal atoms are accessible for chemisorption of hydrogen. The hydroxyl groups in the alumina did not exchange appreciably below 100°C.

Claussen and Wellman prepared a coprecipitated alumina-molybdena catalyst for use in improving the antiknock characteristics of gasoline. Layng and Suman stated that the catalytic action of molybdena is increased by the addition of titania. Polack prepared a reforming catalyst by dry-mixing zinc oxide, alumina, and molybdena, and by calcining at 600 to 750°C for 3 to 16 hours. Sieg prepared a fluid alumina-molybdena reforming catalyst containing from 0.5 to 15% crystalline graphite uniformly dispersed throughout each catalyst particle. Modifications of chromia-alumina catalysts for reforming operations were described by Cornelius and Kirsch, and Strecker and Stine. Worsham and Skarstrom calcined an alumina-molybdena catalyst at above 590°C for at least 2 hours for use as a hydroforming catalyst.

Pines and Chen have described the aromatization of heptane and octane over alumina-chromia catalysts. The dehydrocylization mechanisms possibly involved 5- to 8-membered ring intermediates. Chromia-alumina coprecipitated catalysts that had been calcined at 500 to 1400°C were found by Poole, Kehl, and MacIver to contain various mixtures of γ-Al_2O_3, θ-Al_2O_3, α-Cr_2O_3, and both γ and α-phase chromia-alumina solid solutions. At low chromia concentrations, two principal electron spin resonances

were observed, δ-resonance attributed to electronically iso-
lated Cr^{3+}, and a resonance due to Cr^{5+}. At higher chromia
concentrations an additional resonance was observed, which was
attributed to electronically coupled Cr^{3+} (β-resonance).

Alumina for cracking catalysts, that is, for decomposing
heavy petroleum oils into lighter fractions, may contain sil-
ica (Wilson), usually produced as coprecipitated gels, or as
mixed gels following precipitation. The cracking catalyst may
also consist of alumina or alumina-silica gel containing added
fluorine as SiF_4 (Garrison), as NH_4F (Erickson), or as chromium
fluoride (Hirschler).

Dehydrogenation reactions are performed with alumina im-
pregnated with many metal oxides, among which are the oxides
of chromium, vanadium, cerium, hafnium, thorium, molybdenum,
beryllium, nickel, zinc, copper, magnesium and calcium. Corson
and Webb prepared a catalyst from alumina-silica impregnated
with less than 3% Ni, which maintained dehydrogenation activity
of hydrocarbons at 650°C in the presence of steam. Pitzer im-
pregnated with oxides of molybdenum, tungsten, and vanadium.
Simon et al. (1963) coprecipitated the hydroxides of aluminum
and zinc, and calcined at 300 to 1000°C. This mixture acted
both as a dehydrogenating and a dehydrating catalyst on iso-
propyl alcohol. The spinel formation had dehydrating proper-
ties in an active intermediate stage, associated with the forma-
tion of acid surface groups caused by lattice distortions. The
acid centers were destroyed by heating at higher temperature at
which dehydrogenating properties resulted.

Pis'man et al. investigated the dehydration of butanol to
butene by a catalyst prepared from commercial alumina impregnated
with KOH after activation at 500°C. The optimum production of
butene occurred for the catalyst containing 0.25% KOH, and at
300°C.

Gladrow and Kimberlin prepared an attrition-resistant
hydrogenation catalyst by impregnating suitable metal oxides on
eta alumina microspheres. J. W. Scott (1959) claimed a hydro-
genation catalyst comprising about 1 to 6% cobalt oxide and 6 to
60% molybdenum oxide supported on alumina. Hilaire (1962)
applied alumina calcined at 500°C directly to the hydrogenation
of ethylene and to the decomposition and dehydration of formic
acid.

Folkins and Carr effected the isomerization of saturated

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hydrocarbons by use of an alumina-silica support impregnated
with a minor amount of nickel and the molybdate, phosphate,
borate, chromate, or tungstate of nickel. Ogasawara and
Cvetanovic isomerized the n-butenes by use of alumina impreg-
nated with sodium carbonate (5% by weight). The adsorption
equilibrium constants, the rates, and the activation energies
of the reactions were determined, and the process was fol-
lowed by gas chromatography.

Shepard, Rooney, and Kemball found that the reaction of
propylene on a silica-alumina catalyst at 58 to 200°C involves
both polymerization and cracking, accompanied by isomerization,
hydrogen transfer, and coke formation. Both Lewis and
Brönsted acidity sites were demonstrated.

The synthesis of various nitriles from olefins, vinyl
fluoride from acetylene, hydrazine have been of interest by
catalytic processes. An example is the catalytic synthesis of
acetonitrile in a fluidized bed from acetylene and ammonia.
Ogasawara, Nagai, et al. used 100 to 200-mesh alumina, impreg-
nated with 3 to 4% by weight of sodium carbonate to repress the
side reactions such as formation of pyridine.

A great amount of research has been expended on catalytic
oxidation reactions, many of which have commercial importance.
Examples are the oxidation of methane to methanol, and ammonia
to nitric acid. Oxidation reactions using alumina alone or as
a support for vanadia or other catalysts (Cannon and Welling)
have been investigated as a possible solution to the problem of
air pollution from automobile exhaust gases, but mechanical
combustion equipment presently appears more feasible. Oxida-
tions may involve alumina as a support for other oxides among
which are MoO_3, CuO, CoO, and NiO. Mixtures containing silver,
palladium, and nickel have been used. Waterman prepared an
oxidation catalyst by impregnating alpha alumina with silver
lactate solution and by heating below 425°C to deposit elemental
silver in a highly active form on the alumina surface. Brouwer
presented evidence that the oxidizing properties of silica-
alumina or fluorided gamma alumina are connected with their high-
ly acidic nature. Lewis sites are the oxidizing centers.

Catalytic reactions involving the synthesis of sulfur com-
pounds used Al_2O_3-Cr and Al_2O_3-Mn catalysts (Thacker). Carbon
disulfide is prepared from methane. Desulfurization reactions
are applied to hydrocarbons to remove thiophene and other sulfur
compounds that cause catalyst poisoning and induce corrosion

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in lubricating oils or unpleasant odors in organic compounds. Watkins used alumina impregnated with boric oxide and about 1 to 20% by weight each of a cobalt compound and a molybdenum compound. Hansford used an alumina-silica gel carrier containing about 3 to 25% V_2O_5, and 0.1 to 5% MgO by weight. Metals of high surface area including nickel, chromium, molybdenum, cobalt, and iron are often impregnated on the alumina base. Absorption of the sulfur as the metal sulfide effectively removes it from the sphere of action.

Tung and Mcininch claimed that high-purity alumina possesses good activity for butene isomerization but relatively poor activity for propylene polymerization and for cumene and hexene cracking below 400°C. Above 400°C it has good cracking activity. Dowden related the relative dehydrogenation and dehydration activities of alumina to the number of cation vacancies on the active surface. Holm and Clark observed that typical acid-catalyzed hydrocarbon conversion reactions, such as cracking isomerization, and olefin polymerization, occur most readily on weak acid sites. Alumina has strong sites. Weaker sites are desirable for good catalytic activity because they allow higher surface mobility and permit easier desorption; they can be developed in alumina by additions of fluorine. Cornelius et al. had earlier ascribed the catalytic activity of alumina to highly strained sites of hydroxyl groups.

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5 MECHANICAL PROPERTIES OF ALUMINA

5-1 GENERAL CONSIDERATIONS

Alpha aluminum oxide, both as single crystals and in poly-crystalline sintered form, has remarkable mechanical properties in comparison with conventional porcelains and other single oxide ceramics. None of the likely refractory single-oxide contenders (BeO, CaO, CeO, MgO, Nb_2O_5, SnO_2, ThO_2, TiO_2, ZrO_2, UO_2, and the rare-earth oxides) approaches pure sintered alumina in bending and tensile strengths at room temperature, and only ZrO_2 and ThO_2 are comparable in compressive strength. At about 1000°C, alumina is not approached by them in tensile strength, is matched only by BeO and MgO in bending strength, and is exceeded only by stabilized ZrO_2 in compressive strength (Hague et al., 1963). Many of the advantageous strength characteristics are retained to lesser extent by the high and low-alumina porcelains (Austin, Schofield, and Haldy; Haldy et al.).

The interest in mechanical properties stems from several modern applications such as the possible substitution of alumina ceramics for refractory metal parts in air-borne equipment, or fabrication forms in which high mechanical strength, hardness, or thermal shock resistance is important. The various struc-tures are classified as brittle ceramics.

The mechanical tests of particular significance include: flexural, compressive, tensile torsional, and impact strengths; moduli of elasticity and rigidity; Poisson's ratio and bulk modulus; fatigue, creep, internal friction, thermal shock re-sistance, and flaw detection; and hardness. Shook has presented a critical survey of mechanical property test methods, repre-senting the present state of the art (1963). He discussed the probabilistic nature of brittle failure in terms of Weibull's statistical theory, and Griffith's theory of the existence of microcracks to explain the discrepancy between the theoretical and observed strengths. Orowan developed this theory further. Weibull proposed a semiempirical function of the form:

$$S = 1 - \exp. \left[-V \left(\frac{\sigma - \sigma_u}{\sigma_0} \right)^m \right]$$, in which σ_0, σ_u are the

classical flawless strength and the lower limit stress below which a fracture cannot occur, respectively, m is the flaw den-sity, V is the volume of component subjected to stress, and S is the rupturing stress.

The theoretical strength can be deduced from consideration of the amount of work required to form the new surfaces resulting from fracture of the atomic planes. For alpha alumina this is about 5.5×10^6 psi, but in practice one-tenth of this has not been realized. A large amount of test data in the literature has limited value because of inadequate description (size, surface preparation, ambient test conditions, chemical and physical structure, statistical treatments, grain boundaries, impurities, etc.).

The testing procedures are also subject to criticism because they may not represent pure application of the supposed test. Tensile tests are the least used to evaluate strength of brittle materials. Duckworth observed that the tensile strengths of brittle materials are much lower than the compressive strengths. Bending tests fail in tension, and can be used as a precise method for determining tensile strength. Compressive strength tests usually involve failure in tension and are also surface-sensitive.

Other relevant literature includes articles by Gurney; Salmassy, Schwope, and Duckworth; Glenny and Taylor; D. Weyl; Duckworth and Rudnick; and Bravinskii and Reshetnikov; WADC and other reports by Duckworth, Schwope, Salmassy, Carlson, and Schofield; Salmassy, Duckworth, and Schwope; Salmassy, Bodine, Duckworth, and Manning; Pulliam; and Bortz et al. Books on the subject include, among others, _Property Measurements at High Temperature_, W. D. Kingery; _The Mechanical Properties of Engineering Ceramics_, edited by Kriegel and Palmour; _Mechanical Behavior of Materials at Elevated Temperatures_, edited by Dorn; and _Fracture of Solids_, edited by Drucker and Gilman. The handbook, Refractory Ceramics of Interest in Aerospace Structural Applications ASD-TDR-63-4102 (October 1963) by Hague, Lynch, Rudnick, Holden, and Duckworth shows selected mechanical and thermal properties of aluminum oxide in comparison with other ceramic materials.

Duckworth proposed that the "strength" of brittle materials used in design structures should be based upon a stress corresponding to a given probability of fracture, as derived from a statistical analysis of the test data, rather than on the mean strength obtained from the test data and to which a factor of safety has been applied. The stress corresponding to zero probability of fracture, the "zero strength" is particularly significant.

King found that the microstructure was quite influential

in changing the mechanical properties of hot-pressed poly-crystalline alumina, having a density of at least 3.964 g/ml. The wear resistance increased but impact strength decreased with decreasing temperature of compaction. Samples which had been hot-pressed at 1450 to 1500°C and annealed at 1500°C had marked grain growth after annealing. This growth, which normally does not occur at 1500°C, suggests that residual strain energy from plastic deformations exists after hot pressing.

Weil, Bortz, and Firestone undertook a program to determine the applicability of statistical fracture theories to inorganic ceramics and to define the major parameters affecting fracture strength. They found that the prior thermal history, the specimen finish, the test temperatures, and specimen size had a primary influence on fracture strength. Environmental effects (water content) were significant only for specimens tested at 20°C; at 1000°C, all environmental influences became negligible. Fracture at room temperature is governed by surface-induced failure mechanisms. Both Weibull constants, the flaw-density parameter (m) and zero strength (σ_u), are sensitive to surface treatment and thermal history. Grinding increases the value of m but leaves σ_u unchanged; annealing increases the value of m, but reduces σ_u to zero. Both weaken the material. Weakening is particularly pronounced in annealed specimens. This is thought to result from destruction of beneficial residual stress distribution.

Ryshkewitch (Oxydkeramik, page 192) claimed that rapid cooling by application of an air blast increased the strength of sintered alumina (95% Al_2O_3) by 35% and impact resistance by 30%. Smoke, Illyn, and Koenig; Preist and Talcott; Phillips and DiVita; and Insley and Barczak confirm this effect. Insley and Barczac perform the rapid cooling following a reheating treatment. The proposed mechanism for the strength increase is the prevention of exsolution of components soluble in either a major or minor crystalline phase.

Structural applications of aluminum oxide in the high-temperature field require a knowledge of the effect of temperature on the mechanical properties. Kingery's book, Property Measurements at High Temperature, provides much information on the mechanical properties of aluminum oxide and other high-temperature ceramic materials.

A variety of data on the mechanical properties of alumina are collected in Table 9 and in Figures 8 through 12. The data

Table 9
Mechanical Properties of Alpha Aluminum Oxide

Bending Strength (Modulus of Rupture)

		Temp. °C	psi	
Sapphire	Flame-fused, oriented 0° between optic axis and bar axis (a)	25 600 1000	102,000 27,000 45,000	(1)
Sapphire	Flame-fused, oriented 45° between optic axis and bar axis (a,b)	25 600 1000	72,000 47,000 85,000	
Ruby	Flame-fused, oriented 45° between optic axis and bar axis (a,b)	25 600 1000	50,000 33,000 85,000	

(a) Loading rate 14,200 psi/minute; (b) minimum creep at 45°

Polycrystalline Alumina

$$S_{25°C} = 142,500 \, e^{-11.83P_0 - 0.60} + 3.33P \qquad (18)$$

$$S_{1200°C} = 73,000 \, e^{-11.33P_0 - 0.60} + 3.33P \qquad (18)$$

Polycrystalline Alumina (99.9% Al_2O_3, 98% theoret. density, hot pressed) (2)

Crystal Size (microns)	1-2	10-15	40-50
25°C	67,000 psi	48,000 psi	35,000 psi
400	52,000	37,000	34,000
1000	49,000	37,000	31,000
1350	37,000	16,000	14,000

Commercial Grades of Polycrystalline Alumina

Nominal % Al_2O_3	99.9(5)	99(3)	94(3)	85(3)
25°C	62,000	52,000	46,000	46,000
980	-	23,000	17,000	12,000

Compressive Strength (psi)

	Sapphire	Polycrystalline			
		100% Al_2O_3	99% Al_2O_3	94% Al_2O_3	85% Al_2O_3
	(6)	(7)	(3)	(3)	(3)
25°C	443,000 to	560,000(d)	300,000	300,000	240,000
25°C	495,000	426,000(e)			
400		213,000			
800		185,000			
1000		128,000			
1200		71,000			
1400		35,600			
1600		7,100			

(d) zero porosity; (e) less than 5% porosity

Tensile Strength (psi)

	Single Crystal Orientation 45° to optic axis	Filaments		Polycrystalline		
		Uncoated	Coated	(f)	94% Al_2O_3	85% Al_2O_3
	(9)	(10)	(10)	(7)	(3)	(3)
30°C	71,000 psi	70,000	210,000	37,600	26,000	17,500
300	52,500			36,400		
800	52,500			34,000		
1050				33,800		
1100	88,000			31,400	9,500	8,500
1200				18,500		
1400				4,250		

(f) rupture time less than one minute

Ref.: 1. Wachtman & Maxwell (1959)
2. Spriggs, Mitchell & Vasilos (1964)
3. Coors Porcelain Data Sheet 0001, August 1964
5. Frenchtown Porcelain Co., Bull. 5462
6. Pavlushkin (1957)
7. Ryshkewitch (1941)
9. Wachtman & Maxwell (1954)
10. Berezhkova & Rozhanskii
18. Passmore, Spriggs & Vasilos (1965)

Table 9 Continued

Modulus of Elasticity (E), X 10^6 psi

E (polycrystalline) = 59.49 X $10^6 e^{-3.95P}$, where P = fractional pore volume (8)

| | Single Crystal (12) | | Polycrystalline | | |
	Sapphire	Ruby(0.75% Cr_2O_3)	(11)	94% Al_2O_3(3)	85% Al_2O_3 (3)
25°C	52.6	54.1	59.30	40.2	31.9
500	48.1	49.5	57.27		
1000	43.5	45.1	54.89		
1200	41.9	43.5	53.65		

Elastic Constants (X10^6 psi)		Elastic Compliances (X10^{-13} cm^2/dyne)		(13)
C_{11}	72.05	S_{11}	2.353	
C_{33}	72.24	S_{33}	2.170	
C_{44}	21.40	S_{44}	6.940	
C_{12}	23.73	S_{12}	-0.716	
C_{13}	16.08	S_{13}	-0.364	
C_{14}	-3.41	S_{14}	0.489	

Modulus of Rigidity (G), X 10^6 psi

| | | | Polycrystalline Alumina | | |
	Sapphire (13)	Hot-pressed Zero porosity (14)	Cold-pressed Zero porosity (14)	94% Al_2O_3 Density 3.62 (3)	85% Al_2O_3 Density 3.42 (3)
25°C	23.29 (Reuss) 24.07 (Voigt)	23.26	23.89	17	13

Poisson's Ratio (μ)

μ = 0.257 - 0.35P, where P = fractional pore volume (16)

| | | | Polycrystalline Alumina | | |
	Cold-pressed Zero porosity (16)	Cold-formed 98% Theoret. density (15)	94% Al_2O_3 Density 3.62 (3)	85% Al_2O_3 Density 3.42 (3)
25°C	0.257	0.32	0.21	0.22
1000		0.32		
1400		0.45		

Impact Resistance (In-lb)

| | | Polycrystalline Alumina | | |
| | Slip-cast 92% Theoret. dens. (17) | 96% Al_2O_3 | 90-95% Al_2O_3 | 85-90% Al_2O_3 |
		Charpy Test Method(4)		
25°C	1.2	7.0 to 7.6	6.5 to 6.8	6.3 to 6.5
800	1.0			
1000	0.55			
1600	0.32			

Ref.: 3. Coors Porcelain Data Sheet 0001, August 1964.
 4. Diamonite Products Manufacturing Company (1963)
 8. Knudsen.
 11. Crandall, Chung, & Gray (1961)
 12. Wachtman & Lam (1959)
 13. Wachtman, Tefft, Lam, & Stinchfield (1960)
 14. Lang (1960)
 15. Ryshkewitch (1951)
 16. Spriggs & Brissette
 17. Kingery & Pappis
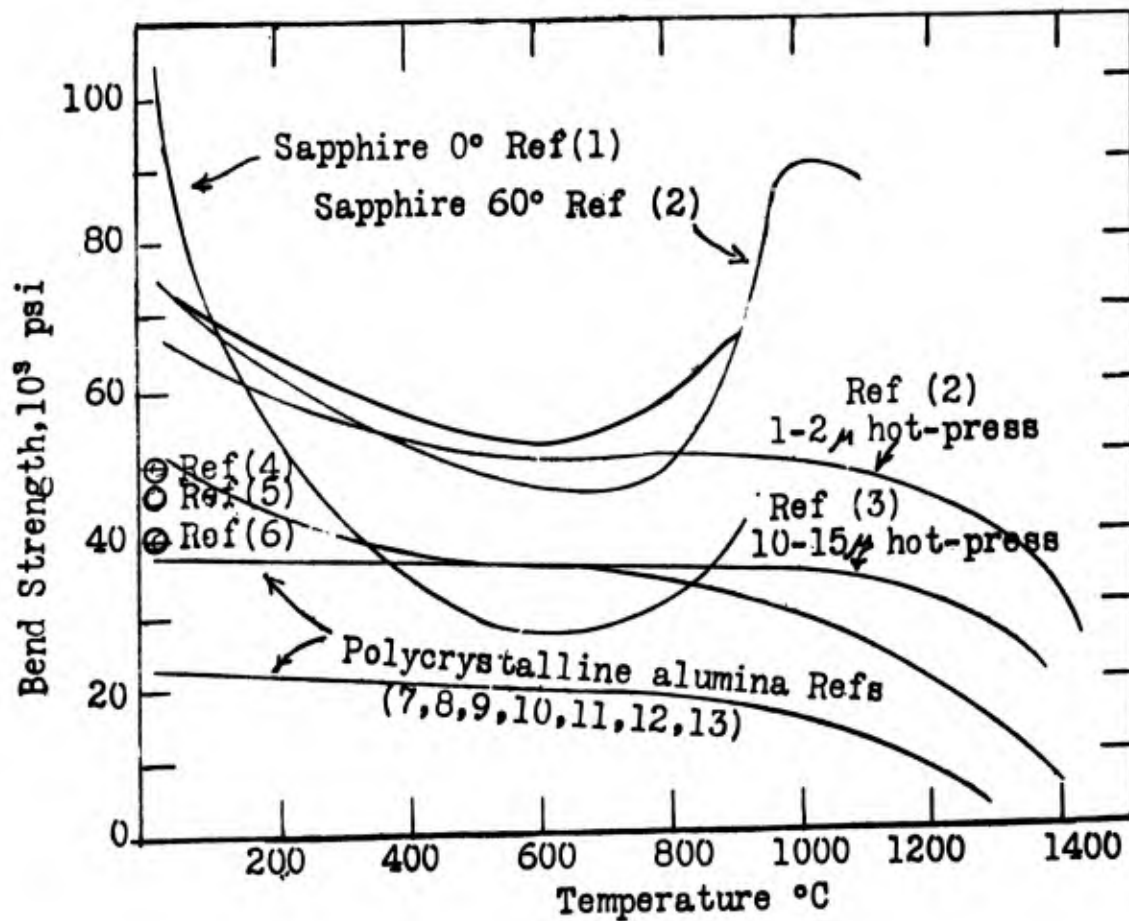
Figure 8b. Bending Strength of Single-Crystal and Polycrystalline Aluminum Oxide
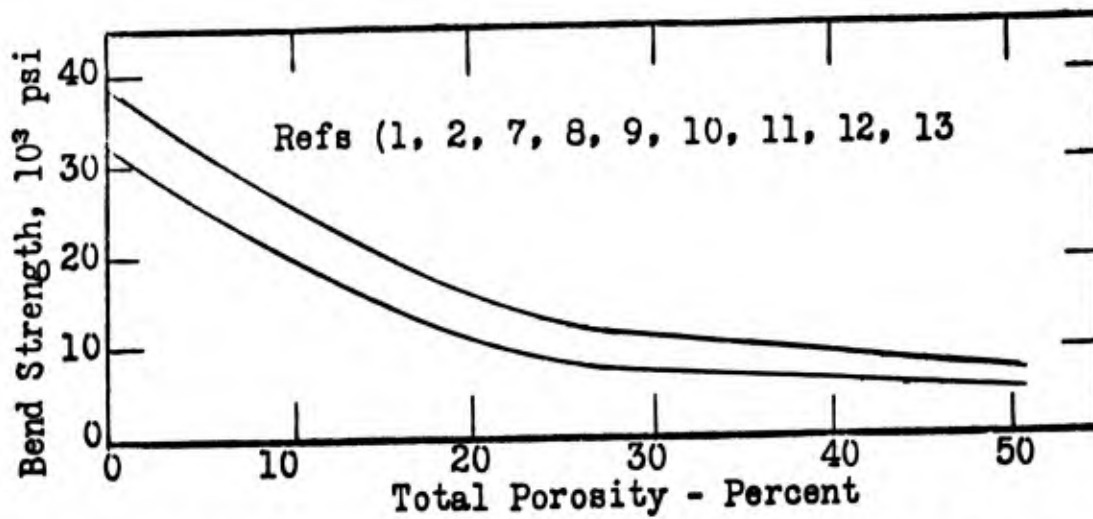
Figure 8a. Effect of Porosity on Room-Temperature Bending Strength of Polycrystalline Aluminum Oxide

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Reference Information for Figure 8

Single-Crystal Alumina

Ref 1 - Wachtman and Maxwell (WADC-TR, 1957). Sapphire rod, 0-deg.
see oriented (crystallographic axis to rod axis); centerless-
ground and flame-polished.

Ref 2 - Wachtman and Maxwell (WADC-TR, 1954). Sapphire rod, 60-
Wachtman and Maxwell (1957). deg. see orien-
tation; centerless-ground and flame-polished; 0-10-inch
diameter, 2.3-inch gauge length, quarter-point loaded at
17000 psi/min.

Polycrystalline Alumina

Ref 3 - Spriggs, Mitchell, and Vasilos (1964). Linde A-5175
alumina 99.9%; hot-pressed at 1700°C; density >98%; speci-
men size 0.25 by 0.15 by 1.75 inch (1.5-inch span); 4-point
loaded at third points, load rate 0.0001 inch per second.

Ref 4, 5, 6 - Alumina Ceramic Manufacturers Association, 96% plus
Al_2O_3, 70 to 96% Al_2O_3, and 80 to 90% Al_2O_3, respectively.

Ref 7 - Coble and Kingery (1956).

Ref 8 - Jackman and Roberts (1953). Commercial recrystallized
Ref 9 - Pearson (1956). alumina; 94 to 95% density;
average grain size about 20 microns; bars 0.25 inch in dia-
meter by 3 inches, 4-point bending, loaded at 30000 psi/
minute.

Ref 10 - Roberts and Watt (1949). Alumina 99.1%, slip-cast and
sintered; 87 to 96% density; 0.16 by 0.16 by 3.2-inch
bars, 4-point bending (load rate not specified).

Ref 11 - Ryshkewitch (1956). Alumina 99.9%; pressed and sintered;
93 to 96% density; 0.14 by 0.14 by 2.75-inch bars, 3-point
bending (no load rate specified); time to fracture, one to
several minutes.

Ref 12 - Tacvorian (1955). High-purity alumina; sintered; about
96% density; bending of 0.16 by 0.16 by 2.66-inch bars
(load rate not specified).

Ref 13 - Tunison and Burdick (1961). Norton 38X alumina; slip-
cast and sintered (sieved naphthalene added to control poros-
ity); average grain size about 23 microns; bars 1/4 inch
in diameter by 3.0 inches gauge-length, 4-point bending,
loaded at 900 psi/minute.
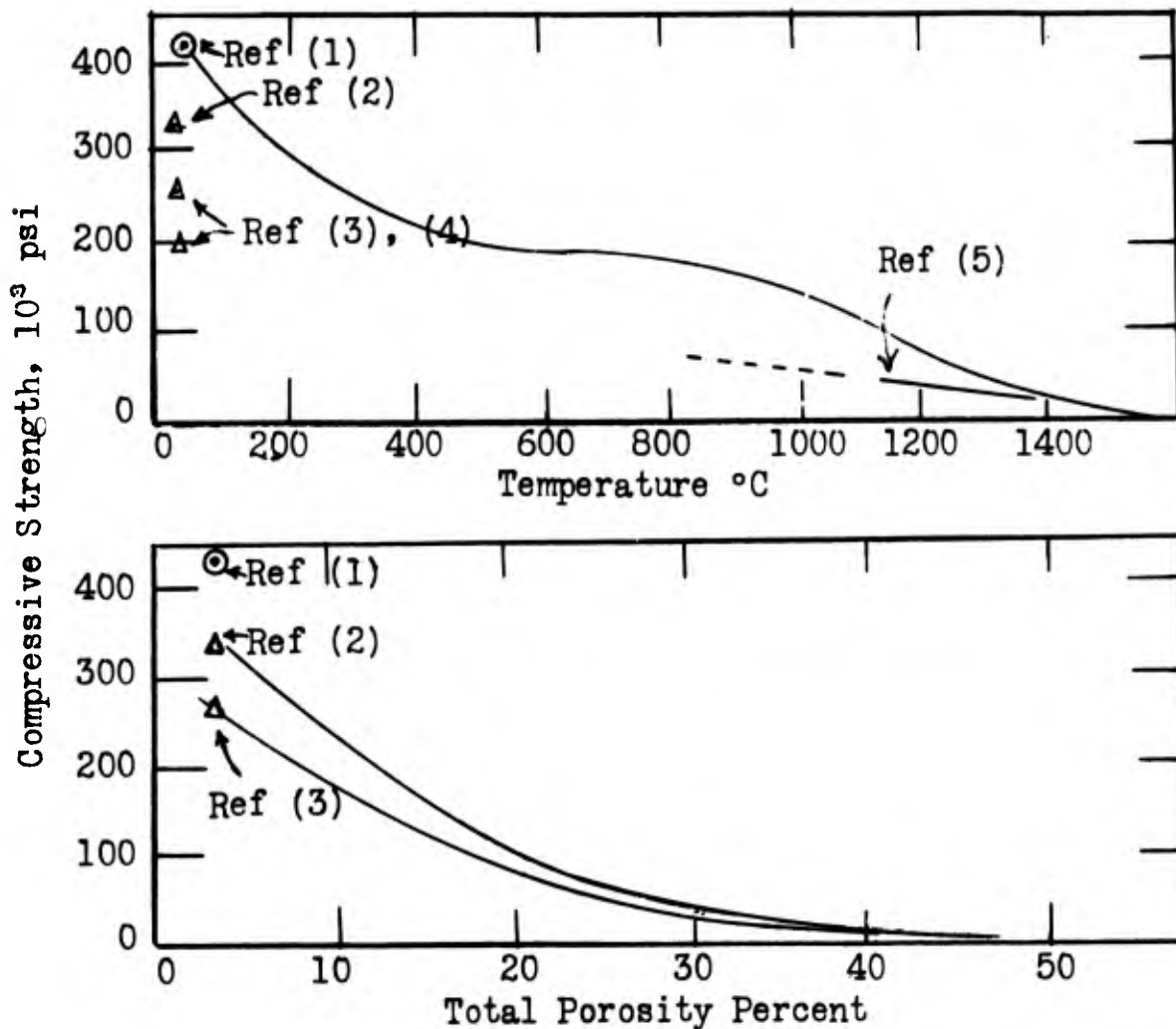
Figure 9. Effect of Temperature and Porosity on Compressive
Strength of Polycrystalline Alpha Aluminum Oxide

Ref 1 - Ryshkewitch (1948). High-purity; 96 to 98% density;
0.25-inch cubes, ground, polished, and graphite coated;
rapid loading in protective atmosphere; load duration less
than 1 minute.

Ref 2, 3, 4 - Ryshkewitch (1953). Slip-cast and sintered; H_2O_2
added to control porosity, 0.5 wt. % MgF_2 added to control
grain size; 97% density:
    Ref 2 - Pores parallel to loading direction
    Ref 3 - Pores perpendicular to loading direction
    Ref 4 - Same as preceding, but 90% density; average of
            parallel and perpendicular pore alignments.

Ref 5 - Schofield, Lynch, and Duckworth (1949). Pressed and
sintered; 78 to 93% density; average grain size 11 to 74
microns.

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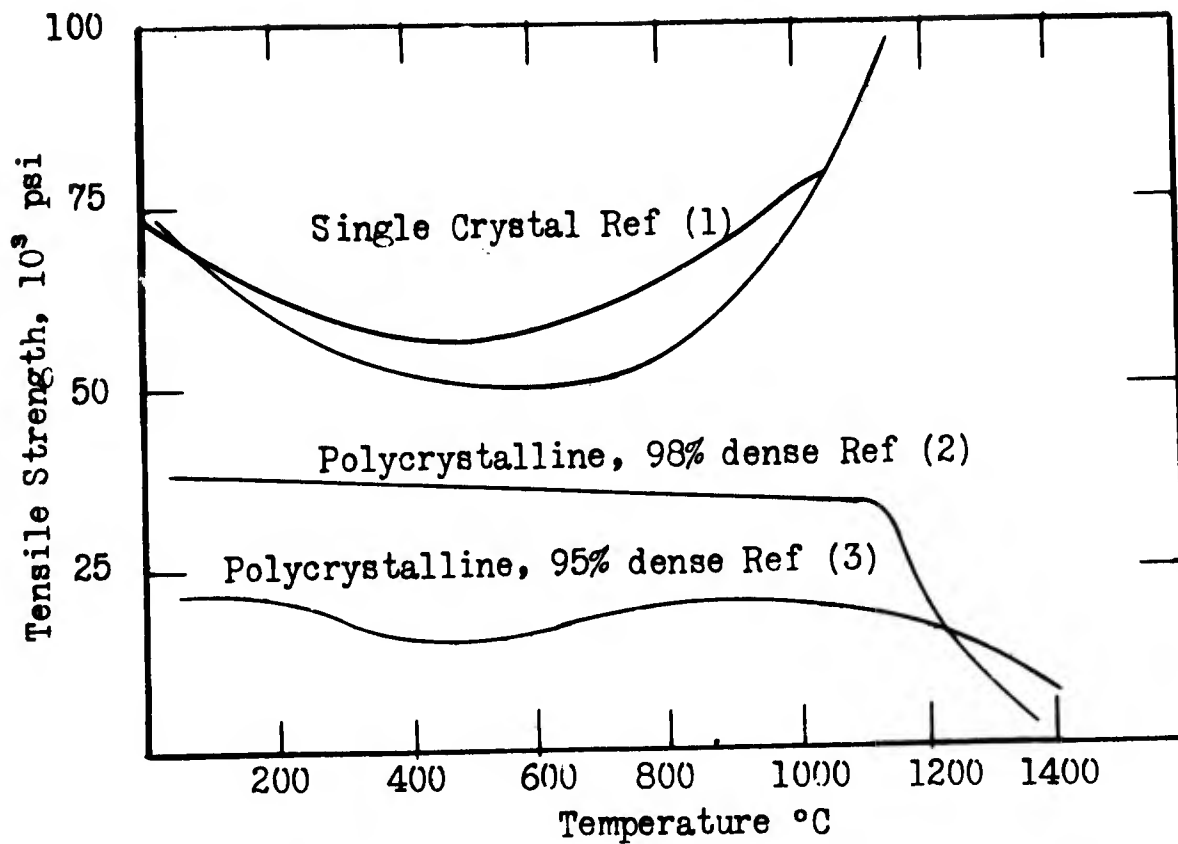
Figure 10. Tensile Strength of Aluminum Oxide

Ref 1 - Wachtman and Maxwell (1954). Flame-polished, single-crystal sapphire rods, 45-degree angle between crystal c-axis and rod axis.

Ref 2 - Ryshkewitch (1941). High-purity, pressed and sintered, about 98% dense.

Ref 3 - Schwartz (1952). Slip-cast, 99% pure, 95% dense; 4-point bending of 5-1/2 by 3/8 by 3/16 inch bars loaded at 13.2 lb/min in flexure.
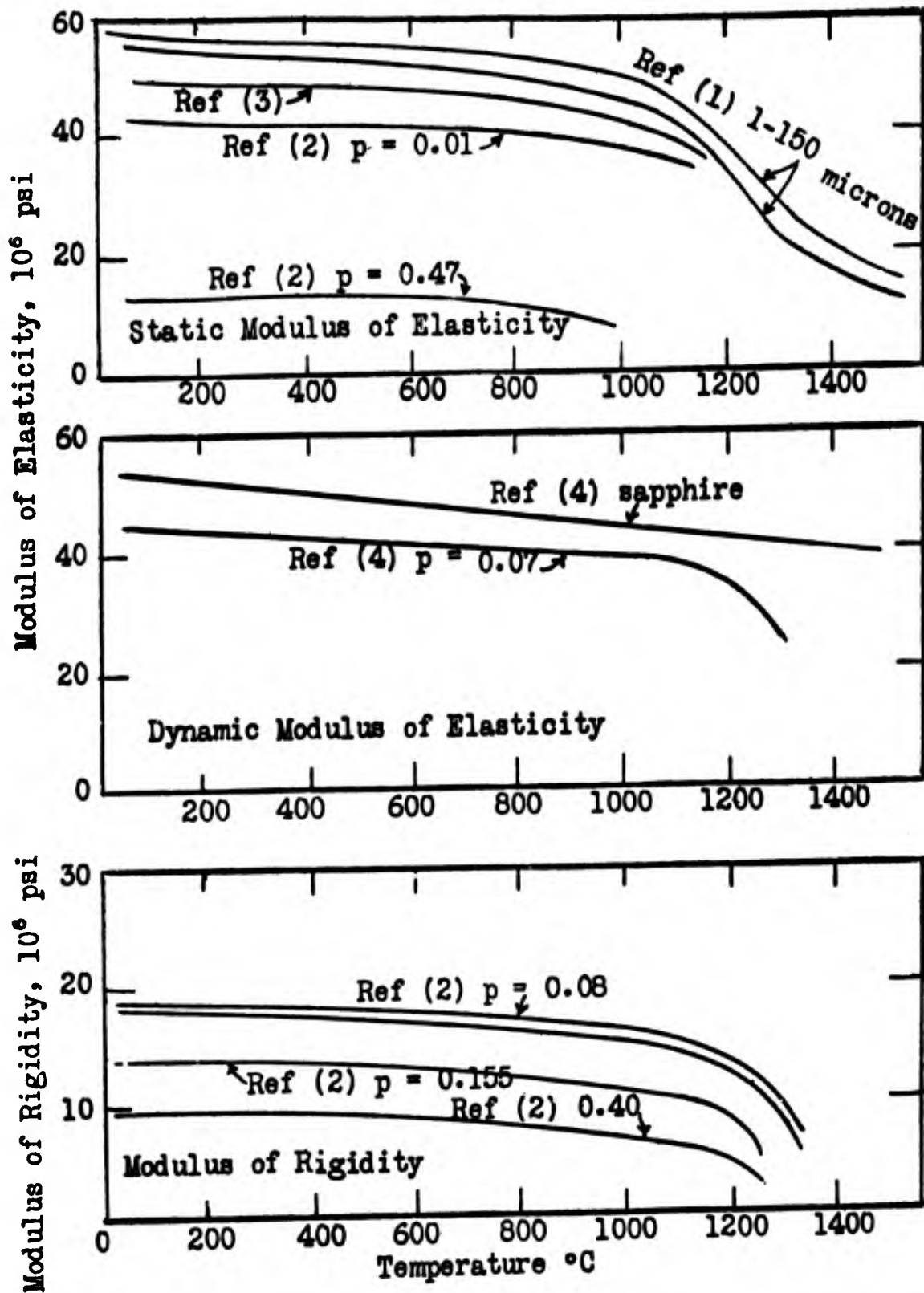
Figure 11. Moduli of Elasticity and Rigidity of Alpha Alumina

Reference Information for Figure 11

Ref 1 - Spriggs, Mitchell, and Vasilos (1964). Linde A-5175 alumina 99.9%; hot-pressed at 1700°C; density >98%; specimen size 0.25 by 0.15 by 1.5-inch span; 4-point loaded at third points, load rate 0.0001 inch/sec.

Ref 2 - Coble and Kingery (1956). Norton 38X alumina, slipcast and sintered (sieved naphthalene added to control porosity), average grain size 23 microns; porosity varied from 0.01 to 0.47 for elastic modulus tests, and from 0.08 to 0.51 for rigidity tests; bars 1/4 inch in diameter by 3.0 inches gauge length, 4-point static bending.

Ref 3 - Schwartz, B. (1952). Alumina plus 99% pure, slipcast and sintered; 95% density; modulus of elasticity determined in 4-point bending (5-1/2 by 3/8 by 3/16 inch bars); modulus of rigidity probably determined similarly.

Ref 4 - Wachtman and Lam (1959). Flame-polished sapphire rods axis parallel to optic c-axis; elastic modulus determined by dynamic sonic method on 0.10-inch diameter by 6-inch specimens. Similar tests on polycrystalline, commercial bars (Norton's La 7365, 3.7 g/ml density = 9.07 porosity, 0.2 by 0.1 by 6 inches.

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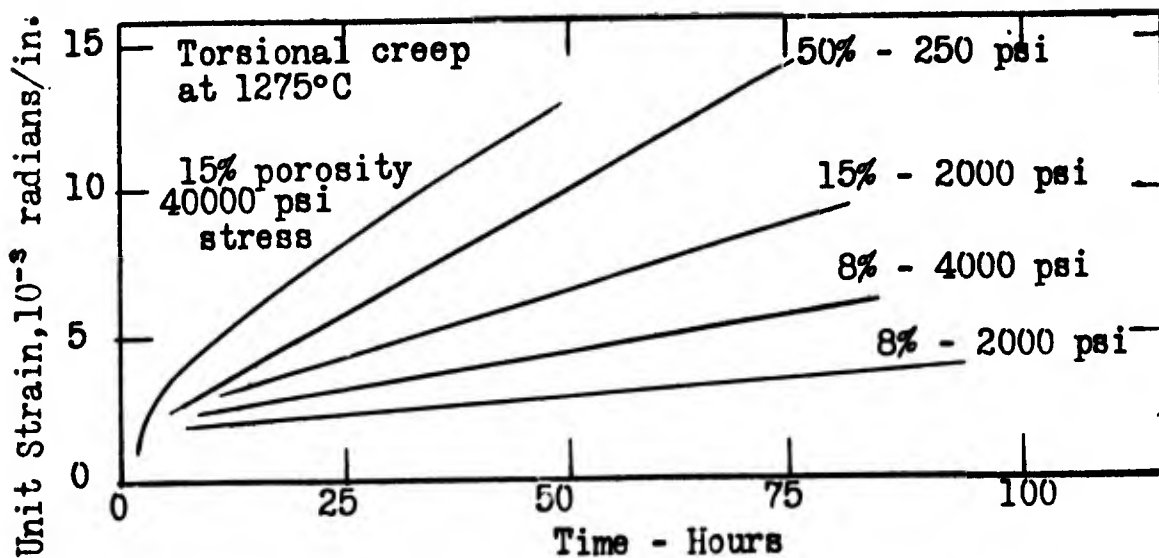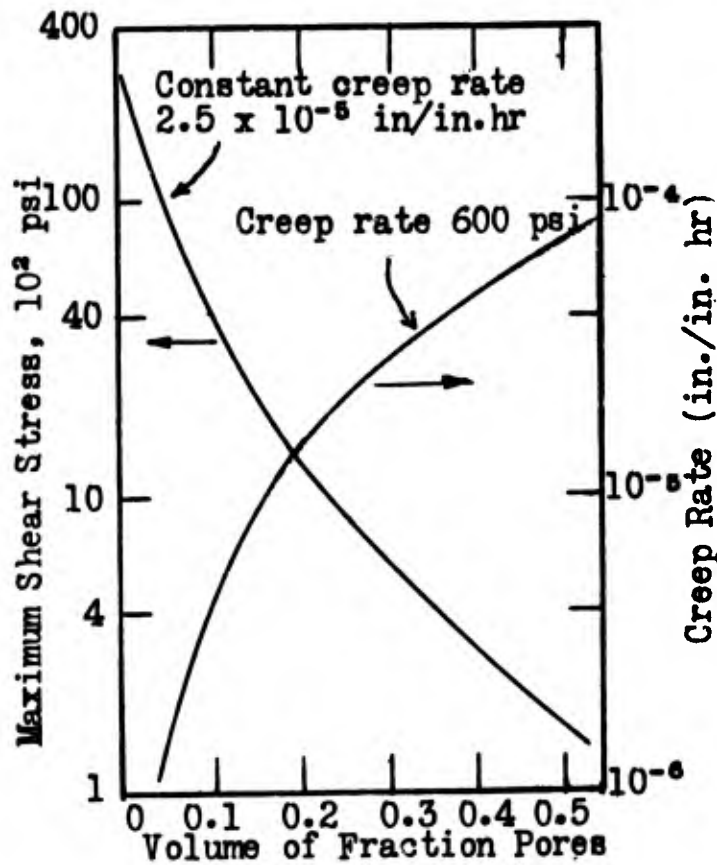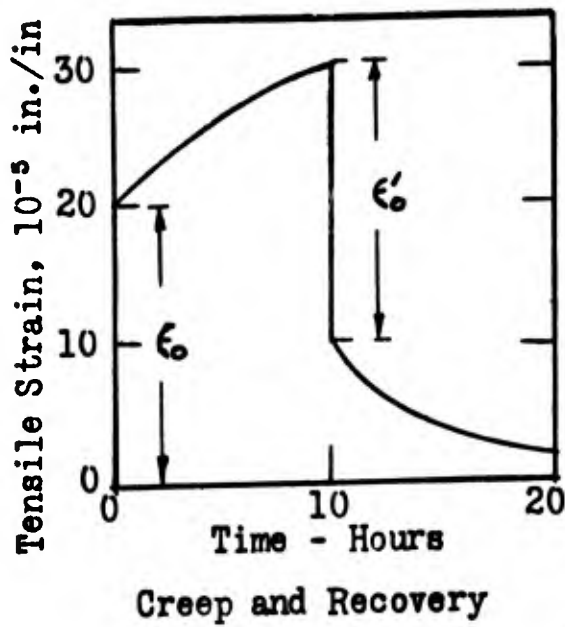
Figure 12. Creep, Creep Recovery, Torsional Creep and Influence of Porosity on Creep

in the table include information taken from the ceramic literature, as well as average values for commercial production, taken from the standards of the Alumina Ceramic Manufacturers Association and the literature of several of its members. The values are typical rather than representative of the highest that have been reported. In much of the ceramic literature, insufficient data have been provided for comparative appraisal of test results by different investigators. In some cases the specimens have been prepared by unsatisfactory forming methods or by excessive heat treatments for optimum strength. Such factors as crystal size, porosity, and vitreous impurities, have contributed to the wide range of strength properties reported. The influence of crystal size appears to be fairly consistent, however, in compositions prepared by different forming methods.

5-2 BENDING, COMPRESSIVE, TENSILE, AND TORSIONAL STRENGTHS

Bending strength involves the placing of some portion of a specimen beam in pure bending according to the expression:

$$\sigma = \frac{Mc}{I}$$, in which σ is the modulus of rupture, M is

the bending moment at the point of rupture, c is the distance from the neutral axis of the beam to the extreme fiber, and I is the moment of inertia of the cross-section about the neutral axis.

The bending strength of sintered alumina specimens is usually determined on several different bar sizes, ranging from the "needle" size of about 80 mils to about 3/8 inch in cross sectional dimensions. The microsize was suggested (H. B. Barlett) to enable determinations on specimens cut from sections of forms that may develop strengths of different values peculiar to the conditions of size and orientation in the form. L. H. Milligan recommended a ratio of span to depth of specimen greater than 10:1, and a loading at the 1/3 or 1/4 point rather than midpoint. Other conditions, particularly symmetrical loading, are commonly used. The microsize specimens usually receive surface polishing to eliminate flaws. Yurchak claimed that the best form is a cylindrical rod 6.5 to 8.6 mm in diameter.

Probably the first determinations of fracture strength on sintered alumina were made in 1933 by H. Gerdian. A flexural strength of about 17,200 psi was obtained on "Sinterkorund," that had been fired at about 1770°C, and having a porosity of about 5% (3.98 g/ml theoretical density of α-Al_2O_3). Ryshkewitch

reported in _Oxydkeramik_ values of about 50,000 psi on cold-pressed bars containing less than 2% porosity, measured at room temperature. The flexural and other strength measurements fell off remarkably when determined at temperatures above 1000°C. In another elaborate 4-point loading, specimens, fired at 1640 to 1780°C (3.48 g/cc bulk density, 12% porosity) developed only 35,500 psi at room temperature, which fell to 22,200 psi at 1000°C.

Ryshkewitch in 1953 found that the strength decreases in an exponential manner with increasing porosity; a 10% increase by volume causes a 50% decrease in strength from initial values. Coble and Kingery confirmed this, and also found that other mechanical properties were similarly affected. Extrapolation of Ryshkewitch's data to 100% theoretical density increases the flexural strength to about 52,500 psi, but this is far from the ultimate strength. Pores perpendicular to the direction of application of pressure decreased strength more than those parallel to the pressure direction.

Ryshkewitch found that the flexural strength of sintered alumina is affected by the crystal size, the finer crystalline material having the higher strength. Cutler used extruded, low-soda alumina specimens containing additives to develop grain growth to different sizes by heating at temperatures below and above the crystallization region. He concluded that grain growth caused a minor decrease in strength, but that porosity was a major factor in decreasing strength in his tests.

Crandall, Chung and Gray; and Spriggs and Vasilos came closer to overcoming the objection of simultaneous changes in porosity and grain size by applying hot-pressing to the forming. The latter's specimens ranged in grain size from about one to 260 microns, and in porosity from about 0.7 to 9.5% by volume. Their relation: Bending strength = $86,000G^{-1/3}$ (psi), fits the room temperature data well, after correcting to zero porosity. G is the grain size in microns. The data indicate that strengths around 100,000 psi are attainable by hot-pressing to obtain a median crystal size of about one micron. At a crystal size of 1000 microns, the strength drops to about 10,000 psi.

Wachtman and Maxwell in 1954 obtained modulus of rupture on synthetic sapphire of 43,000 to 131,000 psi. The scatter is partly dependent on the specimen orientation with respect to the crystallographic axes. Klassen-Neklyudova obtained values of 44,300 to 54,500 psi for bars cut with the length parallel to the base plane (0001), and 99,700 to 115,500 psi for bars cut perpendicular to the base plane. Annealing at 1500 to 1900°C, followed

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by slow cooling to room temperature, increased the strength.

Ryshkewitch (1941) observed that fracture occurs through the crystal as well as at the boundaries, and concluded that the strength of polycrystalline alumina should be substantially the same as that of single-crystal sapphire. Roberts, and Roberts and Watt confirmed Ryshkewitch's conclusion, and observed that transcrystalline failure is more common than intercrystalline. The nature of the fracture changes from transcrystalline to inter-crystalline (grain boundary) at the higher temperatures at which strength decreases rapidly. The impurities even in specimens of better than 99% Al_2O_3 probably concentrate at grain boundaries, in effect to lower the temperature of deformation and fracture. Tunison and Burdick analyzed the fracture of hot-pressed alumi-na by means of the electron microscope and determined that the type of fracture obtained in bending rupture depends upon the re-lation of crystalline to intercrystalline bond strengths. These strengths were equal at 1200°C, the equicohesive temperature at which the fracture was entirely intergranular. It was specu-lated that for high-pressure grinding wheels, agglomerated fine grained alumina could give a lower breakdown rate than the same sized monocrystalline grit used in a bonded abrasive wheel.

Roberts investigated the influence of temperature on the flexural strength of both single-crystal and polycrystalline corundum. A loss in strength of the single-crystal specimens between 300 and 600°C, which was regained at 1000°C, was attri-buted to relief of stresses by microscopic plastic deformations. Wachtman and Maxwell (1959) determined the strengths of single-crystal sapphire and ruby under conditions of orientation of the crystal axes with respect to the direction of application of the pressure which either favored or hindered plastic flow. The data are consistent with the hypothesis of plastic deformation. The initial bending strengths obtained were about 100,000 psi for zero-degree sapphire, 70,000 psi for 45-degree sapphire, and 50,000 psi for 45-degree ruby. These values are less than one-tenth the theoretical strength.

Rasmussen, Stringfellow, and Cutler (1965) found no intrin-sic effect on the strength of polycrystalline alumina by the formation of solid solutions of Cr_2O_3, Fe_2O_3, or TiO_2. The ad-ditions were made in amounts to 2% TiO_2, 20% Fe_2O_3, and 50% Cr_2O_3. The data were corrected to 3.0% porosity and 17.3 microns average grain size.

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Passmore, Spriggs, and Vasilos (1965), from experimental measurements of the coincident effects of grain size G and porosity P on the transverse bending strength S of alumina at 25°C and 1200°C, have derived the following relations:

$$S_{25°C} = 142,500 e^{-11.83P} G^{-0.60} + 3.33P \text{ and}$$

$$S_{1200°C} = 73,000 e^{-11.33P} G^{-0.60} + 3.33P, \text{ respectively.}$$

Brittle fracture in bending at both temperatures appears to be controlled by a Griffith-Orowan mechanism in which pre-existing surface defects, produced during grinding, are propagated to fracture at a critical level of stress.

$$\left(\sigma \cong \sqrt{\frac{EY}{C_0}} \right), \text{ in which } C_0 \text{ is the critical}$$

crack length, E is the elastic modulus, and Y is the effective surface energy for crack propagation. The specimens were prepared by hot-pressing aluminum oxide (99.9 + % pure) of initial average particle size of 0.3 micron at about 1400°C. By heat-treating at 1600 to 1700°C a range of grain sizes up to 100 microns was achieved. The porosity ranged from 2.7 to 6.6% depending upon the heat treatment. The surfaces were diamond-machined and annealed for 24 hours at 900°C to final surface finishes of 0.2 to 2 microns (centerline averages). The defects were thought to have been created by the pulling-out of individual grains during the surface preparation by grinding. Values for the critical Griffith crack length, C_0, were calculated from values of the elastic modulus, E, for each temperature and porosity (Mitchell, Spriggs, and Vasilos, 1963), modified by data shown by Knudsen, and the analytical equations of Spriggs (1961) and of Hasselman. The ratios of crack length to grain size, C_0/G, were plotted as functions of grain size for each temperature and nominal porosity. Interactions between spherical pores and the propagating crack front during brittle fracture inhibited crack propagation apparently by reducing local stresses at the crack front. Increasing pore size, at least up to 5 microns, favored the reduction of stress concentration. Characteristic patterns on the fracture surface were produced by this porosity-crack interaction, which was considered to be responsible for the decreasing dependence of strength with increasing grain size, and the decreasing dependence of grain size with increasing porosity.

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Guard and Romo showed by use of a double-crystal X-ray spectrometer that the fractured surfaces of hot-pressed, 20-micron, polycrystalline alumina exhibit two zones of distortion. Zone 1, of high distortion, extends to a depth of about 10 microns; zone 2, having much lower distortion, extends over 50 microns (in excess of one grain diameter). Both zones are observed in specimens fractured at 20° and at 1700°C. Distortion in zone 1 was believed to result from basal and nonbasal slip in these grains through which a fracture crack passes. Zone 1 has much higher misorientation in the 1700°C fractures than in the 20°C fractures; zone 2 is quite similar at the two temperatures. Zone is observed only in (0330) and (2240) reflections, and was believed to result from basal slip only. The plastic work of fracture was estimated at about 1500 ergs/cm^2, assuming that 1° of misorientation is equivalent to 1% of strain. A fracture stress was assumed to be a tensile yield stress under impact at 35,000 psi at 20°C and 20,000 psi at 1700°C. The value of the critical crack length for the Griffith-Orowan criterion is about 15 microns (about the grain size).

Compressive strength is determined from the expression

Stress at fracture $\sigma = \dfrac{\text{Applied load P}}{\text{Cross-sectional area A}}$, in which the

area A is transverse to the load.

Ryshkewitch reported the measurement of compressive strength of sintered alumina in 1941, in 1953, and also in 1960 in Oxide Ceramics-Physical Chemistry and Technology. As in the case of flexural strength, compressive strength is temperature-dependent and decreases from a room-temperature value of about 425,000 psi to 128,000 psi at 1000°C, and only 7100 psi at 1600°C. The strength at 1000°C is quite impressive, however, in comparison with the strengths of the common structural metals, with which alumina might compete in high-temperature applications. For synthetic sapphire, the room temperature value was 300,000 psi. The influence of controlled porosity on compressive strength was measured on 1.2 cm cubes ranging in porosity from 3 to 60% by volume (Ryshkewitch 1953). The pores were generated by hydrogen peroxide and had an average diameter of 0.4 mm. The spatial arrangement of anisomorphic pores influenced the strength, inasmuch as pores that were parallel to the pressure direction imparted a higher strength than when perpendicular to this direction. The compressive strength decreased in the same exponential manner with increasing porosity as was found for flexural strength.

Pavlushkin in 1957 found the room-temperature strength of polycrystalline alumina to range from 443,000 to 495,000 psi. In one isolated test, a strength of 1,140,000 psi was claimed.

Ryshkewitch (1941) determined the tensile strength of sintered alumina on slender rods, 2 to 4 mm in diameter, expanded on the ends for easy gripping. The rods were made long to avoid error resulting from axial strain. Such thin specimens might suffer from inhomogeneities resulting from unequal heat treatment or marked influence of surface crystallization. His tensile strengths agree well with more recent values obtained on larger specimens, however. He obtained a tensile strength of about 37,500 psi at room temperature, which fell off gradually to 33,800 psi at 1050°C. The strength thereafter decreased rapidly to about 1560 psi at 1460°C. By comparison, however, nickel, as an example of a high-temperature metal, having almost twice the room-temperature tensile strength, retains 1400 psi in tensile strength only to about 700°C.

Roberts and Watt in 1951 used strain gauges on the surface of thicker specimens to enable adjusting the loading axis to avoid strain. The attained room-temperature tensile strength was about 17,400 psi. Pears et al. determined tensile strength on rods 3/8 in. O.D. by 5 in. length, prepared from Wesgo Al-995 (99.5% Al_2O_3) sintered alumina by centerless grinding of formed specimens. (This is a commercial product of Western Gold and Platinum Company, having a bulk specific gravity of 3.89 g/cc, less than 3% porosity, and an average crystal size of 22 microns). Gas bearings were used to provide uniaxial loading. The tensile strength was 35,500 psi at 21°C, and 1,100 psi at 870°C.

Sedlacek applied isostatic pressure to the inside of a sintered alumina ring (Wesgo Al-995) in order to rupture it in tension by an ingenious method that avoided the use of nonyielding constraints in supporting the specimen. He found that the measured values for tensile strength increase with increased rate of applying the load within the range of rates from 70 psi/sec to 4500 psi/sec. At a loading rate of 3000 psi/sec, the maximum room temperature tensile strength was 30,920 ± 1175 psi.

Wachtman and Maxwell (1954) obtained tensile strengths on flame-polished sapphire rods having a 45-degree angle between the axis of the rod and the c-axis of the crystal. The values obtained were considerably higher than those for polycrystalline alumina, amounting to 71,000 psi at 30°C. The specimens exhibited loss in strength above room temperature, gradually recovered

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by heating at about 800°C, and an unusual increase in strength at 1100°C of 88,000 psi. Since strain rate has a definite influence on strength properties, caution should be taken in values obtained from figures 8b and 10.

Berezhkova and Rozhanskii found that the surfaces of filamentary corundum crystals grown from the gaseous phase were covered with twinned corundum coatings which hindered the propagation of cracks through brittle fracture. The room temperature strengths of filaments with a cross-section of 0.1 micron was 210,000 psi in the presence of the coating, and about 70,000 to 140,000 in the absence. The twinning occurs along the (1121) and (1126) faces.

In determining torsional strength, a twisting moment is applied to a cylindrical rod, fixed at one end, or equal and opposite twisting moments are applied. The maximum stress is called torsional strength or modulus of rupture in torsion.

$$t_{max} = \frac{16\,T}{\pi\,d^3}$$

$$\sigma_{max} = \frac{16}{\pi\,d^3}\left(M + \sqrt{M^2 + T^2}\right),\ \text{in which } \sigma_{max} \text{ is the tensile}$$

stress at the surface, d is the rod diameter, M is the bending moment, and T is the twisting moment.

Ryshkewitch; Decker and Royal; and Stavrolakis and Norton investigated the measurement of torsional properties of sintered alumina throughout a range of temperatures. Decker pointed out the advantages of torsion as a quick method for obtaining other strength tests because of the freedom from thermal expansion errors, the absence of the need for close dimensional tolerances, the simplicity of specimen installation in grips, and the ability to make deformation measurements outside the furnace on the cool end of the specimen. Stavrolakis found that the ultimate shear stress conforms with the ultimate tensile stress. Strength in torsion decreases in a slow linear manner from a value of about 29,400 psi at 25°C to 29,300 psi at 500°C. In the temperature region beyond 800°C, torsional strength drops at a rapid rate to about 3350 psi at 1500°C.

5-3 IMPACT STRENGTH

Poor impact resistance of the brittle ceramics has limited their practical use. Factors affecting the strength of polycrystalline oxides are the internal microstresses, porosity, stress

corrosion in damp air, and surface defects. Experience with glass has shown the importance of surface scratches in reducing fracture strength.

Moore measured the impact strength of slip-cast and extruded forms of sintered alumina by dropping a weight from predetermined heights onto 0.5-inch cubes until fracture. The strength was computed from the formula $f = \sqrt{\dfrac{2Ewh}{v}}$, in which E is Young's modulus, w is the weight of the falling load, h is the height of fall, and v is the volume of the specimen cube. The strength for both types of forms was about 43,000 psi.

Kingery and Pappis determined the influence of temperature on the impact resistance of slip-cast cylinders of sintered alumina having about 8% total porosity. The cylinders, 0.5 inch in diameter, were supported across a 4.5-inch span, and were impacted by an alumina-faced pendulum having a velocity of about 41 inches per second at impact. The impact energy of about 1.2 inch-lb at room temperature, fell only slightly until in the region 700 to 1000°C, whereupon it dropped to about 0.5 inch-lb, and continued to decrease slowly until at 1600°C it had reached 0.3 inch-lb.

5-4 MODULI OF ELASTICITY (E), AND RIGIDITY (G)

The modulus of elasticity (Young's modulus) may be determined by measuring a beam deflection for various applied loads within the elastic limits, according to the expression:

$$E = \frac{PL^3}{48\,\delta\,I}$$, in which E is the modulus of elasticity, P is the applied load, L is the span between supports, δ is the deflection, and I is the moment of inertia of the cross-section about the neutral axis.

More recently, sonic and ultrasonic resonant frequency methods, and ultrasonic pulse techniques have been applied. Substantially the same results are obtained by each method at low and intermediate temperatures; the static moduli decrease faster at high temperatures, probably indicating a transition from elastic to plastic strain.

Some factors affecting the modulus of elasticity and the related modulus of rigidity of alpha aluminum oxide are shown in Figure 11. The exposition of these factors appears in the text.

Ryshkewitch (1942); Schwartz; Majumber; Schofield, Lynch, and Duckworth; Duckworth, Johnston, Jackson and Schofield; and Coble and Kingery measured the temperature dependence of Young's modulus of polycrystalline alumina by static bending methods. Ault and Ueltz; Crandall and Bryant; Wachtman and Lam; Lang; Spriggs; Spriggs and Vasilos; Chung; and Kovalev applied either damped or sustained flexural vibration methods.

Ryshkewitch found that the moduli of elasticity of single-crystal sapphire and polycrystalline alumina are about the same at room temperature, from which he concluded that the inter-crystalline bond is about as strong as the intracrystalline bond. Wachtman, Teft, Lam, and Stinchfield determined the zero-porosity modulus of elasticity of polycrystalline alumina to be 59.22×10^6 psi at 4084 kilobars (Voight method), and 57.59×10^6 psi at 3972 kilobars (Reuss method), based on their determinations of the elastic constants of single-crystal sapphire.

Scheetz stated that extrapolation of elastic moduli data for porous ceramic bodies (porosities of 5% or less) lead to values for the fully dense body which lie between those computed by space-averaging of single-crystal elastic stiffness and compliance constants. The elastic properties of composite bodies, including multiple-phase ceramics, may be predicted (with small error for bodies which remain continuous solids) by a method developed by Kerner. The values of elastic moduli for fully dense polycrystalline ceramic bodies should be used rather than the lower values associated with porous ceramics.

The earlier investigators used cold-forming, slip-casting, or extrusion for forming the test specimens. Spriggs and Vasilos, and later investigators applied hot-pressing to obtain fine-grained polycrystalline bodies of density approaching the theoretical. Spriggs, Mitchell, and Vasilos (1964) found that the elastic modulus is essentially independent of grain size within the range 1 to 100 microns, at least, and within a temperature range to at least 1500°C.

The curve relating elasticity to temperature for polycrystalline alumina is similar to those found for flexural and compressive strengths (Figure 11). It decreases in a relatively slow linear manner to above 800°C, followed by a more rapid non-linear decrease at higher temperatures in the range of usefulness. Coble and Kingery suggested that the rapid decrease in mechanical properties around 1000°C is caused by grain-boundary

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slip. This appears plausible, since Wachtman and Lam found that single-crystal sapphire exhibits only linear decrease in Young's modulus from room temperature to the highest temperature measurement.

Spriggs proposed a general equation relating porosity of polycrystalline alumina to Young's modulus, having the form:

$E = E_0 e^{-bP}$, in which E is Young's modulus for the porous polycrystalline specimen, E_0 is Young's modulus for the nonporous body, e is the Napierian number 2.71828...., b is an empirical constant, and P is the fractional pore volume. Knudsen found that the equation:

$$E(\text{in kilobars}) = 4102\ e^{-3.95\ P}$$ approximates the data well except for some, but not all, of the tests in which porosity was obtained by the use of a fugitive particulate filler. The zero porosity value at room temperature is 59.48 X 10^6 psi. Spriggs corrected the equation to compensate for differences in the effects of open and closed porosity. Hasselman, and Piatasik and Hasselman have since proposed a mechanical model for showing the effect of porosity on strength, based on the postulation that a fraction of the material is stress-free owing to the shielding action of the pores.

Lang found that the greatest variation in modulus of elasticity occurs in hot-pressed alumina compositions (mainly commercial specimens), although the averages were higher than for other forming methods. The dynamic elastic constants determined by the sonic vibration method are more sensitive than bulk density measurements as indicators of homogeneity.

Rao; Bhimasenacher; Mayer and Hiedemann; and Wachtman, Tefft, Lam, and Stinchfield determined the six elastic compliances and elastic constants of single-crystal corundum. Wachtman et al. applied a resonance technique at frequencies in the range 1 to 45 kcps in the evaluation. Values for the elastic constants are shown in Table 9. The variations of Young's modulus and of the shear modulus with crystal orientation were determined from the elastic compliances.

The modulus of rigidity (shear modulus) may be visualized as the distortion resulting from a compression of one diagonal of a specimen and the stretching of the other. The determination is most readily achieved by placing a cylinder in torsion, and is measured by the expression:

$$G = \frac{TL}{\theta J}$$, in which T is the twisting

moment, L is the specimen length in strain, θ is the angle of twist in radians, and J is the polar moment of inertia of cross section.

The modulus of rigidity is related to the modulus of elasticity by the expression:

$$G = \frac{E}{2(1+\mu)}$$, in which G is the modulus of rigidity, E is the modulus of elasticity, and μ is Poisson's ratio (dimensionless). This is applicable only to isotropic bodies.

The resonant frequency of a beam in its fundamental mode of torsional vibration is related to the modulus of rigidity by:

$$G = \rho\left(\frac{WL}{\pi}\right)^2$$, in which G is the modulus of rigidity, ρ is the mass density, W is the resonant frequency of the fundamental vibration, and L is the beam length.

Ryshkewitch in 1942, and in 1951; Stavrolakis and Norton; Coble and Kingery; and Lang obtained data on polycrystalline alumina. Wachtman, Tefft, Lam, and Stinchfield obtained data on single-crystal sapphire at room temperature. The modulus of rigidity of polycrystalline alumina changes with temperature in the same manner as the modulus of elasticity, that is, a slow linear decrease to about 800°C, followed by a very rapid decrease at high temperatures. The change with increasing porosity is also similar. This follows from the Poisson's ratio relationship between the two moduli.

Spriggs and Brisette computed the zero-porosity modulus of rigidity for polycrystalline alumina from the values of Lang, and Coble and Kingery on specimens prepared by cold-pressing, slip-casting, and hot-pressing, by use of an exponential expression similar to that used in determining the influence of porosity on modulus of elasticity. The expression has an empirical constant that varies with the fabrication technique. An average value of 23.68 X 10⁶ psi was obtained, which agrees well with the average of the values calculated by Wachtman et al. from the single crystal constants, 23.29 X 10⁶ by the Reuss theory, and 24.07 X 10⁶ by the Voigt theory.

Spinner and Valore found that the empirical determination of the relationship between shear modulus and the fundamental torsional resonance frequency, mass, and dimensions of bars of rectangular cross-section is lower than the theoretical approximation given by Pickett by an amount increasing to about 1.75% as the cross-sectional width-to-depth ratio of the bars approaches 10.

5-5 POISSON'S RATIO (μ)

When a material is strained in one direction, it undergoes strain of opposite sign in the transverse directions. The ratio of transverse strain to principal strain is Poisson's ratio (μ).

The changes can be shown as volume changes.

Ryshkewitch (1960) computed Poisson's ratio for sintered alumina from the relationship: $\mu = \dfrac{E}{2G} - 1$, and obtained a value of 0.32 for temperatures up to about 1000°C, increasing above that temperature to about 0.5 at 1900°C. Alumina exhibits pronounced creep under these higher temperatures. Lang, Coble and Kingery, and Knudsen found that Poisson's ratio is porosity-dependent, decreasing with increasing porosity. Spriggs and Brissette derived a linear relation between Poisson's ratio and porosity, calculated from the exponentially dependent relations of elastic modulus (E) and of shear modulus (G). The equation has the form: $\mu = \mu_0 - mP$, in which μ_0 is Poisson's ratio of the nonporous specimen, P is the volume fraction of porosity, and m is an empirical constant which must be derived for each type of specimen fabrication. For cold-pressed, sintered alumina the equations: $\mu = 0.257 - 0.350\,P$, provides a close fit.

5-6   CREEP CHARACTERISTICS

Creep is the slow and progressive deformation of a material with time under constant stress. Related phenomena include stress relaxation, internal friction, dynamic elastic modulus relaxation, and grain-boundary relaxation of polycrystalline materials.

Bridgman showed that aluminum oxide as well as other hard, brittle materials creep at room temperature under pressures of 30,000 atm. Ryshkewitch (1957) observed evidence of plastic flow on a microscale for the coiled chips of sapphire, ruby, and quartz glass that had been cut with a diamond tool at room temperature. Gorum predicted that the most likely brittle materials to possess ductility are the ionic solids having cubic crystal structures. Weinig, and Parker and associates investigated atmospheric and impurity factors affecting the limited ductility of brittle oxides. Sintered alumina does not presently appear to have useful room-temperature ductility.

McDowall and Vose discussed methods for determining pyroplastic deformation during heating of ceramic bodies. They found a relationship for sag of a rod specimen showing that Sd^2/L^4 is a characteristic constant. S is the sag at the center of the rod of circular section, d is the diameter, and L is the length between suspensions.

Wygant (1951) stated that polycrystalline alumina has superior creep resistance to hydrostatically-pressed magnesia, thoria, zircon, and mullite. Alumina probably has the best creep resistance (around 0.13×10^{-5} at 1300°C, 1800 psi) of all the oxides, but is exceeded at high temperatures by covalent materials such as silicon carbide and graphite (Coble 1960). Poluboyarinov and

Kalliga measured the deformation under load for alumina-silica compositions containing from 39 to 99% Al_2O_3, and from 0.5 to 4.7% fluxes. The temperature of deformation under controlled loading increased with increasing content of Al_2O_3. Partridge found that the creep rate of polycrystalline refractories containing a glassy phase is governed by the viscosity of the glassy matrix.

Stavrolakis and Norton found that the recovery of short-time creep of torsional stress in polycrystalline alumina was complete at 1200°C within 12 hours after removal of the load (unspecified); at 1300°C the deformation was permanent.

Wachtman and Maxwell investigated the creep rates of both polycrystalline and single-crystal alumina. Dense sintered alumina and sintered alumina containing 1.4% Cr_2O_3 developed an instantaneous strain, ϵ_0, under load (8530 psi), which continued to increase with time, as shown in Figure 12. When the strain was released after 10 hours, an instantaneous recovered strain ϵ_0, was obtained, which was about equal to the initial, instantaneous strain. This was followed by a partial time-dependent recovery within 10 hours. In the case of the single crystals, plastic deformation is caused by slip of the base plane (0001) in the [1120] direction. The creep curves under constant load consist of an initial period of increasing creep rate commencing above 900°C, followed by a period of decreasing creep rate, a period of constant creep rate, and finally, a period of increasing creep rate. The stress required to initiate creep falls uniformly from about 11,000 psi at 900°C to about 1850 psi at 1400°C.

The "steady-state" creep of sapphire crystals was investigated by Chang in 1960, and was analyzed according to three mechanisms; dislocation climb, micro-creep, and the Peierls stress. Dislocation climb is the motion of dislocation into an adjacent plane. Weertman's theory of dislocation climb states that diffusion vacancies between dislocations are rate-controlling. The change in the free energy caused by a change in the number of vacancies equals the change in the elastic energy occurring during the dislocation climb. The Peierls stress is the force necessary to move a dislocation along its slip plane, believed to be very much less than the observed shear strength of the softest crystals (in metals). The dislocation climb mechanism fits the data best. The Peierls stress mechanism is apparently not rate controlling. The ratio of Peierls force to shear modulus is about 0.00002, or about one-tenth that of face-centered cubic metals.

Kronberg, Westbrook, and May; and Kronberg stressed the function of temperature and strain rate in controlling the flow properties. The tensile deformation of sapphire between 1200 and 1700°C and at a strain rate of 0.001 to 0.01 in/in. min. was relatively sharp. The specific temperature of transition from brittle fracture to massive plastic flow in this rate change

increased from about 1270°C to 1520°C. The stress-strain relation for plastic flow was characterized by a pronounced drop in the yield-point. The stress required for starting macroscopic flow was about double that required for subsequent flow. Both the upper and lower values for yield stress were temperature-sensitive; both decreased approximately exponentially with increasing temperature for a given strain rate. The fracture stress before yielding, however, was essentially independent of both temperature and strain rate, falling within a range of about 16,000 to 20,000 psi. The transition temperature between ductile and brittle behavior corresponds to the temperature at which the upper yield stress equals the fracture stress.

Conrad, Stone, and Janowski find that the deformation rate (γ) of sapphire from 900 to 1700°C fits either of two equations:

(1) $\quad \gamma = \left(A/T\right) (\tau^*)^n \exp{-(H_0/RT)}$

(2) $\quad \gamma = \nu \exp\left[- H (\tau^*)/RT\right]$

A, n, and ν are constants. In equation (1), n is approximately 3 to 7 and H_0 is 90-125 kcal/mole. In equation (2), H is 120 kcal/mole and $\nu^* = -dH/d\tau^*$ and is $110b^3$ at $\tau^* = 1$ kg/mm², decreasing with stress. Equation (1) agrees with the dislocation climb mechanism; equation (2) supports the Peierls-Nabarro mechanism.

Seigle applied the Nabarro-Herring mechanism to creep and sintering phenomena of alumina. According to this mechanism, deformation results from diffusional flow away from a boundary of compressive force toward boundaries having tensile stress. Grain boundaries were found to be significant in the densification. The data did not support void shrinkage in the absence of grain boundaries. Folweiler investigated the creep of pore-free polycrystalline alumina as a function of temperature, grain size, and strain rate (ϵ). Deformation was found to occur not by basal slip, but by the Nabarro-Herring mechanism. Warshaw and Norton found that grain size is an important factor in creep. Fine-grained aluminum oxide (3 to 13 microns) is of viscous behavior; the strain rate is inversely proportional to the square of the grain size; and the creep behavior is by the Nabarro-Herring mechanism. Coarse-grained aluminum oxide (50 to 100 microns) behaves plastically when deformed; the plastic flow probably occurs through a dislocation or glide mechanism.

Coble and Guerard obtained good agreement with the diffusion coefficients obtained from the data of Warshaw and Norton. They

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also found good agreement between measured and calculated aluminum-ion diffusion coefficients. The observed grain-size dependence for creep is satisfied by a lattice-diffusion model. Addition of Cr_2O_3 reduces the temperature at which the transition to a multiple slip process occurs. Orlova and Kainarskii found that the rate of deformation of polycrystalline alumina containing 0.25% talc or 0.07% MgO was similar to that of the pure corundum, and the the rate approached linearity with time, suggesting the diffusion mechanism.

Particularly at high temperatures, but also for rapidly applied stresses, the strain does not instantaneously come to equilibrium. This is called anelasticity, and the time required to attain equilibrium is the relaxation time. Chang, and Chang and Graham measured the activation energies for both steady-state creep and grain-boundary relaxation in polycrystalline aluminum oxide; the values were approximately 200,000 cal/mole and 120,000 cal/mole, respectively.

In both single-crystal and polycrystalline specimens, a controlled amount of solid solution was claimed to cause increased hardening and greater creep resistance. The addition of about 1 to 2% (by weight) of Cr_2O_3 or La_2O_3 to the alumina introduced additional grain-boundary relaxation peaks at lower temperatures (800 to 900°C), reduced the grain-boundary viscosity, and improved the ductility at temperatures around 1100°C. Evidence that grain boundary effects are the predominant factors challenges the diffusional-creep theory.

Beauchamp; and Beauchamp, Baker, and Gibbs measured the deformation of polycrystalline sintered compacts of doped Gulton Alucer MC alumina in 3-point beam loading in the range 1000 to 1350°C. The creep consisted of a transient deformation superposed on a steady-state deformation. The steady-state creep rate of specimens doped with 50 to 5000 ppm (wt) of MgO or $MnCO_3$ was fitted to the expression: $A \exp(-E/KT)$, in which the activation energy (E) is 130 kcal/mole, independent of the added impurity. The constant (A) is independent of the $MnCO_3$ addition, but is decreased by a factor of 3 to 5 in samples doped with MgO. Gibbs, Baker et al. concluded that the steady-state creep is controlled by diffusion of vacancies.

Coble and Kingery observed the influence of porosity on the torsional creep rate of polycrystalline alumina having porosity in the range about 5 to 50%, induced by addition of different amounts of crushed naphthalene during the forming operation. The induced pore size was about 100 microns, in comparison with an

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average grain size of 23 microns. The creep rate (at constant stress and constant temperature) following a suitable relaxation interval at temperature, increased with increasing porosity.

McClelland derived a linear expression relating porosity to creep of sintered alumina, based on the Mackenzie-Shuttleworth plastic flow model, having the form:

$$p_\varepsilon = p \left(\frac{1}{1 - P^{2/3}} \right), \text{ in which}$$

p_ε = effective pressure in closing pores, p = the externally applied pressure, and P = the volume fraction porosity. Spriggs and Vasilos (1964) have derived an explicit equation to show the relation in terms of the Nabarro-Herring diffusional creep equation, having the form:

$$\varepsilon = \text{strain rate} = \frac{10 \sigma D \Omega_0 \frac{1}{1 - P^{2/3}}}{r^2 k\, T}, \text{ in which } \sigma = \text{the}$$

stress, D = the lattice diffusion coefficient, Ω_0 = the vacancy volume, P = the volume fraction porosity, r = the grain radius, k = Boltzmann's constant, and T = the absolute temperature.

5-7 THERMAL SHOCK

Poor resistance to thermal shock in comparison with the refractory metals limits the usefulness of the brittle ceramic oxides. Thermal stresses are particularly harmful during sharp cooling, in which the cooler exterior of the ceramic develops tensile stresses resulting from differential volume changes of the different parts of the structure. Since the compressive strength of ceramics may be about eight times the tensile strength, failure from compressive stresses is not important.

General reviews of the factors affecting thermal shock resistance of ceramics are given by Kingery (1955), and by Manson. Manson has shown good correlation between the theoretical and experimental values of thermal shock resistance of some brittle materials. The theoretical solution is based on the concept of an infinite plate at uniform temperature that is immersed in a cooling medium. The cooling is expressed in terms of a dimensionless heat-transfer coefficient β, termed Biot's modulus, defined as: $\beta = \frac{ah}{k}$, in which a = 1/2 the plate thickness, h = the heat transfer coefficient, and k = the thermal conductivity of the plate. In general, the thermal stress resistance determining the temperature difference between initial and final conditions

that just induces failure at different rates of thermal shock
is represented by the equation:

$$\Delta T_f = \frac{k\ (ts)\ (1 - \mu)S}{E\ a}$$, in which ΔT_f is the

temperature difference just causing failure, k is the thermal
conductivity, ts is the tensile strength, μ is Poisson's ratio,
E the elastic modulus, a the coefficient of expansion, and S
a shape factor. The thermal conductivity, k, enters the equation
only at relatively low values of heat transfer ratio β.

Present heat-shocking methods include: the plasma arc; the
arc imaging furnace; a gas-air blast directed onto the specimen;
rocket motor exhaust; fused quartz heating lamps; and exposure
to heating or cooling fluids. The increasingly severe demands
for heat-resistant materials in high-duty vehicles or for re-
entry into the earth's atmosphere have taxed the present tech-
nical capability.

Manson and Smith found that the failure in thermal shock
materials is not entirely the result of attainment of a defi-
nite critical stress but is dependent upon the stress distribu-
tion within the body, and can be accounted for on the basis of
Weibull's statistical theory of strength. J. White concluded
that the largely theoretical consideration of the thermal shock
behavior of brittle materials, the factors involved, and the
basis of a quantitative treatment are complicated by the fact
that the properties of the material vary with the temperature
and because there is no unequivocal definition of strength of a
brittle material. The maximum stress criterion of failure was
compared with the statistical concept of strength, based on the
assumed presence of flaws in the material. White concluded that
stresses set up under slow conditions of heating or cooling are
also influential. Wenger and Knapp derived a stress formula
based on work by Lidman and Bobrowsky, and concluded that (1)
prestressing increases the relative resistance to thermal shock,
and (2) the internal flow theory offers an explanation of the
failure by tension upon cooling. Hummel found that the low-
expansion materials suffer from one or more of the disadvantages
of high cost, insufficient refractoriness, poor thermal con-
ductivity, poor strength, and anisotropic expansion behavior.

Schwartz selected a hollow cylindrical shape heated uniform-
ly from the inner surface for testing sintered alumina specimens
in thermal shock. The resistance to heat shock was found to be
a function of (1) the physical properties of the alumina, (2) the

temperature range of testing, and (3) the temperature distribution within the specimen. Crandall and Ging described a method and the theoretical considerations involved in using a solid spherical shape (Coors grinding balls, type AB-2). The test consisted of plunging the heated sphere into a medium (salt bath) at a different temperature, and determining the time to fracture and the temperature difference causing 50% of the spheres to fail. These agreed well with the theoretical calculations based on the determined physical properties: Poisson's ratio, Biot's modulus, Young's modulus, the coefficient of thermal expansion, the breaking tensile stress, the surface heat-transfer coefficient, and the sphere radius. Hasselman determined the thermal shock on balls of this same composition by radiation heating. The emissivity of the material was shown to be as important as the thermal and mechanical properties usually considered in thermal-shock theory. The calculated and experimental values of the maximum radiation temperature to which the body could be subjected without fracture (T_{max}) at 95% stress level were in good agreement, as for example, 1255 and 1250°K for the 3-inch ball diameter, respectively, and 1564 and 1644°K for the 1.25-inch balls, respectively. Buessem and Bush used the ring shape, 2 in. in outside diameter by one in. in inside diameter, by 1/2 in. in length, and stacked rings for test, heating from the inside and cooling from the outside by a calorimetric chamber. Upon increasing the gradient slowly, failure eventually occurred. The thermal stress resistivity constants were determined from the maximum gradient at thermal fracture and from the thermal conductivity.

Baroody et al. characterized the thermal fracture of hollow cylinders in terms of two factors: M, the material, and S, the shape. Changing the dimensions (but not the ratios of dimensions) by as much as 1.6 times did not affect the shape factor. Using theorems derived by Biot, it was shown that the product relationship of the two factors S and M hold for a considerably wider variety of shapes than the simple circular tube.

Tacvarian claimed that a correlation exists between the ratio of the transverse strength before and after thermal shock and the difference in temperature of the heat shock, and proposed this as a simple method for evaluating thermal shock resistance.

Glenny and Royston found reasonable agreement between theory and experiment in calculating the transient thermal stresses in sintered alumina cylinders produced by rapid heating and cooling in fluidized beds.

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Rubin found that for moderate cooling rates, the high thermal conductivity of beryllia gives a higher thermal shock resistance than that of alumina, but at high cooling rates, the higher strength of alumina provides greater resistance. Walton and Bowen claimed that the thermal shock resistance of slip-cast fused silica was superior to that of Pyroceram, which in turn was found to be superior to sintered alumina in the thermal shock environment provided by the exhaust of a small O-H rocket motor.

Hasselman and Shaffer investigated the material properties which affect the thermal shock resistance of polyphase ceramic systems composed of a continuous phase of high Young's modulus containing a dispersed phase of low Young's modulus. The model system investigated was zirconium carbide-graphite. The principal effect of the dispersed phase (graphite) on the thermal shock resistance of the zirconium carbide was to reduce the extent of damage resulting from fracture. The graphite, while decreasing the strength and Young's modulus, decreased the elastic energy stored at fracture, and at higher volume fractions of graphite, increased the extensibility, that is, the strain at fracture. Emissivity (absorptivity) was introduced as a variable affecting the thermal shock resistance of ceramic materials. Some metal-reinforced ceramics, ceramic fiber-reinforced plastics and metals are combinations that offer possible improvements over single component materials.

Reinhart claimed to improve the thermal shock resistance of sintered alumina by incorporating a small amount of the boride of zirconium or titanium.

There has been a general opinion that increased porosity improves thermal stress resistance of ceramic materials because greater flexibility or extension before fracture is obtained. Much of the early experience related to the effect on strength or spalling resistance of refractory brick. Variations due to forming methods and other causes probably were greater than those due to porosity. Coble and Kingery (1955) investigated the effect of porosity on the thermal shock resistance of sintered alumina under conditions believed to represent only this variable. The porosity was obtained by adding ground naphthalene to a slip-casting composition. All samples were fired together to the same temperature so that crystal growth and grain boundaries would be equally developed. Pore size was uniform. Within the range from 4 to 50% porosity, the thermal stress resistance was found to decrease with increasing porosity; resistance to thermal stress at 50% porosity was only about one-third of that estimated for zero porosity.

5-8 INTERNAL FRICTION

In a perfectly elastic system (Hookean) with stress proportional to strain, cyclic energy loss occurs only under dynamic adiabatic conditions. Kelvin established the difference between adiabatic and isothermal conditions of elasticity, $E_a - E_i$, by the expression,

$$\frac{a^2 T E_i E_a}{\rho s},$$ in which a is the coefficient of

thermal expansion, T is the absolute temperature, ρ is the density, and S is the specific heat. Real solids depart from the Hookean concept. Differences larger than predicted from the formula (about 0.01%) are ascribed to internal friction.

The relaxed(static) strain is greater than the instantaneous strain, and the relaxed modulus of elasticity is correspondingly higher; that is, the material is more rigid under rapid loading. Under sinusoidal loading, the energy loss per cycle is proportional to a function of the phase angle θ by which the strain lags the stress; it reaches a maximum when the relaxation time matches the period of vibration, so that the energy absorption is sensitive to frequency. The width of a natural resonant peak at 0.707 maximum amplitude, f, is measured, since $\Delta f/f$ approximately equals tangent θ, defined as the measure of internal friction. Internal friction may also be determined by measuring the decay in amplitude of free vibration (logarithmic decrement).

Dew, Wachtman and Lam; and Huber investigated the internal friction of polycrystalline alumina. Dew found a rapid broadening of the resonant peak widths above 800°C, which he regarded as an indication of increasing internal friction. Dew ascribed this to plastic deformation, on the basis of torsion tests made at about 20 cycles per second. Wachtman and Maxwell (1957) and Chang concur in the more likely belief that the cause is grain-boundary slip.

Asbury and Davis showed the influence of porosity on the internal friction in terms of the phase difference between stress and strain in cyclic deformation. The phase displacement increases with increasing porosity but decreases with increasing frequency of vibration. For perfect elasticity, the phase angle is zero. For ordinary electrical porcelain, the value ranges from 0.3 to 1.0 radian; for polycrystalline alumina, a value of about 0.01 to 0.03 radian is found; and for single-crystal alumina and quartz, below 0.01 radian.

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5-9 FATIGUE

The hysteretic energy absorbed during cyclic stress of a body is largely absorbed in regions of local stress concentration. Failure may occur at some critical stress level. The endurance limit is the greatest stress that can be applied repeatedly without causing failure; its measurement, statistically, has a band width of about one logarithmic order of magnitude. Fatigue fracture of the cyclic type is rare in ceramics.

Static fatigue, or delayed fracture, is more common in ceramics. There is a marked dependence upon the ambient atmosphere. Brittle fracture is of most significance. Williams; Pearson; Roberts and Watt; Wachtman and Maxwell (1954); and Charles and Shaw investigated the embrittlement by moisture, or other factors affecting the delayed failure of both polycrystalline and single-crystal aluminum oxide. Mountvala and Murray found that exposure of sapphire to moisture at elevated temperatures (above 180°C) caused the formation of hydrates, which impaired the strength measured at room temperature. The strength was recovered when the moisture-exposed specimens were heated to 400°C. Polycrystalline alumina (Lucalox) having an average crystal size of 30 microns did not decrease significantly in bend strength (from 33,300 to 28,000 psi) following steam spraying at 180°C for 52 hours. The strength of single-crystal alumina was unaffected by exposure to nitrogen at 1000°C, or hydrogen at 800°C.

Delayed fracture (steady-load) data have been correlated with fatigue (cyclic-load) results and with the short-time determination of modulus of rupture. Both types of corundum exhibit strong delayed failure characteristics which depend upon the atmosphere, temperature, and strain rate. In normal atmosphere the effect was found to depend on the time for which the stress was applied. Under constant load, the average time to fracture increased from one second to about 11 days when the stress was reduced by 22%. This type of delayed fracture could be largely eliminated by heat-treating and testing in a vacuum. The delayed-fracture effect reappeared, however, when the vacuum heat-treated material was again exposed to atmosphere. The effect was absent at liquid nitrogen temperatures, and decreased at temperatures above room temperature until it disappeared around 900°C.

A fatigue theory involving stress corrosion of an elastic continuum was applied to the low-temperature data on sapphire to obtain reasonable concordance.

5-10 HARDNESS AND ABRASIVENESS OF ALUMINA

Hardness has been defined as the resistance of the surface layers of a body to penetration under the effect of external mechanical forces concentrated in a restricted area of the body (Koifman). A clear understanding of the hardness range of minerals existed at least 200 years before Mohs devised his arbitrary scale about the year 1820 (Gradzinski). On the Mohs scale, corundum is fixed at 9.0 and diamond at 10. The scale has since been revised by Ridgway, Ballard, and Bailey, and by Markes, to show quartz 8, topaz 9, garnet 10, fused zirconia 11, corundum 12, silicon carbide 13, boron carbide 14, and diamond 15 or 15.1.

A more quantitative evaluation of hardness than the Mohs scale has been determined in terms of valence number and atomic volume or the interatomic distances (Friederich; Plendl and Gielisse; Kick; and E. Meyer). The different surface-indentation tests (Vickers, Knoop, Tukon, Rockwell) are based on the relation between hardness and the load required to produce a definite indentation. The methods differ in the shape of the diamond indenter and in the loading (Ludwik; Smith and Sandland; Brinell; and Knoop, Peters, and Emerson).

A distinction is made between macrohardness and microhardness determinations made with the diamond indenter. The former requires from 10 to 20 kilograms of loading, and the indentation diagonal usually covers many crystals. The determination is more or less independent of the load value. Microhardness determines the indentation on single crystals usually, and at loadings of about 5 to 100 grams the hardness is dependent upon the loading (Hanemann and Bernhardt).

Hardness (H) is determined as the loading (P) per unit of superficial area of penetration derived from the length of the diagonal of the indentation (d):

$$H = \frac{kP}{d^n} \text{, in which n is 2 for}$$

macrohardness determinations, and varies from about 1.7 to 2.5 for microhardness determinations. The factor k relates the length of the diagonal of penetration to the area of indentation, and has a value of about 1.8544 for the Vickers indenter.

The Bierbaum equipment is sometimes used for measuring the hardness of ceramic materials. It measures the width of scratch produced by a diamond cube corner under standard loading, usually three grams.

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Tabor found that the hardness of abrasives (except diamond) on the Mohs scale (M) correlates closely with the indentation hardness (H) by the expression: $\log H = 1.6 M$.

Knoop et al. obtained a hardness of alpha aluminum oxide of about 3000 kg/mm². Ryshkewitch claimed that fused alumina has a distorted structure which weakens its mechanical strength. Thibault and Nyquist obtained an average value for abrasive alumina of 2050 by the Knoop indenter at 100 gram loading, in comparison with 820 for quartz, 1340 for topaz, 2480 for silicon carbide, 2760 for boron carbide, and 8000 to 8500 for diamond.

Attinger, and Stern determined the directional hardness of synthetic corundum. The faces parallel to the optic axis were harder than those perpendicular to it. Sapphires with pores normal to the optic axis were the softest. Fissures were usually at 45° to the optic axis. Maximum hardness is claimed to be at about 60 degrees to the c-axis (Klassen-Neklyudova) and both minima occur at 0° and 90° to this axis. The abrasion resistance is also greater in the direction parallel to the optic axis. The average hardness was about 2000 kg/mm² ($Knoop_{200}$).

The hardness of corundum containing about 3% Cr_2O_3 in solid solution is higher by about 10% than that of pure sapphire, but decreases at higher chromia contents. The hardness is strongly anisotropic. Schrewelius found that for an expanding unit cell of fused alumina, caused by a change in the titania content up to 0.6%(mole), the microhardness ($Knoop_{100}$) dropped from 2300 at 5.126A to only 1800 kg/mm² at 5.130A. Titania is added to fused bauxite compositions to about 2 to 3% by weight to increase the toughness of the grain (Parché). Baumann showed that such grain has large crystalline areas of alpha alumina with slag-like inclusions of siliceous groundmass and numerous included microcrystals of titanium and aluminum compounds. He ascribed the toughness of the abrasive grain to this residual matrix. Schrewelius obtained only 2000 to 2200 kg/mm² for beta alumina in comparison with 3000 for alpha alumina by the Zeiss microhardness test. Jorgensen and Westbrook obtained a microhardness of 2500 kg/mm² for polycrystalline alumina sintered from Linde A alumina powder (0.3 micron) fired for 16 hours at 1830°C. When sintered with 0.05 to 0.25% MgO by weight, the bulk hardness (crystal face) was about 2550 kg/mm² and the crystal-boundary hardness about 2800 to 2900 kg/mm². The adsorption of water on the surface of the polished specimens affected the hardness

values. Specimens dried in oxygen for 16 hours at 200°C and measured under toluene gave consistent values. This effect together with the differences in crystal orientation and in solid solution of impurities perhaps accounts for the differences in hardness reported by different investigators.

Whitney attempted to measure hot hardness using a Tukon tester equipped with a temperature-controlled furnace in a hydrogen atmosphere.

Pemberton determined the hardness of alumina abrasives simply by measuring the load in grams required to crush a sufficient number of single grains, 290 to 340 microns in size for statistical significance. Abrecht et al. measured the toughness of the grain by throwing sized grain continuously (by recirculation) from a centrifugal device against an impact surface. The number of cycles required to halve the number of grains of the original size was arbitrarily taken as the measure of impact resistance. The loss in weight of the impact surface measured the abrasiveness. Mann determined the crushing resistance of synthetic abrasives by milling uniform grit sizes (2000 to 125 microns) with steel balls, and by calculating the fraction of attrition. The order of decreasing resistance for various 2000-micron abrasives was: dark silicon carbide, brown corundum, white corundum, boron carbide, and light silicon carbide, designated a,b,c, d, and e, respectively. The order for 125-mesh grits was: d,e, a,c,b, possibily indicating that strain or partial cracking upon crushing may differ for different sizings of the materials.

Cadwell and Duwell, and Stotko measured the friability by crushing with steel balls in grinding operations.

Several synthetic abrasive materials are harder than corundum. Among these are silicon carbide, boron carbide, boron, boron nitride (cubic), and, of course, diamond. While silicon carbide is harder than corundum, it is more brittle. Alumina is therefore recommended for grinding operations on materials of high tensile strength, while silicon carbide is used on materials of low tensile strength.

Giessen (1959) reviewed the available methods for determining the tenacity of abrasives and recommended the use of impact methods, and sample sizes of about 160 to 200 grams.

H. W. Wagner in 1950 stated that an abrasive yields higher grinding value when its penetration hardness is higher, when its body strength permits fracture (self-sharpening) of the grain at

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the proper degree of dullness, and when its attrition resistance is higher. Dulling of abrasive points is influenced by solubility of the abrasive in the work material being ground. The effect of oxidation in grinding is small compared with that of solubility. In molten steel, boron carbide and silicon carbide dissolve rapidly, but aluminum oxide is practically insoluble. In molten glass, aluminum oxide dissolves more rapidly than silicon carbide. Brown, Eiss, and McAdams confirmed that chemical mechanisms are involved in the wear of single-crystal sapphire on steel. Duwell and McDonald measured the wear and cutting performance of sixteen abrasive minerals, and found that wear may be by attrition and fragmentation. Lubricants can increase the rate of cut and decrease the rate of wear. Carbides and borides have less resistance to attritional wear on steel than oxides because of their chemical instability. Steijn; Coffin; Sibley, Mace et al.; Riesz; and Riesz and Weber investigated the mechanism of wear of sapphire as a bearing material. A statistical correlation exists between the measured wear rates and the coefficient of friction, the thermal-stress resistance, and the thermal diffusivity of the mated materials for unlubricated wear resistance at high sliding speeds (100 to 200 fps). During high-speed sliding, wear appears to be induced by the inability of ceramic and cermet materials to resist thermal stresses produced by temperature gradients within each rubbing surface between small asperities or hot spots in frictional contact. Corundum and Cr-Mo cermets appear to be promising materials for high-temperature, high-speed sliding bearings and seals. Friction and wear of single-crystal sapphire, sliding in vacuum from 30 to 1550°C, was influenced by surface cleanliness. High coefficients of friction and "stick-slip" sliding occurred up to 300°C. At 300 to 1000°C, lower coefficients and smooth sliding occurred. In the region from 1000 to 1350°C, stick-slip reappeared at lower coefficients. Chevron-shaped subsurface fractures of the sapphire plate were observed below 300°C, their formation being orientation-dependent. In the absence of fracture, adhesions were noted. Under high vacuum, a weld-adhesion mechanism of sliding friction was observed, particularly above 1000°C. High surface temperatures occur coincidently with the friction process, but direct evidence of an adhesion mechanism is inconclusive. Parker, Grisaffe, and Zaretsky used a five-ball fatigue tester to study the behavior of hot-pressed and cold-pressed-and-sintered alumina balls under repeated stresses applied in rolling contact. The failures that developed were shallow eroded areas unlike fatigue spalls found in bearing steels. The room-temperature load capacity of hot-pressed aluminum oxide was about one-fifteenth that of a typical bearing steel and seven

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times that of cold-pressed-and-sintered alumina. Preliminary
tests at 1000°C with molybdenum disulfide-argon mist lubrication
indicate that polycrystalline aluminum oxide is capable of
operating satisfactorily under high-temperature rolling contact
conditions.

Wear of sintered alumina grinding balls in which both
sliding contact and impact are involved appears to be dependent
on surface crystal size, the rate of wear increasing with in-
creasing average crystal size.

Groszek found that preferential heats of adsorption of
various wear-reducing agents on different types of porous solid
surfaces correlated with their wear-reducing action on sliding
steel surfaces.

The abrasiveness and wear resistance of alumina has been
the subject of investigation because of the importance of
applications as abrasives, lathe tools, bearings, gauge blocks,
dies, etc. These applications involve alumina both in partic-
ulate form and in massive shapes.

The Bayer process hydrates, calcined aluminas, and tabular
aluminas together with fused alumina cover a remarkable range of
abrasive properties. These effects are related to a wide varia-
tion in hardness between the different alumina phases, and an
extended range of particle or crystal size. Changes in texture
and in the bond holding crystallites together in the Bayer grain,
particularly in the transition alumina structures, afford various
degrees of abrasiveness in the polishing range. Both Bayer alumi-
na trihydrate and kappa alumina (Broge, Hedley) have been claim-
ed as dental polishes. "Gamal," a gamma alumina structure, and
"microid" (Griffin and Tatlock) are finely divided metallographic
polishes. Manuilov and Zimbal recommended a 2-hr calcination at
1300°C in the alpha aluminum oxide range for metallographic pol-
ishes. "Sira", a coarsely crystalline sharp alpha-alumina, pro-
duced from Bayer hydrate, relies on the soft bond of the Bayer
grain to produce fine scratching in the polishing of glass
(Carlisle). McAleer, Powell, and Klein discussed the properties
of polishing grades prepared from Bayer alumina and fused alumi-
na.

The polishing aluminas were developed initially for finish-
ing chrome plate and stainless steel. The ware is buffed on
rapidly rotating wheels of sewed canvas layers to which the pol-
ishing compound has been applied. The compounds consists of

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proprietary mixtures of the ground alumina in stearic acid and other greases in the proper consistency for holding on the wheel, but with minimum coating of the ware with a wax film. Polishes of different grades are designated "cutting" for fast surface removal, and "coloring" for high polish development. The abrasive action is thought to depend upon a combination of partial disintegration of Bayer agglomerates having the proper crystal size and the development of a suitable Bayer grain bond for the specific operation. The Bayer grain provides backing for producing scratches, but the Bayer particle bond is weak, and disrupts easily under pressure. Russell and Lewis showed the range of abrasiveness of aluminas derived from the Bayer process in terms of a standarized air-blast test. Tabular alumina (sintered alumina) was found to be about as abrasive as fused alumina by this "one-shot" test.

6 THERMAL PROPERTIES

Several excellent compilations of thermal properties of
alumina and other materials have appeared within recent years.
Among these are Goldsmith, Waterman, and Hirschhorn, Handbook of
Thermophysical Properties of Solid Materials, The Macmillan
Company, New York, 1961, 5 volumes; Bradshaw and Mathews, Proper-
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chemical Tables, Vol. I; Fieldhouse, Hedge and Lang, Measurements
of Thermal Properties," PB Rept. 151583, furnish some thermal
data on sapphire. Rossini, Wagman et al. (compilers), Selected
Values of Chemical Thermodynamic Properties, N.B.S. (US) Circu-
lar No. 500 (Feb. 1952) provides thermodynamic properties of
some alumina phases.

A selected set of thermal properties of the aluminas has
been collected in Table 10.

Table 10

Thermal Properties

Property	Phase	Value		Reference
Melting Point	α-Al_2O_3	2072°C		(1)
Boiling Point	α-Al_2O_3	3530°C		(2)
Vapor Pressure		T °K	Atm	(2)
		2309	8.7×10^{-6}	
		2325	1.03×10^{-5}	
		2370	1.66×10^{-5}	
		2393	1.68×10^{-5}	
		2399	2.15×10^{-5}	
		2459	3.78×10^{-5}	
		2478	5.81×10^{-5}	
		2487	9.10×10^{-4}	
		2545	2.00×10^{-4}	
		2565	1.29×10^{-4}	
		2605	3.23×10^{-4}	

Property	Phase	Value	Entropy at 298.15 (kcal/mole)	Reference
Heat of Formation at 298.15°K (kcal/mole)				
	$\alpha-Al_2O_3 \cdot 3H_2O$	-612.8	33.51	(5,3)
	$\beta-Al_2O_3 \cdot 3H_2O$	-609.4		(4)
	Amorphous $Al(OH)_3$	-304.2		(3)
	$\alpha-Al_2O_3 \cdot H_2O$	-471.8	23.15	(4)
	$\beta-Al_2O_3 \cdot H_2O$	-	8.43	(3)
	$\alpha-Al_2O_3$	-400.4	12.16	(7,6)
	AlO	-138		(2)
	Al_2O	-248		(2)

Heat of Fusion

$\alpha-Al_2O_3$	26	(3)

Heat of Sublimation   456.0 at 298.15°C   (2)

Heat of Vaporization   150.1 at 1950°C   (8)
                             443   (2)

Enthalpy at 705°C

$\gamma-Al_2O_3 \longrightarrow \alpha-Al_2O_3$ - 5.3 kcal/mole	(9)
$K-Al_2O_3 \longrightarrow \alpha-Al_2O_3$ - 3.6 kcal/mole	(9)
$\delta-Al_2O_3 \longrightarrow \alpha-Al_2O_3$ - 2.7 kcal/mole	(9)

Heat of Immersion at 25°C (cal/m² surface area)

(Ref. 28) Type Alumina	A Tabular T-60	B Alucer MC	E Alucer HSB	F Alon C	G Alucer MA	H Act.Alumina F-20
Phase	$\alpha-Al_2O_3$	$\alpha-Al_2O_3$	$\alpha-Al_2O_3$	$\gamma-Al_2O_3$	$\gamma-Al_2O_3$	-
Area m²/g	0.22	2.72	4.56	65.2	109	
Degassing Temp °C						
100	0.157	0.139	0.127	0.098	0.092	0.077
300	0.202	0.222	0.170	-	0.150	0.123
400	0.206	0.241	0.170	-	0.172	0.153
450	0.208	0.257	-	0.200	0.177	0.163

Table 10 Continued

Property	Phase	Value		Reference
Specific Heat (cal/g°K)				
	α-$Al_2O_3 \cdot 3H_2O$	$0.2694 + 6.43 \times 10^{-4}t$ (a)		(10)
		0.2855 at 25°C		
	α-Al_2O_3	$0.34833 - 8.02 \times 10^{-6}T - 47.852/T$ (a,b)		(11)
		°K	cal/g°K	
		100	0.03010	(11)
		200	0.11988	
		273.16	0.17149	
		298.16	0.18521	
		300	0.18614	
		400	0.22545	
		500	0.24857	
		600	0.26371	
		700	0.27431	
		800	0.28204	
		900	0.28788	
		1000	0.29240	
		1100	0.29594	
		1200	0.29868	
		1318.1	0.2783	(12)
		1510.0	0.3364	
		1660.2	0.3814	
		1787.4	0.4196	
		2350	0.468	(13)
Diffusivity		Temp,°C	cm²/sec	
		25	0.091	(26,27)
		100	0.055	
		200	0.043	
		400	0.024	
		800	0.018	
		1000	0.015	
		1500	0.0063 to 0.0108	
		1600	0.0106 to 0.0184	
		1700	0.0130 to 0.0224	
		1800	0.0170 to 0.0294	

Notes: (a) T = °Kelvin = $273.16 + °C$; $t = °C$
      (b) Range 400 to 1200°K

Table 10 Continued

Property	Phase	Value	Reference

Thermal Expansion, Linear $(X \ 10^{-6}/°C)$

α-$Al_2O_3 \cdot 3H_2O$ (Perpendicular to specified crystal
plane)
25 to 100°C(010),10.9; (001),15.4; (100),13.1;
10$\bar{1}$),39; (101), -5.6   (16)

α-Al_2O_3

Temp.Range	Single-Crystal (14) Orientation		Polycrystalline	
	C-axis 0°	90°	(14)	(15) AD-94
-273 to 0	1.95	1.65	1.89	
-73 to 0	4.39	3.75	4.10	
0 to 127	6.26	5.51	6.03	
327	7.31	6.52	6.93	
527	7.96	7.15	7.50	
927(c)	8.65	7.80	8.08	
1127	8.84	7.96	8.25	7.95
1327	8.98	8.12	8.39	
1527	9.08	8.20	8.49	
1727	9.18	8.30	8.58	

(c) Data obtained by extrapolation

β-Al_2O_3

25 to 200°C 5.1 to 5.7 $X \ 10^{-6}/°C$ (17)
600 to 700°C 6.0 to 7.6

ζ-Al_2O_3

25 to 200°C   6.0 $X \ 10^{-6}/°C$
600 to 700°C   7.7

Table 10 Continued

Property	Phase	Value		Reference

Thermal Conductivity (cal/sec cm °C)

α-Al_2O_3 (dense)

Temp °C		cal/sec cm °C	Coors AD-995	AD-94	(15,18,19, 20,21,22, 23,24,25)
-263		3			
-253		9			
-233		14			
-223	°K	12			
25	(298)	0.086	0.080	0.046	
100	(373)	0.069			
300	(573)	0.038			
500	(773)	0.025			
700	(973)	0.018	0.018	0.011	
900	(1173)	0.015			
1100	(1373)	0.014			
1300	(1573)	0.014			
1500	(1773)	0.013			
1700	(1973)	0.014			
1900	(2173	0.015			

α-Al_2O_3 (23.4% porosity)

25	0.055
100	0.049
300	0.029
500	0.018
700	0.013
900	0.012
1100	0.008

α-Al_2O_3 (48.7% porosity)

25	0.0397
100	0.0312
300	0.0191
500	0.0104
700	0.0070
900	0.0062
1100	0.0070

Table 10 Continued

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(4)	Russell et al (1955)		
(5)	Barany & Kelley	(19)	Weeks & Seifert
(6)	Kerr, Johnston & Hallett	(20)	Francis, McNamara, Tinklepaugh
(7)	Mah		
(8)	Wartenberg	(21)	Adams
(9)	Yokokawa & Kleppe	(22)	Charvat & Kingery
(10)	Roth, Wirths, & Berendt (1942)	(23)	McQuarrie (1954)
(11)	Furukawa et al.	(24)	Norton (1951)
(12)	Shomate & Naylor	(25)	Berman
(13)	Steindlin (1964) 0.46 cal/g °K at 2570°K	(26)	Plummer, Campbell, & Comstock
(14)	Wachtman, Scuderi, & Cleek(1962)	(27)	Paladino, Swarts, & Crandall
(15)	Coors Porcelain AD 995		
(16)	Megaw (1933)	(28)	Wade & Hackerman (1960)

6-1 THERMOPHYSICAL AND THERMOCHEMICAL CONSTANTS

Many investigators have determined the melting point of alpha aluminum oxide, among whom are included Kanolt; Geller and Bunting; Geller and Yavorsky; Trombe; and Lambertson and Gunzel. In general, they have striven for high sample purity, but their estimations have been vitiated in some cases by the heating conditions or the method for detecting incipient melting. Some investigators, including Kanolt, used graphite resistor tubes, which in the presence of reducing atmospheres water vapor might have caused reduction of the alumina. In other cases, the direct observation of melting indicated a lack of black body conditions and a temperature gradient in the test furnace (Schneider,1963).

Geller and Yavorsky (1945) obtained apparently low values ranging from 2000 to 2030°C on fused and recrystallized alumina 99.99% pure, melted in an oxidizing atmosphere, but based on the visual observation of edge deformation, believed unsatisfactory. Ryshkewitch (1960) had pointed out that an alumina rod in the

horizontal position, fastened at one end, deforms at 1400°C, and that pyrometric cone 42 is pure alumina, which deforms at 2000°C.

Kanolt's painstaking determination, 2050°C, has been erroneously corrected to 2040°C for the changes in the International Temperature Scale of 1927 to that of 1948 (about 6° at 2000°C), and has been considered valid until recently. The present temperature scale could not be established within 3° at 2000°C between leading national standardizing laboratories as recently as 1957 (Kostkowski). Kanolt's alumina was probably of high purity (0.001% Fe_2O_3, 0.001% SiO_2, 0.005% chlorides, and 0.001% sulfates). His calibration was not based on the International Scale, however, but on his determination of the melting point of platinum at 1755°C rather than the presently accepted 1769°C. Schneider (1963) has appraised the earlier investigations on the basis of the present temperature scale and on the relative freedom of the alumina from decomposition, and finds that Kanolt's determination, corrected on the basis of the present platinum melting point to 2072°C, still appears to be the most probable melting point.

Diamond and Schneider obtained 2025°C as the melting point of alumina in a solar furnace, but do not recommend this method.

Markovskii et al. suggested a micromethod for determining the melting point of refractory materials using hot-pressing equipment.

Lambertson and Gunzel obtained 2034 ± 16°C for the melting point of tabular alumina T-61, indicating the high purity of alumina from Bayer sources.

Brewer and Searcy (1951) found 3530 ± 200°C as the boiling point of alpha alumina; Wartenberg (1952) obtained 3300°C, based on extrapolation of the vapor pressure. Ruff and Konschak (1926) had obtained 2980°C. The data are all questionable because of the claimed decomposition of the alumina by tantalum containers used by Ruff (Brewer and Searcy), and by tungsten containers used by Brewer and Searcy (Wartenberg; Ackermann and Thorn).

Treadwell and Terebesi (1933) stated that the heat of formation of alpha aluminum oxide is fairly independent of temperature, citing 392 kcal/mole at 25°C, and 387 kcal/mole at 2300°C. Roth, Wolf, and Fritz (1940) obtained 402.9 kcal/mole, Snyder and Seltz 399.0, and Holley and Huber 400.29. Schneider and

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Gattow (1954) claimed that the value of Snyder and Seltz was too low because of incomplete conversion to alpha alumina in the oxygen pressure bomb. They corrected on the basis of about 25% transition alumina having a heat of transition to alpha alumina of 10 kcal/mole, and estimated 402 kcal/mole for the heat of formation of alpha alumina. The value, 400.4, obtained by Mah in 1957, appears to be more trustworthy, because the product of combustion was shown to be alpha aluminum oxide by X-ray.

Wade and Hackerman (1960) determined the heats of immersion of aluminas varying in surface area from 0.22 m²/g for tabular alumina (T-60) to 221 m²/g for activated alumina (F-20). The data are shown in Table 10. Morimoto, Shioma, and Tanaka (1964) found that the curves for heat of immersion have maxima at about 600 to 650°C. The heats of hydration calculated from the heats of immersion were 15.8 kcal/mole for α-Al_2O_3 and 9.60 kcal/mole for γ-Al_2O_3. Rehydration of the dehydration sites is an important factor in immersion.

Kingery (1959) found the density of liquid alumina, by the pendent drop method, just above the melting point to have a mean value of 2.97 g/l, somewhat higher than the 2.5 g/ml reported by Wartenberg, Wehner, and Saran in 1936. Kirshenbaum and Cahill measured the density at 2100 to 2350°C (2375 to 2625°K) by use of a molybdenum crucible and a tungsten sinker. Their data fit a linear curve having the form: $D = 5.632 - 1.127 \times 10^{-3}T$, in which T = °K. The calculated liquid density at the melting point is 3.053 g/ml. The increase in volume found by Kingery was 20.4% and by Kirshenbaum 22%, assuming the correctness of Ebert's solid data. Wartenberg's value, 33%, seems unlikely in comparison with the expansion of other ionic solids. Hasapis, Panish, and Rosen found the viscosity at 2200°C to be only 13 poises, in comparison with 104.4 poises for fused silica at 2560°C. Kingery (1959) measured the surface tension by the pendent drop method (from a molybdenum rod) and obtained a mean value of 690 dynes/cm.

The surface energy of solid aluminum oxide was 905 ergs/cm at 1850°C, or about 885 ergs/cm² at the melting point (Norton, Kingery, Economos, and Humenik). Livey and Murray (1956) considered these values low, and probably due to the formation of a low-energy surface consisting of oxygen ions highly polarized by the submerged and powerful cations. The surface energy is low in comparison with several thousand ergs/cm² for diamond and silicon carbide. Livey and Murray (1959) reported a value of -0.2 erg/cm²/°K for the surface energy for crack propagation, γ, which

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would make the room temperature value of surface energy about 1270 ergs/cm².

6-2 SPECIFIC HEAT

The variation in specific heat of alpha alumina with temperature has been determined by many investigators, among whom are Shomate and Naylor (1945); Kerr, Johnston, and Hallett; Ginnings and Furukawa; Furukawa et al.: J. I. Lang (1959); Hoch and Johnston (1961); Ewing and Baker; and Kirillin, Sheindlin, and Chekhovskoi (1964). In general, the method of dropping the specimen from an equilibrium temperature into a water or ice calorimeter has been used. The specimen usually has been sapphire. Agreement between the different investigators has been close in the temperature region from near absolute zero to about 1200°K. The data of Furukawa et al., according to the empirical equation: $c_p = 0.34833 - 8.02 \times 10^{-6}T - 47.852/T$, is generally accepted in the temperature region from near 400 to 1200°K, in which c_p is the specific heat in calories per gram °K or closely Btu per pound °R. T is 273.16 + °C in °K. The results are tabulated for 5° intervals in the reference. Dawson (1963) obtained values only 0.3% higher than these N.B.S. values.

In the region above 1200°K, there is increasing variance between different investigators. At 1700°K, the scatter ranges from extrapolated values of about 0.295 cal/g °K for the data of Lucks and Deem, to 0.390 cal/g °K for that of Rodigina and Gomelskii. Goldsmith, Waterman, and Hirschhorn plotted a most probable average curve from the data prior to 1959, which conforms to the data of Ginnings and Furukawa from the absolute zero to 1200°K. The values of Shomate and Naylor continue the curve slope smoothly to about 1800°K. Sheindlin et al. found a value of 0.4677 cal/g °K for the melt at 2350 to 2800°K, indicating an upsweep to the curve, which makes Rodigina's data appear high. In their method, the corundum melt, heated diathermally in a molybdenum container in argon, was mixed in a massive metallic calorimeter. Alternatively, tests in vacuum gave closely similar values for specific heat.

Fieldhouse, Hedge, and Lang found only slightly higher results for polycrystalline alumina than for sapphire by the drop method in the temperature region 1300 to 1800°K.

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6-3 THERMAL EXPANSION

The linear thermal expansion of various specimens of alpha aluminum oxide has been determined by many investigators, and using different methods. Austin determined the expansion of single-crystal natural sapphire by the interferometric method. He reported that alumina expands anisotropically, with the expansion 7 to 15% higher parallel to the c-axis. Austin claimed that the expansion of an aggregate of nonisotropic crystals often shows hysteresis which is not observed in single crystals.

Schwartz (1952) obtained values ranging from 5.5×10^{-6} at 25°C to 10.0×10^{-6} at 1300°C by telemicroscopic sighting on the ends of slip-cast pure alumina rods having about 5% porosity after sintering. Smoke (1949) determined expansions on six alumina spark plug porcelains by dilatometric measurements against silica on 8-inch bars. Shevlin and Hauck similarly measured the expansion of bars prepared from Alcoa T-61 to about 700°C. Whittemore and Ault obtained data to about 1500°C on 7-inch bars prepared from fused alumina (99% Al_2O_3), sintered alumina (99% Al_2O_3), and clay-bonded fused alumina (88% Al_2O_3). Their values for the expansion coefficients were: (6.7, 5.9, and 4.4) $\times 10^{-6}$/°C, respectively, in the range 25 to 900°C; and (10.2, 9.6, and 8.7) $\times 10^{-6}$/°C, respectively, in the range 25 to 1500°C.

Coble and Kingery (1956) found no difference in the thermal expansion of polycrystalline alumina ranging in porosity from 4 to 49%.

Shalnikova and Yakovlev (1956) reported that alumina expands isotropically, from X-ray measurements of the lattice expansions. Zimmerman and Allen reviewed the use of a simple back-reflection X-ray camera to determine the expansion, and concluded that the accuracy of measurement was adequate. Beals and Cook applied the method to reagent-grade alumina, and reported the following average values: (9.39, 9.48, and 9.50) $\times 10^{-6}$/°C in the temperature ranges, 20 to 200°C, 20 to 600°C, and 20 to 1200°C, respectively. These values are on the high side of the average curve. They claimed that the change in the ratio of crystallographic axes, c/a, is insignificant. Mauer and Bolz measured the expansion of two orientations of sapphire and a commercial-grade alumina (0.50% Na_2O) in neon atmosphere by the X-ray method, and obtained values on the low side of the curve. They ascribed this to inadequate thermal calibration for samples of lower thermal conductivity. Klein claimed that the anisotropy of alpha aluminum oxide is low, and that within a small limit of error, the ratio

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c/a is constant. This was believed to confirm that the expansion is substantially isotropic.

Engberg and Zehms extended the telemicroscopic evaluation to 1600°C by use of a graphite tube in which the carbon gases were swept away from contact with the alumina specimens by a small flow of argon, introduced through a tantalum tube. Consistent values were obtained on cold-pressed, extruded, and single-crystal melts of alumina on the low side of the average of previous investigations. The average coefficients of linear thermal expansion found for alumina in comparison with several other high-temperature materials is as follows:

Material	$\bar{a} \times 10^{-6}$	Temp. range °C
Al_2O_3	7.5 ± 0.4	1000 to 1600
BeO	10.1 ± 0.6	1000 to 2000
MgO	12.6 ± 0.5	1000 to 2000
B_4C	6.02 ± 0.51	1000 to 2400
SiC	5.68 ± 0.11	1000 to 2400
TiC	8.31 ± 0.68	1000 to 2600

All BeO specimens that had been heated to above 2050°C had very large expansions. The specimens were bent and cracked. The alumina specimens exhibited irreversible behavior above 1600°C, probably representing additional sintering contraction, particularly of those specimens having a cold-pressed density of 3.83 g/ml, and an extruded density of 3.81 g/ml. Peculiarly, the single-crystal alumina (density 3.98 g/ml) also exhibited irreversible shrinkage, and on a different slope than the ascending curve.

Campbell and Grain investigated the c/a ratio rigorously by X-ray diffractometer methods and found that alpha alumina expands anisotropically, with the expansion coefficient parallel to the c-axis about 10% higher than that parallel to the a-axis, in substantial confirmation of Austin's data. The c/a ratio determined at 25, 200, 400, 600, 800, and 1000°C was 2.7294, 2.7298, 2.7303, 2.7307, 2.7312, and 2.7316, respectively.

Burk measured the thermal expansion of several specimens of sintered alumina, Coors AD-85, AD-94-E, AD-99, and AP-100, in the low temperature range from about 73°K to 273°K. In these compositions the number signifies the approximate alumina content. In this region, the coefficient of expansion was in the range 2 to 4 X 10^{-6}, in comparison with 6 to 8 X 10^{-6} from room temperature to 100°C. The specimen with almost 100% Al_2O_3 and

porous, AP-100 (18 to 21% porosity), had the highest thermal expansion coefficient. The lowest coefficient was found for the specimen having the lowest Al₂O₃ content, owing to the presence of spinel or silicate phases.

Wachtman, Scuderi, and Cleek (1962) measured the linear thermal expansion of polycrystalline alumina (Lucalox containing 0.1 to 1% MgO) and of sapphire (0.01 to 0.1% Si) in two orientations by the interferometric method in air. The orientations of sapphire were for an angle (ω) between the crystallographic c-axis and the direction of measurement equal to 10 degrees, and for the angle equal to 90 degrees. Values were computed for the orientation 57.6 degrees, which is frequently used for sapphire rod dilatometers. Measurements obtained at 100 to 1100°K were fitted to Grüneisen's statistical mechanical equation using a Nernst-Lindemann energy function. The closeness of fit made it reasonable to extrapolate the values to 2000°K. The values for the polycrystalline alumina fell intermediate between those for the two orientations of sapphire, the higher value being for the 10 degree orientation. Their data agree with those of Mauer and Bolz, but are on the low side of the curve of probable values shown by Goldsmith et al.

Neilson and Leipold (1963) investigated the thermal expansion of hot-pressed, slip-cast, and isostatically pressed polycrystalline single-phase alumina heated in air in an automatic, recording dilatometer. Expansion measurements above 1100°C in air were made in an oxide induction furnace. The hot-pressed alumina (98.5% theoretical density) developed crystal growth during testing, increasing in size from 3 microns original size to 17 microns at 1700°C, 20 to 50 microns at 1900°C, and 80 to 200 microns at 2040°C. The isostatically pressed alumina (Norton AW1F) having a grain size initially of about 45 microns, developed growth to about 65 microns around 1900°C. The coefficient of expansion was not affected by the crystal size or by the fabrication techniques. The samples showed stability of weight and lattice parameters, but developed permanent expansion when heated above 1500°C, which is well below the melting point. It appears that an oxidizing ambient during initial heating causes a permanent expansion and correspondingly higher values for the coefficient, while a reducing atmosphere causes permanent shrinkage and lower values for the coefficient (Engberg and Zehms). The effect repeats to some degree with continued cycling.

The marked differences between the results of various investigators probably results in part from the differences in

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grain growth or sintering activity of the polycrystalline alumi-
nas. These changes are of particular significance in high-
temperature applications. Further elucidation is required of
the factors affecting expansion. More consideration should pro-
bably be given to data obtained under oxidizing conditions than
reducing, because of the lesser likelihood of reduction of the
alumina.

Stutzman, Salvaggi, and Kirschner (1960) have collected the
literature on the reversible thermal expansion of crystalline
ceramics.

Filonenko and Kuznetsova observed anomalous thermal ex-
pansion of electrocorundum, which they ascribed to oxidation of
titaniferous ferroalloys at 400 to 600°C. This is accompanied
by a considerable decrease in density. Wenzel investigated the
effect of the anomalies in thermal expansion on the quality of
abrasives. Titanium carbide is the most damaging impurity;
titanium nitride and iron alloys, which are also detrimental,
may be removed by proper calcination at 1200°C. Mischke and
Smith determined the thermal conductivity of alumina catalyst
pellets of different densities as a function of the macropore
volume fraction. Values were measured under vacuum and also
under atmospheric conditions to 150°C. Low conductivities in-
dicated that severe temperature gradients are likely in porous
catalysts. The area of contact between the powder particles and
in the pellets is more significant than the conductivity of the
solid phase itself.

Kingery (1957) noted that the thermal expansion of two-
phase compositions is not simply the averages of the end
member values, but agrees quantitatively with calculations based
on the assumption of substantial residual microstresses result-
ing from the constraint of each phase on cooling.

Schneider and Mong investigated the thermal expansion of
certain refractory castables, using a sapphire rod dilatometer.
Ruh and Wallace (1963) have extended the determinations to many
types of refractory brick, including alumina brick in the
classes from 60% to 99% Al_2O_3, and ranging in porosity from 19.5
to 23.4%. The data for the high-purity alumina brick agree well
with that of Wachtman, Scuderi, and Cleek for Lucalox. As the
alumina content decreases, the thermal expansion also decreases,
which indicates the importance of the chemical composition and
the mineral phases present, as well as their distribution.

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The 99% Al_2O_3 brick had a linear expansion of about 1.2% for the range from room temperature to 1300°C (2400°F). This is less than the expansion of the magnesia types (fused, forsterite-bonded, spinel-bonded, spinel, magnesia-chrome, and chrome-magnesia), and less than the expansion of superduty silica-alumina and superduty silica brick. Stabilized zirconia is about in the same range, while zircon and clay-bonded silicon carbide have lower expansions.

6-4   THERMAL CONDUCTIVITY

The thermal conductivity of alpha aluminum oxide is relatively high for ceramic materials, which helps to explain its good thermal shock resistance. It is exceeded, however, by several materials among which are beryllia, magnesia, and silicon carbide. The variation of thermal conductivity of alumina with temperature is typical of dielectrics. The heat conduction is apparently mainly by lattice vibration of the crystals in quantized units called "phonons." The temperature region below 100°K is of unusual interest because of the influence of the marked variation in mean free path, and the effect of various factors on scattering (Umklapp processes). Berman found a peak of very high conductivity, about 15 cal/sec cm °K, for a sapphire crystal at about 40°K. The conductivity of polycrystalline alumina varies near this maximum, dependent on the lattice defects, crystallite size, impurities, etc., in the specimen. The thermal conductivity then falls to a minimum of about 0.012 cal/sec cm °K with increasing temperature to about 1700°K (the reciprocal temperature rule). Above 1700°K, radiation contributes to increased thermal conductivity.

Jaeger (1950); Francl and Kingery; McQuarrie; and Sutton have described methods and equipment for testing thermal conductivity. The usual methods involve the determination of steady-state heat flow through a cube or rod form by comparison or substitution of standards or the direct determination dynamically of heat flow or temperature rise. The heat source in some cases has been enclosed within an ellipsoid-shaped envelope (Norton et al.,1950). It may consist of a thermocouple-resistance unit embedded in the specimen symmetrically (Haupin).

Determinations of the variation of thermal conductivity of alumina with temperature have been made by many investigators, among whom are Knapp (1943), Norton, Fellows, et al.; Norton and Kingery; and Kingery, Klein and McQuarrie. Weeks and Seifert

compared the thermal conductivity of synthetic sapphire against
Armco iron standards in a vacuum, and found that in the
direction 60 degrees from the c-axis, the thermal conductivity
is 0.065 cal/sec. cm °C at 90 to 100°C, in good agreement with
the average curve (Goldsmith, et al.). Knapp earlier had ob-
tained low values for native corundum and synthetic sapphire,
both normal and parallel to the c-axis, by a similar method.

Kingery (1954) found that the thermal conductivity of
polycrystalline alumina by the spherical envelope and cylinder
methods gave values in close agreement with other methods.
Adams obtained values in the region 780 to 1570°K by the prolate
spheroid method on slip-cast sintered alumina (porosity 6.3 to
7.1%) that conformed closely with the average curve. McQuarrie
(1954) fitted the previously published data for alumina to
an empirical equation. The experimental data depart from the
reciprocal temperature law at higher temperatures, believed to
result from increased passage of radiant energy. Jamieson and
Lawson (1958) fitted the data by an equation which was exponen-
tial in reciprocal temperature, and ascribed the deviations
to the flow of excitons. Excitons are electron-hole pairs of
insufficient energy to allow the electrons to leave, but which
can transfer energy from point to point. Whitmore (1960)
concluded that phonon electronic heat transfer, as well as
transport by electron-hole pairs, excitons, and dissociated
gas molecules contribute to the heat flow, and estimated the
possible magnitude of these effects. R. E. Taylor (1962)
found that beryllia follows exactly the reciprocal temperature
relation to 1700°C. At this point several competing phenomena
occur. These include grain growth and the approach of the mean
free path to interatomic distances.

Francl and Kingery measured the influence of porosity
on thermal conductivity. It was well known that at low
temperatures pores have a lower conductivity than any solid
phase. At temperatures below 500°C, the conductivity of a
sample with isolated pores in any given direction k_p was found
to be approximately equal to the solid structure conductivity
k_s $(1-P_c)$, in which P_c is the cross-sectional pore fraction.
At higher temperatures, the pore size and emissivity become
significant. The effect of isometric approximately spherical
pores was quite different from that of anisometric cylindrical
pores. Pore orientation was found to affect the thermal
conductivity remarkably. The "structure factor" for porous
bodies varies from infinity for parallel orientation to zero
for series orientation in the direction of heat flow (Torkar).
Convection becomes important when the pores are larger than
several millimeters (Kingery). Kingery, Francl, Coble, and
Vasilos applied a correction factor on this basis to obtain
thermal conductivity at zero porosity. Schwiete, Granitzki,

and Karsh found that the rate of decrease in thermal conductivity was highest below 800°C. Charvat and Kingery found that the conductivity of polycrystalline alumina rods (9 and 12 micron average crystal size, data corrected to zero porosity) is the same as that of monocrystal sapphire at temperatures below 300°C, at which point radiant heat transfer begins. At 1000°C, the value for sapphire was about 0.018 cal sec^{-1} cm^{-1} °C^{-1}, and for polycrystalline alumina about 0.008 cal sec^{-1} cm^{-1} °C^{-1}. Tinklepaugh, Truesdale, Swica, and Hoskyns (1961) found that the thermal conductivity of sintered alumina decreased slightly but significantly as the average grain size was decreased from 10 to 4 to 2 microns, in the temperature range from 100 to 1000°C. Francis, McNamara, and Tinklepaugh determined the thermal conductivity between 200 and 700°C of a commercial high-purity sintered alumina (Wesgo Al-300, 97.6% Al_2O_3, density 3.68 g/ml). Members of the Alumina Ceramic Manufacturers Association furnish values for thermal conductivity of their high-alumina ceramics.

Cowling, Elliott, and Hale (1954) concluded from a large number of production control tests that there was a relationship between bulk density and thermal conductivity of specific types of refractory insulating bricks that was sufficiently accurate for appraising thermal conductivity for most practical purposes. Lasch observed an increase in thermal conductivity of firebrick containing up to 50% added corundum. Brick with high corundum content (80%) showed a comparatively rapid decrease in conductivity with increasing temperature.

Ruh and McDowell determined the thermal conductivity of many types of refractory brick, including high-alumina types, using apparatus modified from the ASTM C201-49 specifications. The measurements covered mean specimen temperatures from about 90 to 1090°C. The apparent porosities of the specimens varied from about 16 to 23.5%. The thermal conductivities increased with increasing alumina content from about 0.0034 cal/sec cm °C at 150°C mean temperature for 60% Al_2O_3 to about 0.0137 cal/sec cm °C at 150°C mean temperature for 99% Al_2O_3. At a mean temperature of 1100°C, the values were 0.0034 cal/sec cm °C and 0.0060 cal/sec cm °C, respectively.

Hansen and Livovich investigated the thermal conductivity of both insulating and dense refractory cement (Lumnite) concretes. The data for the concretes generally were in good agreement with a curve establishing a relationship between thermal conductivity and bulk density. Some deviation in excess

of 5% in the direction of higher conductivity apparently indicated larger than average pore size. Well dispersed pores provide better insulation than the same quantity in a poorly dispersed condition. Ruh and Renkey also determined the thermal conductivity of refractory castables of both dense fireclay and high-alumina types, as well as of several insulating castables. These tests, covering mean specimen temperatures of about 90 to 1090°C, indicated that the thermal conductivity of a castable material varies with its thermal history. Castables merely dried at 110°C and retaining their constitutional water have high initial thermal conductivities, but when the combined water was driven off between 200 and 800°C, usually associated with loss of strength, the thermal conductivity was also lowered. As the temperature was further raised beyond 1100°C, the formation of a ceramic bond caused an increase in the thermal conductivity. In actual castables in service, these effects take place in layers that merge into each other.

6-5   THERMAL DIFFUSIVITY

Thermal diffusivity is defined as the ratio of thermal conductivity to the product of specific heat and density. The measurement in the CGS system is in cm^2/sec. Thermal conductivity is important in those cases which involve steady-state conditions. Diffusivity is of more significance in those cases where transient heat flow is important, as in spalling of refractories. Thermal diffusivity is also of more fundamental significance with reference to phonon scattering because the mean free path of the scattered phonons is more directly related to diffusivity. Diffusivity methods which have been used are the periodic heat flow methods, Biot's modulus method, the radial flow method, and the infinite solid method (Plummer, Campbell, and Comstock).

Fitzsimmons (1950) determined the diffusivity of alumina at 400 to 700°C. Paladino, Swarts, and Crandall covered the range 1500 to 1800°C, and Plummer, Campbell, and Comstock the range from room temperature to 1000°C. Rudkin, Parker, and Jenkins (1963) have reported high-temperature measurements. The values vary from about 0.091 cm^2/sec at 25°C to 0.0063 at 1500°C, and 0.0294 at 1800°C.

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7 SONIC EFFECTS IN ALUMINA

7-1 VELOCITY OF SOUND IN ALUMINA

The longitudinal velocity of sound in solids is related to Young's modulus of elasticity (E) and the density (d) by Newton's equation, $V = \sqrt{E/d}$. This elastic modulus is specifically defined for slender rods whose lateral dimensions change according to Poisson's ratio (μ) when a longitudinal stress is applied. According to Hueter and Bolt, Sonics, page 25, the velocity of sound in solids varies, dependent on the degree of constraint of the lateral dimensions. For an infinite solid body in which the lateral dimensions are constrained by stiffness, the stiffness (or bulk) modulus (E_b) is higher than E, from theoretical considerations, by an amount determined by $E/E_b = 1-b$, in which $b = 2\mu^2/(1-\mu)$. For sintered alumina of theoretical density, μ may be assumed to be 0.257, d 3.987, and E 58.5 X 10^6 psi. On these assumptions, the calculated velocity of sound (V) in unconstrained aluminum oxide is about 33,000 ft/sec, and the bulk velocity (V_b) is about 36,300 ft/sec. The velocity in thin plates (V_p) is about 34,100 ft/sec, derived from the expression,

$$V_p = V \sqrt{1/(1-\mu^2)}.$$

In a reversal of the preceding methods, the velocity of sound is measured in order to determine the modulus of elasticity. Young's modulus is also determined by measurement of the fundamental resonant frequency of the sound waves generated in a bar of suitable geometry. This also involves the speed of sound in conformity with the expression, $N = (m^2 k/2\pi L^2 \sqrt{E/d}$, in which E = Young's modulus, d = density, k = radius of gyration, L = bar length, and m is a constant representing the mode of vibration (Powers, 1938). As the frequency increases, and the wavelength of the sound diminishes to about twice the diameter of the rod, the dominant wave form changes from longitudinal to transverse (shear). The shear velocity (V_s) = $V \sqrt{1/2(1+\mu)} = \sqrt{E_s/d}$, in which E_s is the shear modulus of elasticity. For alumina, V_s is about 20,800 ft/sec.

7-2 ULTRASONIC ABSORPTION

Ultrasound can be applied to the study of dislocations, internal friction, stress effects, relaxation, fatigue, and superconductivity of solids (Redwood, 1959).

The attenuation of sound (acoustical damping) in solids depends on imperfections which cause scattering. In crystalline materials, foreign impurities occur in the lattice as a substitute

for the solvent, or in interstitial positions. A small number
of foreign atoms markedly affects the physical properties. Two
kinds of single point defect structure represent atoms out of
normal position, that have moved to the surface (Schottky) or into
an interstitial position (Frenkel). Line defects (dislocations),
hysteresis, and relaxation also contribute to ultrasonic attenua-
tion (Hutchison, 1960). The relaxation process involves a
characteristic rate.

Sligh and Bixby observed that the ultrasonic energy absorbed
is converted to heat. Solid particles acquire high velocity and
acceleration, cavitation occurs in liquids. These effects have
been applied to ceramic processes to obtain improved dispersion
of slips, to provide heat during the application of glazes, to
cut and drill hard ceramics, and to detect flaws in heat-fused
ware, among others (Dickinson, Gibbs).

Fitzgerald, Chick, and Truell found that the ultrasonic
attenuation for ruby was higher than for sapphire in the low-
temperature region, conforming with the prediction from the
corresponding effect of impurities on the thermal phonon re-
laxation time. Ciccarello and Dransfield found, contrary to
some theoretical expectations, that the absorption of longitu-
dinal waves in the low-temperature region was stronger than that
of transverse waves. This was ascribed to 3-phonon processes.

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8 ELECTRICAL PROPERTIES OF ALUMINA

8-1 ALUMINA INSULATOR TYPES

The first major commercial application of polycrystalline alumina was electrical insulators for spark plugs. H. Gerdian and R. Reichmann (1927) developed an early electrical insulation composition which was substantially pure alumina. Because of the poor forming properties of the alumina, except by slip casting, and the high firing temperature required, it was expedient to resort to the addition of fluxes in the early commercial spark plug operations. These compositions contained from 10 to 20% vitreous components, although compositions containing from 95 to 97% Al_2O_3 had been developed which could be fired at feasible temperatures between 1620 and 1700°C.

The spark plug manufacturers became interested in the electrical conductivity, or its inverse the electrical resistivity, at elevated temperatures. A common criterion in appraising the insulating value is the determination of T_e, a designation for the temperature at which the resistance of a one-centimeter cube falls to one megohm. Other electrical measurements of significance mainly in high frequency applications include the determination of the dielectric constant, the power factor, the loss factor, and the dielectric strength or breakdown voltage.

Electrical compositions containing as little as 23% added Bayer alumina, present substantially as undissolved aluminum oxide particles in a glassy matrix, have been investigated (Austin, Schofield, and Haldy). When substituted for the usual flint additions in standard dry-process compositions, the alumina provided certain advantages that could not be ascribed merely to its finely divided condition. Although increasing amounts of alumina tended to increase the over-all thermal expansion (30 to 1000°C), evidence of the alpha-to-beta quartz inversion in the thermal-expansion curve decreased with increasing alumina content. The inversion was not evident beyond 20% alumina addition, even though the raw body still contained a relatively large amount of potter's flint, thus allowing more rapid firing schedules. The use of alumina lengthens the firing range because the glass phase is stiffer at a given temperature than in a conventional body. The tendency for pyroplastic flow is decreased decidedly, but not necessarily the warpage. Translucency is reduced, which is to be expected, because of the fine particle size and high index of refraction of the alumina. Strength was increased as much as 200% when 40% alumina was added. Modulus of rupture above 22,000 psi was obtained, in comparison with about 4000 psi for unglazed, dry-pressed ware, or 12,000 psi for unglazed extruded ware of the common feldspathic types. Zircon

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porcelains range in flexural strength from 10,000 to 20,000 psi. It was particularly advantageous on strength to substitute alumina completely for flint, and nepheline syenite for feldspar, in order to remove as completely as possible sources of free quartz. Selsing claimed strengths of 26,000 psi in flexure for such bodies containing in excess of one percent quartz to which a flux is added containing sufficient sodium silicates ($Na_2O:SiO_2$ at least 1:10) to reduce the quartz content on firing to no more than one percent.

Blodgett (1961) prepared high-strength alumina porcelains (average flexural strength 31,000 psi) using 65% Alumina A-2, minus 325 mesh, 10% nepheline syenite, 2% each of lithium manganite and whiting, and 21% ball clay. A significant factor was the wet grinding of all components together for 14 hours. This is presently not a conventional practice in preparing electrical porcelains. Commercial porcelains are prepared for forming by blunging the ingredients in water suspension and by screening out the coarse oversize, including organic carbonaceous material.

All bodies containing from 20 to 60% Bayer alumina can be fired similarly to cone-12, feldspathic, electrical porcelains. Dielectric strengths are as high as 300 volts/mil, and the power factor is approximately 0.01 to 0.03 at 60 cycles, and 0.001 to 0.002 at 1 megacycle.

Haldy, Schofield, and Sullivan investigated high-alumina porcelains in the concentration range from about 80 to 99% Al_2O_3. The flux consisted of 2.5 parts dolomite, 2.5 parts flint, and 15.0 parts kaolin clay. The specimens were dry-pressed at 7500 to 10,000 psi. The maturing temperature applied to obtain apparent porosity of not over 0.1%, varied from 1540°C for the 80% Al_2O_3 compositions to 1810°C for the 99.0% Al_2O_3 compositions. Flexural strengths ranged from 30,000 to 40,000 psi. The room-temperature resistivities, measured with a capacitance bridge, were as high as 10^{17} ohm-cm. The T_e values were affected by the residual soda contents in the alumina, being higher with decreasing alkali. The power and loss factors were quite low, falling in the classification grade of excellent insulators for radio and other communication equipment. The dielectric constant, calculated from capacitance measurements, increased with increasing alumina content of the specimens.

Kato and Okuda (1960, 1962) discussed the physical properties of alumina porcelains prepared from three different alumina sources, namely, calcined ammonium alum, Bayer process, and electrically fused alumina fines. When using 2% MnO_2 and TiO_2 as additives, the microscopic examination of specimens fired above 1400°C revealed a mosaic structure for the calcined alum and the fused alumina, but an intergranular structure for the Bayer alumina. The effects of the addition of 2 to 5% (wt) of various

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oxides including MgO, Co_3O_4, Fe_2O_3, Cr_2O_3, TiO_2, or MnO_2 were investigated. The electrical properties of specimens containing MnO_2, such as insulating resistance and dielectric loss at 1 megacycle, were superior to those of the others (see Luks, 1942). The electrical properties were poor for specimens containing Fe_2O_3 or TiO_2, and intermediate for those with MgO or Co_3O_4.

Most commercial electrical insulator compositions in the high-alumina class have been based on the use of Bayer process alumina of reduced alkalinity (below 0.2% Na_2O). The compositions may contain from 80 to 95% aluminum oxide. Aluminum silicates and alkaline earth oxides usually comprise the major portion of the remaining constituent but many metal oxides have been claimed to provide additional favorable improvements in the properties. A competent review of the electrical insula-tion compositions would embrace a majority of all spark plug compositional patents which have issued since 1929. This is considered more fully in the section on electrical applications (Section 19).

8-2 ELECTRICAL CONDUCTIVITY OF ALUMINA

Many investigators have determined the variation in elec-trical conductivity and other electrical properties of alumina with change in temperature, both on single-crystal and polycrys-talline specimens. Some data on the electrical properties of pure alumina and commercial compositions are shown in Table 11.

Cited among the contributors to the literature on the electrical conductivity of single-crystal and polycrystalline alumina are: Diepschlag and Wulfestieg; Wartenberg and Prophet; Podszus; Backhaus; Rochow; Shul'man; Rögener; Arizumi and Tani; Oreshkin; and Pentecost, Davies, and Ritt. Doelter (1910) classed corundum as an insulator at ordinary temperatures, and an electrolytic conductor at higher temperatures, showing notice-able polarization. Later investigations, even to the present time, have been undertaken with marked variations in purity, porosity, thermal history, ambient conditions during test (air, gases, vacuum), contacts to the test specimens, and test methods (both ac and dc). It is therefore quite understandable why the data of different investigators show a divergency as great as six orders of magnitude for both single-crystal and polycrystal-line alpha aluminum oxide (Figure 13).

The conductivity in mhos is the reciprocal of the bulk
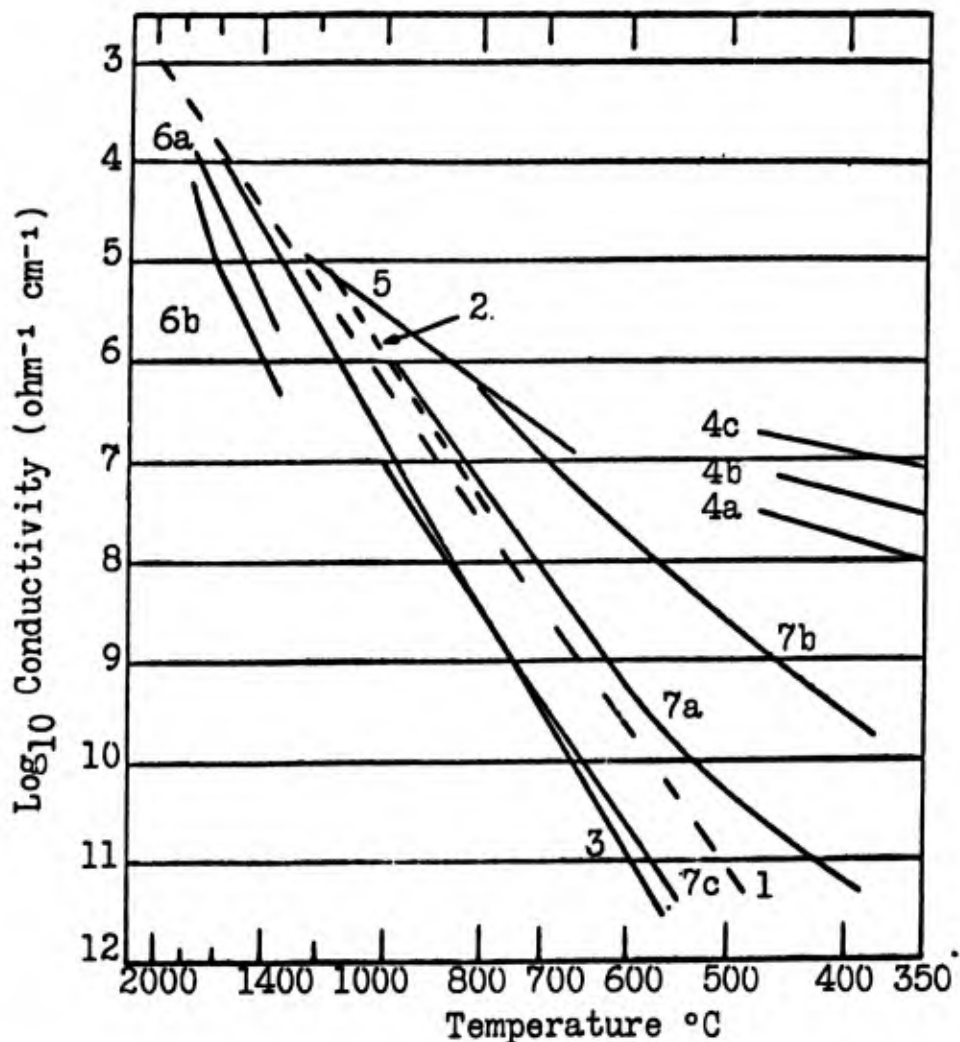
Figure 13. Electrical Conductivity of Alpha Alumina

Variation in electrical conductivity with temperature. Solid lines represent polycrystalline alumina, dotted lines single-crystal sapphire; (1) Linde Air Products; (2) Wachtman and Maxwell (1957), annealed at 1800°C for 4 hours, tested in air; (3) Heldt and Haase (1954), vacuum sintered 99.97% Al_2O_3, tested in vacuum; (4) Hartmann (1936) a, b, c, repeated tests in vacuum at increasing conductivity, 4c represents equilibrium; (5) Hensler and Henry (1953), porosity 27%, acid treated specimens, ac test in air; (6) Pappis and Kingery (1961), isostatic-molded Linde powder, sintered at 1900°C for 7 hours to 3% porosity, a in oxygen at one atm., b in oxygen at 10^{-5} atm.; (7a) Coors Porcelain Company, AD-995, (7b) Coors Porcelain Company, AD-85, (7c) Coors AD-99C.

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resistivity. When the logarithm of electrical conductivity is plotted vs. the reciprocal of the absolute temperature, a straight line is generally obtained, the slope of which is proportional to the activation energy. A substantial amount of data has been found to obey an expression having the form:

$\theta = Ae^{-E/kT}$, in which θ is the conductivity, A is a constant, k is the Boltzmann constant, T is the absolute temperature, and E is the activation energy. Ford and White summarized the fundamental knowledge relating to ionic conductors in 1952. Cohen reviewed the literature on conductivity in 1959. Florio (1960), and Pappis and Kingery (1961) also reviewed the temperature dependence of the results of conductivity of earlier investigators.

At room temperature the conductivity of alumina is extremely low, around 10^{-17} mhos. In common with other insulators, the conductivity increases with increasing temperature. At high temperatures the insulator acquires the characteristics of a semiconductor. Shul'man (1940) noted a break in the conductivity curve between 1200 and 1500°C, and stated that it was not caused by structural changes, but was a real change in conductivity. The reported activation energies vary from about 0.250 ev to above 5 ev, but are generally close to 2.8 ev. Cohen concluded, from the point of view of electrical conduction, that the distinction between an insulator and a semiconductor may be considered one of degree rather than of kind. There is no abrupt change in resistivity to separate the two classes.

Hartmann in 1936 had observed that the electrical resistance of sintered alumina at high temperatures increases with increasing oxygen in the atmosphere, and had concluded that conduction is an oxidation process. Heldt and Haase (1954) measured the electrical resistance in vacuum of very pure alumina (less than 0.03% total impurities) that had been sintered in vacuum, and compared the results with similar measurements made on less pure specimens (about 0.06% impurities) that had been sintered in a gas furnace. The "pure" material had a linear curve with an activation energy of 2.50 ev. The less pure specimens yielded curves which exhibited a break at about 1100°C. Below 1100°C the activation energy was 2.38 ev; above 1100°C it was 2.5 ev. The conductivity above 1100°C was designated intrinsic to imply real semiconduction substantially by electron transfer and mechanisms associated with the pure oxide. Extrinsic conduction, largely impurity-controlled, was believed to occur below 1100°C.

Heldt and Haase also investigated the effect of air and vacuum on resistance. When the alumina was removed from the vacuum and aged in air the resistance decreased, being the lowest for high humidity. At room temperature, the resistance in air was 10^9 ohms, at 10^{-1} mm Hg 10^{12} ohms, and in vacuum, following heating at 1500°C and cooling to room temperature, 10^{14} ohms.

Pappis and Kingery measured the electrical conductivity of both polycrystalline and single-crystal aluminum oxide at 1300 to 1750°C, and at oxygen partial pressures of 10^0 to 10^{-10} atmospheres. At 10^0 atmosphere the activation energy was 2.97 ev, and the conductivity was p-type; at 10^{-5} atmosphere the activation energy was 2.62 ev below 1627°C and 5.5 ev above, with intermediate-type conductivity; and at 10^{-10} atmosphere the activation energy was 2.84 ev below 1627°C and 5.8 ev above, and the conductivity was n-type. They concluded that the conductivity of alpha aluminum oxide does not result from any single simple process over wide ranges of temperature and oxygen partial pressure. The increase in conductivity at high and low oxygen pressures indicated that alumina is a nonstoichiometric semiconductor. Kroger and Vink suggested possible structures by which changes in the conductivity can be interpreted. These are limited, since interstitial anions are unlikely in alumina.

Vest studied the transport mechanism by electrons and ions in various oxide compositions including $Cr_2O_3-Al_2O_3$. He concluded that because the bonding in metal oxides is partially ionic, there is always an ionic component of the total measured conductivity. Hensler and Henry measured the influence of controlled additions of small amounts of Cr_2O_3 on the electrical resistance of polycrystalline alumina, measured in air. The specimens were dry-pressed, 0.4 cm-thick disks fired at 1500°C for 10 hours. X-ray patterns showed the Cr_2O_3 to be in complete solid solution. With additions to about 6% Cr_2O_3, the log resistivity vs. reciprocal temperature curves behaved similarly to that of the pure alumina, being approximately linear and having about the same slope. The calculated activation energy was about 1.0 ev. Specimens containing up to 6% Cr_2O_3 had higher resistivities than the pure alumina, with a maximum at about 1%. Another peak resistivity occurred at 92% Cr_2O_3. Chiochetti and Henry found that the electrical resistance of commercial refractory brick (alumina-silica mixtures, fireclay brick, high-alumina brick, mullite-type brick, and fused-cast brick containing some chromite) are similarly straight line curves. Fused-cast alumina containing mixtures of alpha and beta aluminas exhibits a different type of curve.

Barta, Bartuska et al. investigated the influence of purity and crystal size on the specific resistance in the range 400 to 700°C. Alkalies decreased the specific resistance considerably, but small quantities of SiO_2, CaO, TiO_2, Fe_2O_3, V_2O_5, or Cr_2O_3 had no significant effect. MnO and calcium compounds increased the specific resistance. Fine-grained sinters had a higher resistivity than coarse-grained sinters.

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Yamauchi and Kondo (1950) investigated the effects of several mineralizers on sintered alumina disks that had been fired at 1550 to 1700°C. Pure sintered alumina had greater resistance to dc at high temperatures than other ceramics. The electrical conductivity was claimed to result from the alkali present in the vitreous component. Iron oxide also decreased the electrical conductivity, while lime and silica increased it and decreased its temperature coefficient.

Starokadomskaya et al. appraised the electroconductivity of alundum, 90% Al_2O_3-10% BeO, and Al_2O_3 plus 1% Cr_2O_3 as materials for thermocathode preheaters at working temperatures of 1600 to 1800°C. All specimens behaved as semiconductors, with changes in the type of conductivity indicated at 1200 to 1400°C. The sharp increase in conductivity begins at much lower temperatures for the mixtures than for the pure substances. Calcination in vacuum decreased both the conductivity and the scatter in the measurements.

Budnikov and Tresvyatskii found that corundum refractories prepared with 2.5% clay bond reduced the electrical resistivity to one-tenth that of shapes without clay. Further addition to 20% dropped the resistance only to 0.4. The resistivity depends very little on composition for a clay content of 20 to 50%. Eremenko and Beinish correlated the electrical conductivity of binary refractory oxides with their chemical analysis. Garn and Flaschen applied electrical conductivity to the detection of phase transformations.

Schwab (1962) investigated the semiconductor properties of aluminum oxide from the standpoint of its use as a catalyst in gas reactions. The conductivities of both alpha and gamma aluminas increased with doping with any foreign cations. These properties were not affected markedly by oxygen. Both p- and n-doped oxide rectification was obtained, suggesting that both alumina phases are intrinsic semiconductors.

Reported values for the electroconductivity of single-crystal alumina are about in the same range as that for polycrystalline alumina. Rochow (1938) measured the dc conductivity of sapphire from 600° to 1200°C, and obtained an activation energy of 1.8 ev. Wachtman and Maxwell (1954, 1957) determined the effect of plastic deformation on the electroconductivity of Linde sapphires and found that deformation increased the resistivity. The activation energy for the undeformed portion was 1.5 ev and for the deformed portion 2.7 ev. The resistivity curves (extrapolated) crossed at about 1800°C. Annealing the deformed specimens at 1600°C did not affect the conductivity significantly, but annealing at 1800° reduced the resistivity even lower than the original curve. This is interpreted to indicate that resistivity in the original crystal caused by strain and subsequent resistivity caused by work-hardening of plastic deformation is eliminated at high temperature. Linde Air Products Company obtained the same activation energy

(about 1.5 ev) as for the unannealed sapphire.

Tucker and Gibbs observed a narrow peak in the conduction current of sapphire at about 250°C, and exponentially decaying pulses of about 10^9 electrons at 400 to 550°C, when the sapphire was exposed to water-saturated nitrogen. Both the peak and pulses were absent on cooling from 1000°C, or on reheating in dry nitrogen. Similar impurity effects at different temperatures were observed for HCl, NaCl, and $Mg(NO_3)_2$. The Verneuil-type crystals normally contain about 10^6 dislocations/cm^2, as indicated by etch-pit studies. Bending through a radius of about one centimeter introduces about 2×10^7 dislocations in the (0001) slip plane, the length of which lie parallel to the axis of bending. Gibbs (1959) concluded that the impurities penetrate into the body of sapphire along dislocation lines. This provides high-conductivity "tubes" which surround the dislocation lines. The high-conductivity regions also cause dielectric-loss peaks, but these can be eliminated by heating to volatilize the impurity atoms.

Harrop and Creamer (1963) found an activation energy of 4.64 ev in the range 1280 to 1480°C for the low-voltage, dc conductivity of sapphire. When chromium was present as an impurity, the conductivity was lower and the activation energy was 4.26 ev. They concluded that the charge carriers were p-type, in agreement with earlier investigators, but ascribed the conductivity mechanism to impurity effects, specifically traces of iron, rather than to intrinsic behavior, as suggested by Pappis and Kingery.

Champion (1964) continued the investigation of the conductivity of alumina containing chromia in air at 20 to 850°C by a 2-terminal dc method. When first heated, all specimens showed peaks and pulses in conduction current similar to those described by Tucker and Gibbs for clear sapphire. After several heating cycles, the variation of conductivity with temperature became reproducible. The activation energy averaged 0.5 ev at 200 to 450°C, and 1.7 ev at 450 to 850°C. Conductivities of 1×10^{-9} ohm^{-1} - cm^{-1} for clear sapphire and of 2×10^{-10} ohm^{-1} - cm^{-1} for pink ruby were compatible with the values obtained by Harrop and Creamer, but their suggestion that trace impurities of iron control the conductivity was not confirmed.

Chang (1963) found that electrical resistivity decreases initially during transient creep. During steady-state creep at 1525°C and a pressure of 2175 psi, the resistivity increased almost linearly with strain. This was ascribed to the creation of carrier-trapping point defects in the wake of moving dislocations.

The current-voltage characteristics of very thin barrier layers (20 to 40 Å thick) of aluminum oxide between aluminum electrodes was investigated by Nakai and Miyazaki. Conduction results from a quantum-mechanics tunneling effect. The tunneling current at constant applied voltage increases with increasing temperature.

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Peters determined the electrical conductivity through junctions in single-crystal sapphire formed by sintering together two single crystals with a 50% $CaCO_3$-50% SiO_2 bond at 1750°C in air. A large barrier to current flow was found to exist across the junction. Peters suggested several mechanisms for the junction barrier including: (1) differences in work functions between the sintered layer and the sapphire, (2) diffusional effects, and (3) a difference in the type of charge carrier between the junction region and the sapphire region.

Matiasovsky et al. (1964) found that the specific conductivities of cryolite and of melts in related systems decreases with increasing concentration of dissolved alumina in the melt. The addition of sodium chloride increases the specific conductivity of cryolite and of the system $Na_2AlF_6 \cdot Al_2O_3$ also. The influence of the sodium chloride is most pronounced at low concentrations of NaCl and at higher concentrations of Al_2O_3.

8-3 DIELECTRIC CONSTANT AND LOSS FACTOR OF ALUMINA

The dielectric constant (k) or relative permittivity of crystalline insulator materials is characterized by a combination of electronic, ionic, and dipole orientations that cause polarization of the insulator in electrical fields. For an alternating field, polarization shows as a phase retardation of the charging current. The complex dielectric constant, $k = k' - ik''$, in which k' is the relative dielectric constant, i is the imaginary, $\sqrt{-1}$, and k'' is the loss factor. If θ is the dielectric phase angle, 90-θ is the dielectric loss angle (δ); tan δ is the dissipation factor (D); and k' tan δ is called the dielectric loss factor (k''). The rate of dissipation of electrical energy lost as heat is proportional to the ac conductivity (σ); $\sigma = fk''/1.8 \times 10^{12}$, in which f is the frequency.

In the optical frequency range, electronic orientations are present. The relative dielectric constant $k'_\theta = \eta^2$, in which η is the index of refraction (Maxwell). The value is about one-third the measured value. A common method for measuring the dielectric constant is by substitution of a specific geometrical form in a capacitance bridge circuit.

The dielectric constant and the dielectric loss factor are of significance in alumina ceramics applied principally in frequency applications, as for example, capacitor and electronic insulating elements, and transparent radar windows.

Glemser (1939) determined the dielectric constants of several hydrated aluminas by an immersion method. The values ranged from 20.6 for amorphous alumina hydrate (49.6% ignition loss) as well as for alpha monohydrate (17.4% ignition loss), to 9.4 for beta trihydrate, and 8.7 for alpha trihydrate. On heating, the values either decreased or increased in the direction of 12.3, the value

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found by Glemser for either native or artificial corundum (Table 11).

Ebert (1962) examined the dielectric loss of gamma alumina containing sufficient water of hydration corresponding to a bi-molecular layer at temperatures from -60 to +60°C and at 100 kcps to 10 Mcps. Several sharp maxima, traceable to resonance, were observed in the curves of tan δ vs. frequency. The dielectric constant vs. temperature curves agreed with calculations made by modifications of the Debye relaxation equations. Dekker and van Geel found no difference in dielectric constant of the amorphous and crystalline layers formed by anodic oxidation of aluminum.

Bogoroditskii and Polyakova based the low dielectric losses for corundum on the polarization effects being ionic and electronic. Variations in dielectric properties were attributed mainly to the formation of beta alumina, in which structural polarizations are marked because of the open crystal lattice. Calcination under reducing conditions was thought to convert the beta alumina to alpha alumina, possibly by favoring the volatilization of contained soda. Bogoroditskii and Fridberg ascribed large dielectric losses in alumina insulators at temperatures below 200°C to moisture retention in submicroscopic pores.

Bowie (1957) described apparatus for measuring the dielectric constant and dielectric losses at 3000 Mc/sec and at temperatures to about 1600°C. The average dielectric constants for several commercial, nominally 95% Al_2O_3 bodies in the temperature range, 250 to 850°C, were found to be between 8.4 and 8.9.

Cohen (1959) had indicated the presence of a high-resistance transition layer at the dielectric-electrode interface on sapphire as a complicating factor in bridge methods for determining the value.

According to von Hippel (1958) the dielectric constant of pure sapphire at 25°C is 9.34 perpendicular to the optic axis, and 11.55 parallel to this axis. It increases slowly with temperature to about 10.40 perpendicular to the optic axis and 13.50 parallel to it at 800°C. It is substantially independent of frequency to about 500°C, but slight increases in value are observed at frequencies below 10^4 cps. The dielectric loss tangent (dissipation factor) showed no particular trend with orientation. The values were very low, being of the order of 0.00001 at 25°C. The loss was both frequency- and temperature-dependent, generally decreasing with increasing frequency, and increasing temperature to a value as high as 0.23 for 100 cps at 600°C. The dielectric constant of dense, polycrystalline alumina (99.9% Al_2O_3) fell intermediate between the values for the two orientations of sapphire. Relatively high values for both the dielectric constant and the loss tangent were obtained at temperatures above 300°C, and at frequency 10^3 cps. Differences in the value of the dielectric constant were obtained for differences in orientation of the test specimen with respect

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Table 11
Electrical Properties of Alumina

Resistivity (ohm-cm)

% Al₂O₃	Single-Crystal +99.5%	Polycrystalline 99.97%	99.0%	99.5%	94%	85%
Ref.	(1)	(2)	(3a)	(3b)	(3c)	(3d)
Temp °C						
200				2.0×10^{12}	1.0×10^{15}	4.0×10^{11}
400			1.0×10^{13}	1.2×10^{10}	3.0×10^{10}	3.5×10^{9}
500	1×10^{11}	1×10^{13}	6×10^{11}	1.5×10^{9}	3.0×10^{9}	4.0×10^{8}
800	-	5×10^{8}	3×10^{8}	8×10^{6}	1.0×10^{7}	1.2×10^{6}
1000	1×10^{6}	7×10^{6}	8×10^{6}	8×10^{5}	5.0×10^{5}	
1500	1×10^{4}	1×10^{4} (extrapolated)				
2000	1×10^{3}	-				

Dielectric Strength (volts/mil)

Conditions	Test Thickness	Value (v/mil)	Reference
Anodized films, tested at			
15°C	<100 A	27,500	(4)
	>100 A	15,000	(4)
-75°C, 33,000 cps	100-2000 A	34,060	(5)
27°C, 33,000 cps	100-2000 A	40,500	(5)
100°C, 133,000 cps	100-2000 A	42,100	(5)

		99.5% Al₂O₃ (3)	94% Al₂O₃ (3)	85% Al₂O₃ (3)
ASTM Method D116-63	0.250 in.	230	230	230
	0.125	330	330	330
	0.050	400	500	-
	0.025	425	550	-
	0.010	450	600	-

Dielectric Constant

Phase	Preparation	Per Cent Loss on Ignition	Dielectric Constant	Reference
Amorphous	Stock	49.6	20.6	Glemser
Alpha Trihydrate	Fricke & Wullhorst	34.6	8.7	Glemser
Beta Trihydrate	Fricke & Wullhorst	34.6	9.4	Glemser
Alpha Monohydrate	Fricke & Severin	17.4	20.5	Glemser
Amorphous	Heated 13 hr 600°C	21.4	9.3	Glemser
Amorphous	Heated 13 hr 800°C	....	9.6	Glemser
Amorphous	Heated 13 hr 1200°C	....	11.3	Glemser
Beta Trihydrate	Heated 13 hr 600°C	0.88	13.1	Glemser
Beta Trihydrate	Heated 13 hr 1000°C	....	11.8	Glemser
Alpha Monohydrate	Heated 13 hr 600°C	0.13	10.6	Glemser
Alpha Monohydrate	Heated 13 hr 800°C	....	10.0	Glemser
Alpha Monohydrate	Heated 13 hr 1000°C	....	10.0	Glemser
Alpha	Synthetic or Corundum	....	12.3	Glemser

Temp °C	Frequency cps	Sapphire ⊥	Sapphire ∥	99.9%	99% 3.83 g/ml	94% 3.62 g/ml	85% 3.42 g/ml
		Ref (7)		(7)	(3)	(3)	(3)
25	10^{3}	9.3	11.5	10.5	9.5	8.9	8.2
	10^{5}	9.3	11.5	10.5	9.5	8.9	8.2
	10^{9}				9.5	8.9	8.2
	10^{10}	9.3	11.5	9.6	9.4	8.8	8.2
300	10^{3}	9.6	12.1	21.6			
	10^{5}	9.6	12.1	11..			
	10^{9}						
	10^{10}	9.6	12.1	9.9			
500	10^{3}	9.9	12.5	59	11.3	11.8	13.9
	10^{5}	9.9	12.5	13	10.0	10.1	8.9
	10^{9}				10.0	9.2	
	10^{10}	9.9	12.5	10.1	10.0	9.1	8.3

(1) Linde Air Products
(2) Heldt & Haase (1954)
(3) Coors Porcelain Company (a,b,c,d)
(4) Lomer
(5) Kawamura & Azuma
(7) von Hippel (1958)

Table 11 Continued

Temp °C	Frequency cps	Sapphire Orientation to Optic axis ⊥ ‖	99.9%	99% 3.83 g/ml	94% 3.62 g/ml	85% 3.42 g/ml
		Ref (7)	(7)	(3)	(3)	(3)
800	10^3					
	10^5					
	10^9			10.5		
	10^{10}	10.4 13.5	-	10.4	9.4	
		60° orient. Ref. (8)				
1000	10^3	12.2		-		
	10^5	10.7		30		
1100	10^3	15.5		-		
	10^5	11.3		31		

Dielectric Loss Tangent (Dissipation Factor)

| | | Single-Crystal | | Polycrystalline | | |
| % Al_2O_3 | | Orientation Ref 7 | 99.5 | 99.0 | 94 | 85 |
Temp °C	Frequency cps	⊥ ‖	(3)	(3)	(3)	(3)
25	10^2	0.000012	-	0.0054	0.00018	0.0015
	10^6		0.0001	0.0008	0.00012	0.0009
	10^9		0.0001	0.00014	0.0008	0.0014
	10^{10}	0.00003 0.000086	0.0001	0.00019	0.0009	0.0019
500	10^3	0.005 0.0035	-	0.15	0.215	0.580
	10^6		0.0023	0.0047	0.008	0.024
	10^9		0.0002	0.0003	-	-
	10^{10}	0.00009 0.00015	0.0003	0.0002	0.002	0.003
800	10^6		-	-	-	-
	10^9		0.0003	0.0005	-	
	10^{10}	0.00043 0.00021	0.0006	0.0006	0.004	
24 X 10^{10}			0.0007	0.0003	0.006	
50 X 10^{10}			-	-	-	

Miscellaneous Electrical Properties

Secondary Electron Emission

2.5 to 3.5   (9)

Conditions: 30 to 500 microsecond pulses at 50 pulses/sec., at 500 volts; specimen 10 microns thick, spectroscopically pure

Activation Energy for Electrical Breakdown

5 ev   (10)

Single-crystal sapphire
200 to 450°C   0.5 ev   (11)
450 to 850°C   1.7 ev   (11)
1280 to 1480°C   4.64 ev   (12)
Single-crystal ruby
1280 to 1480°C   4.26 ev   (12)

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(3) Coors Porcelain Co. (a,b,c,d)
(7) von Hippel (1958)
(8) Florio (1960)

(9) Shul'man & Rosentsveig (1959)
    Shul'man, Makeslonskii, & Yaroshetskii (1953)
(10) Miyazawa & Okada
(11) Champion (1964)
(12) Harrop & Creamor (1963)

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to the forming operation, indicating an influence of preferential crystal orientation in forming.

Above 900°C, the dielectric constant is far from constant. Florio used a 3-electrode guard-ring to determine the value at 900 to 1300°C. The dielectric constant of sapphire became increasingly frequency-dependent, as was also the case for the loss factor, which decreased at a rate about proportional to 1/frequency. The dielectric constant of polycrystalline alumina containing significant amounts of impurities (0.1% Fe, 0.1% Si, 0.08% Na, 0.1% Mg, and 0.1% Ca), confirmed von Hippel's finding that the measured values become very high for low frequencies at elevated temperatures. The observed dielectric losses were ascribed to free-electron conduction mechanisms. Large thermal activation energy values suggested that the conductivity is intrinsic; the energy band gap was calculated to be about 7.3 ev. Anomalous dispersion, in which the dielectric constant decreases with increasing frequency, was encountered in the alumina insulating applications. Types of polarization which yield anomalous dispersion curves include: orientation polarization due to polar molecules, distortional polarization due to a displacement of bound ions, and interfacial or space-charge polarization produced by traveling charge carriers (Florio 1960).

Tallan, and Detwiler and Tallan observed dielectric loss maxima of clear sapphire at frequencies between 10^2 and 10^4 cps, and at temperatures between -160° and 400°C. It was observed that the loss process was more pronounced with the optic axis in the direction of the applied field than with it perpendicular to the field. With careful balancing of the bridge-guard circuit system used, no significant conduction loss was observed. They suggested that the conduction loss commonly observed in the upper part of this temperature range for unguarded sapphire samples is a surface rather than bulk effect.

Sang (1958) discussed the application of high-strength dielectric materials in different types of air-borne equipment for Mach 3 to 6 operations. Fallon (1960) described the preparation of sapphire dielectrics.

Atlas, Nagao, and Nakamura (1962) determined the dissipation factors and dielectric constants of polycrystalline alumina ceramics containing less than 100 ppm of impurities and of specimens doped with Si, Ti, Ca, Mg, Fe, and Cr ions at 25 to 875°C, and at 10^2 to 8.5×10^9 cps. Disks, 0.2 in. thick for frequency measurements to 10^7 cps and disks 0.6 in. thick for microwave determinations at 4000 Mcps were cold-pressed from calcined aluminum chloride prepared from 99.999% pure aluminum ingot. The aluminum chloride was precalcined at 1000°C (75.6 m²/g) to 1300°C (5.7 m²/g). The impurity additions in the form of oxides or carbonates were wet-milled with the alumina portions for one or more days in plastic jars. The specimens fired at 1800 to 1950°C achieved a maximum density of only 3.7 g/ml. Unresolved discrepancies in the

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analyses of the wet-ground alumina compositions were ascribed to impurities introduced during firing and to errors in the spectrographic analysis, but not to the prolonged wet grinding. Multiple regression analysis of the data obtained at 500°C and at 10^8 cps showed a linear relationship between the impurity concentration and tan δ with a correlation coefficient of 0.93. The greatest increase in tan δ was caused by Si ions, followed by Mg and Ti, and Ca. Cr and Fe had no significant effect. These effects decreased with rising frequency and became negligible in the microwave region. Activation energies of conduction for the pure and doped alumina compositions were calculated from measurements of the loss tangent at 10^5 cps and 500°C. Values between 1.2 and 1.6 ev were calculated for all compositions except the one containing Mg^{2+} ions, for which 2.0 ev was obtained. At low frequencies, an exponential rise of the dielectric constant (k') with temperature was interpreted as reflecting a like rise in the number of free charge carriers contributing to interfacial polarization. At higher frequencies, the temperature coefficient was not affected by low concentrations of impurities, but could be compensated effectively without excessive loss by additions of 10 to 20% strontium titanate. None of the data showed clear evidence of dipole rotation loss mechanism.

Ioffe et al. (1964) investigated the electrical conductivity of cerium aluminate ($CeAlO_3$) and some solid solutions based on it in weak and strong electric fields. Some specimens having anomalous dielectric properties showed hysteresis loops in which the electrical conductivity varied exponentially with the field intensity. Reversible dielectric constant was found to be independent of the intensity of the displacing field.

Smoke et al. (1962) determined the dielectric constant and loss tangent of alumina in comparison with about 30 ceramic materials over a range of frequencies from 100 to 12,000 Mc/sec and at 25 to 816°C. Basic formulas were derived for a range of low to high loss.

Variation in loss tangent with temperature of commercial alumina compositions are shown in Figure 14b. Variations in dielectric constant with frequency and temperature are shown in Figure 15.

8-4 DIELECTRIC STRENGTH

Ueda and Okada obtained 2×10^6 v/cm (5000V/mil) for the dielectric strength of alumina at 50 cps. Lomer measured the dielectric strength of anodized films on aluminum at 15°C in vacuum. The value decreased from 11 megavolts/cm for films less than 1000 Å thick to 6 megavolts/cm for films greater than 100 Å. Kawamura and Azuma measured the breakdown of thin films 100 to 2000 Å thick with a rectangular pulse of 30 microseconds. Measurements at 198, 300, and 373°K gave breakdown voltages of

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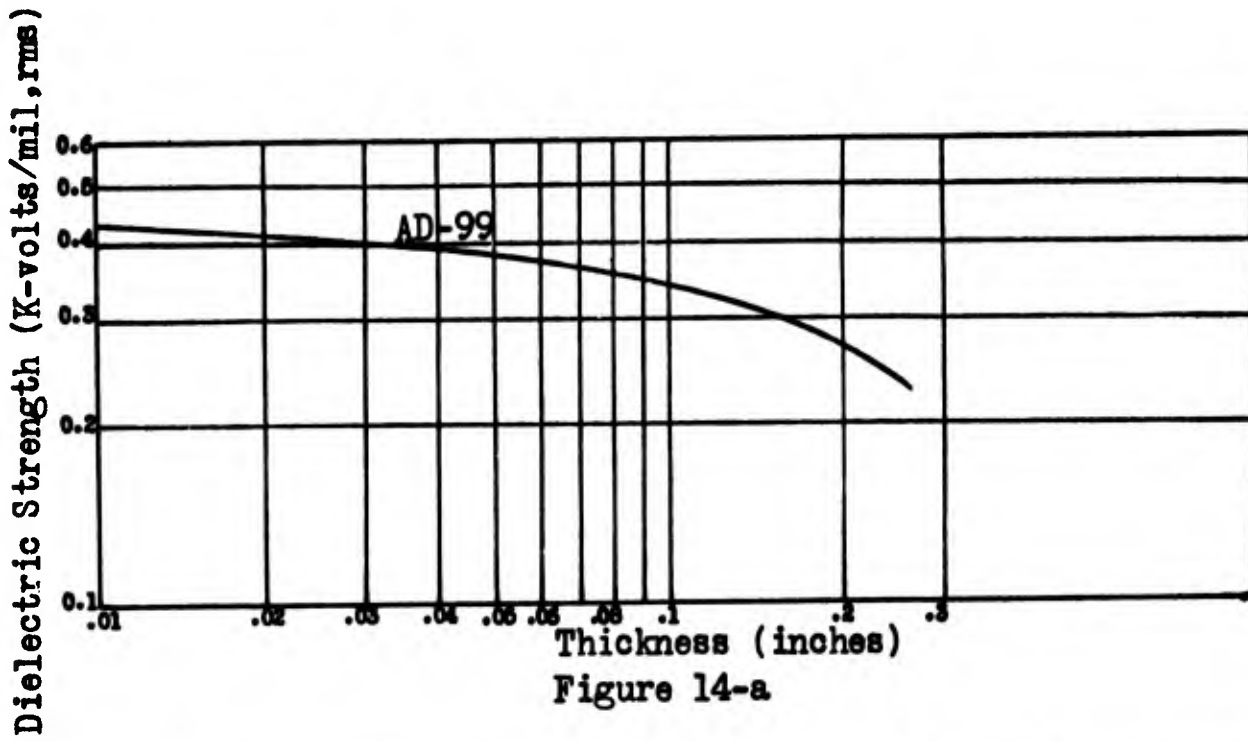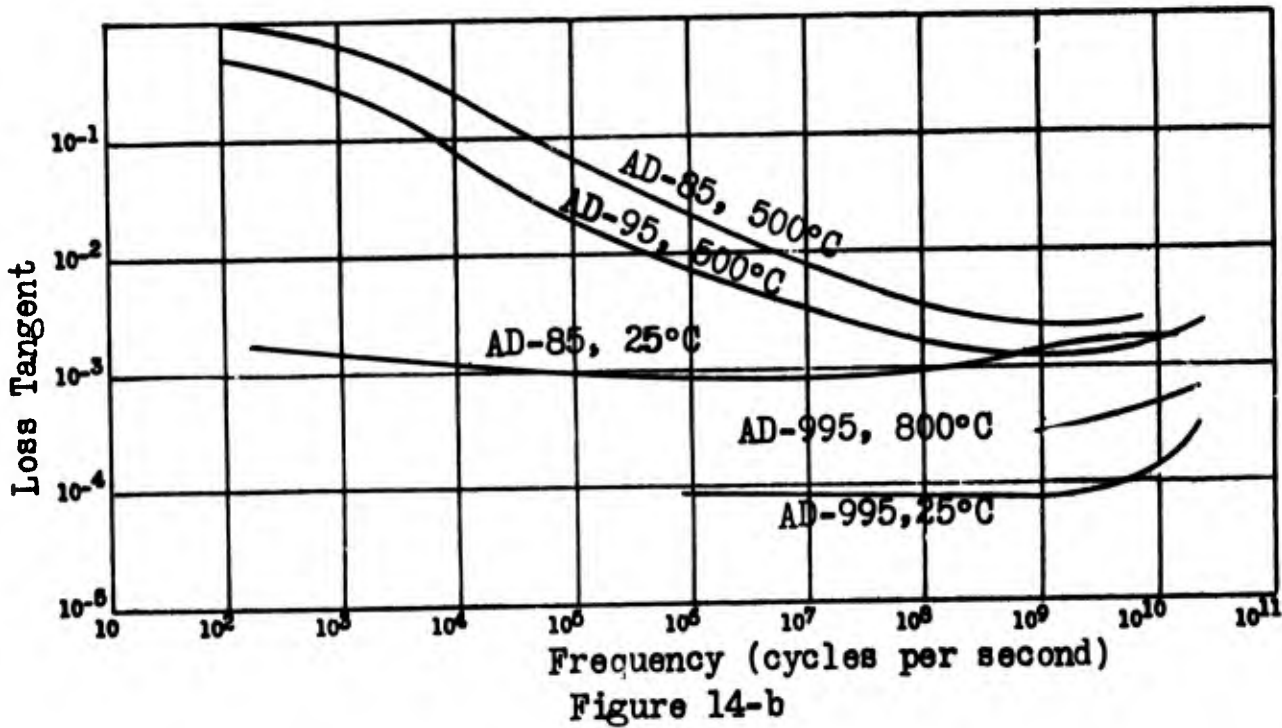
Figure 14-a

Figure 14-b

Figure 14. Dielectric Properties of Alumina

The composition number represents the nominal Al_2O_3 content.
Courtesy Coors Porcelain Company.
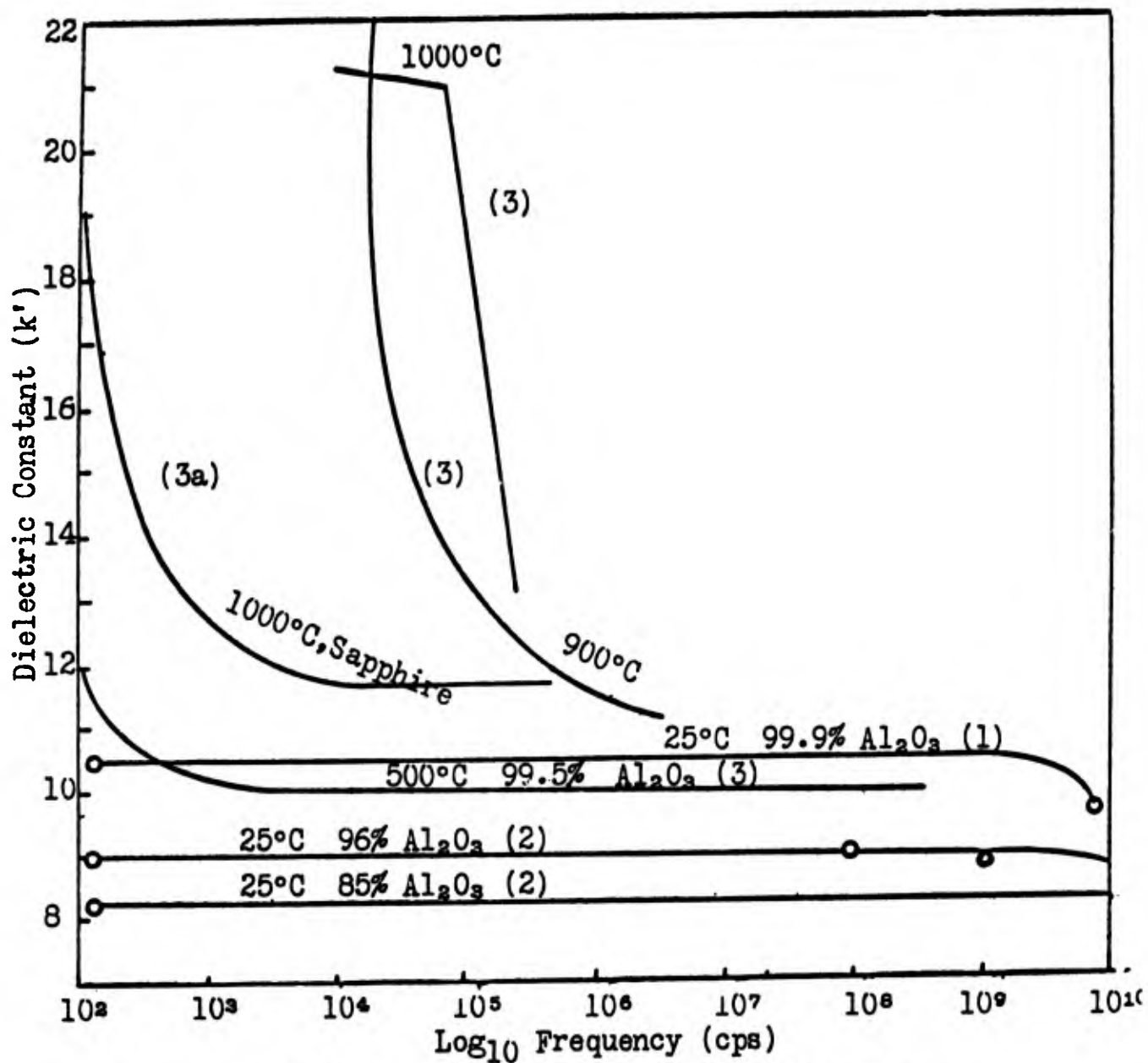
Figure 15. Dielectric Constant of Alumina

All specimens dense polycrystalline alumina except 3a, sapphire, oriented at 60° to optic axis. References: (1) von Hippel (1958); (2) Coors Porcelain; (3) Florio (1960).

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1.36 X 10⁷, 1.62 X 10⁷, and 1.85 X 10⁷ v/cm, respectively, for the three temperatures.

Kainarskii et al. (1964) observed that both the dielectric strength and the mechanical strength are affected by the microstructure of the alumina. The microstructure is determined by the sintering, which in turn depends on the mode of preparation of the alumina. An increase in the area of individual crystals to above 0.02 mm² (140 microns diameter) was found to increase the breakdown voltage from 70 kv/cm (175 v/mil) to 170 kv/cm (425 v/mil). These values appear somewhat low, but unless careful precautions are observed, values in this range are likely to be obtained at room temperature.

Commercial manufacturers of high-alumina electrical insulators obtain dielectric strength values ranging from about 200 to 600 v/mil, depending on the purity of the alumina composition and the extent of sintering. Typical data are shown in Table 11 and Figure 14a. These values are much lower than are obtained from measurements on thin films. The determination is quite sensitive to the thickness of specimen tested.

9 MAGNETIC PROPERTIES OF ALUMINA

9-1 MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility (X) is the ratio of the intensity of magnetization produced in a substance (M) to the magnetizing field intensity producing it (H). Magnetic permeability (μ) is the ratio of magnetic induction (B) to the field intensity (H), and $\mu = 1 + 4\pi X$. Substances having magnetic permeability less than that of air (about one) are said to be diamagnetic, in contrast to those having higher values, called paramagnetic. The pure alumina phases are diamagnetic. As shown in Table 12, the susceptibility is very small, less than 10^{-6}. Pascal (1924) investigated the magnetic susceptibility of the precipitated hydrous phases and their dehydrated products as a means of determining changes in the content of constitutional water. A definite correlation was found, confirmed by Zimens. The value changed from about -0.35×10^{-6} for the calcined product to -0.62×10^{-6} for aluminum hydroxide containing about 72% H_2O. The negative sign denotes the diamagnetic property. Selwood obtained substantially the same values. The method has been recommended for determining rates of hydration of various materials, as for example, of cements.

Table 12

Magnetic Properties of Alumina

Magnetic Susceptibility ($X\ 10^{-6}$)

	Pascal	Ziemens	Selwood	Rao & Leela
α-Al_2O_3 (polycrystalline)	0.35	-0.30	-0.23	
Synthetic sapphire $\perp$				-0.25
Synthetic sapphire $\|\|$				-0.21
Synthetic ruby $\perp$				+0.38
Synthetic ruby $\|\|$				+0.41
Natural ruby $\perp$				-0.20
Natural ruby $\|\|$				-0.15
γ-Al_2O_3		-0.28	-0.34	
α-$Al_2O_3 \cdot H_2O$			-0.37	
α-$Al_2O_3 \cdot 3H_2O$	-0.50		-0.43	
$Al(OH)_3$ 20% H_2O	-0.42			
$Al(OH)_3$ 71.6% H_2O	-0.62			

Rao and Leela (1952, 1953) observed a slightly lower diamagnetic susceptibility for pure synthetic sapphire in the direction of orientation parallel to the optic axis than at a

right angle to this axis. Native ruby, containing a maximum of about 0.27% Cr_2O_3, was also diamagnetic, and showed about the same disparity in effect of orientation. Synthetic ruby containing 0.82% Cr_2O_3, however, was strongly paramagnetic.

Cirilli (1950) precipitated a continuous series of mixtures of hydroxides of Al_2O_3 and Fe_2O_3, subsequently heat-treating at 600°C. The magnetic susceptibility increased to a maximum at a content of 90.4% Fe_2O_3, and then decreased abruptly for higher iron oxide contents. The γ-Fe_2O_3 alone changes to α-Fe_2O_3 at 300°C, but if it contains Al_2O_3 in intimate mixture, it changes at 550°C.

Gorter (1954) investigated the magnetization of various mixed crystal oxides, including $NiFe_2O_4$-$NiFeAlO_4$. Selwood (1956) presented information on the magnetic properties of solid solutions of Cr_2O_3 and Fe_2O_3 in alumina. Shirikov and Kirillov investigated the magnetic properties of mixtures of Al_2O_3 and NiO prepared either by repeated impregnation of gamma alumina with $Ni(NO_3)_2$ solution to different concentrations, or by grinding together NiO and Al_2O_3 pastes in HNO_3. Both series were calcined at 300, 500, and 700°C. In both cases, the susceptibility was maximum at 6 to 15 mole % NiO, and it fell off continuously up to 65 mole %.

9-2 MAGNETIC RESONANCE OF ALUMINA

Nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) have been investigated by Varian Associates Instrument Division (1961) and others. In nuclear magnetic resonance spectroscopy, isotopes of the elements can be identified by their nuclear gyromagnetic constants. Isotopes whose spins do not equal zero have a magnetic moment. The ratio of the values of magnetic moment to spin constitute the gyromagnetic ratio. In application, the specimen, immersed within a magnetic field of variable field strength, is excited by a coil in the circuit of a small radio-frequency transmitter. A second coil in a sensitive receiving circuit, having substantially zero coupling with the transmitter, receives any induced signal voltage in the specimen, and detects it on a voltmeter, an oscillograph, or a graphic recorder. A suitable system amounts to a high-resolution, crystal-controlled, fixed-frequency spectrometer.

Saito (1942, 1960) determined the NMR of bayerite and gibbsite and their dehydration processes through change in the shape of the magnetic resonance line. Both were the same. The second moment for bayerite is 13 to 14 gauss², and is independent of the dehydration temperature to 220°C. It decreases gradually to 4 to 5 gauss² at 400°C, remains constant to 550°C, and then

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gradually decreases. This agrees with the sequential phase transformations of bayerite through boehmite and eta alumina.

Osiowski thought that NMR should be particularly useful in identifying the different forms in which water can be found in cements, and for following the kinetics of cement hydration.

Pecherskaya, Kazanskii, and Voevodskii applied electron spin resonance (ESR) to alumina catalysts containing 0.3 to 11.4% (wt) Cr_2O_3. Samples of low chromium content show a second narrow line of 30 to 40 gauss width, which was attributed to a dilute 2-dimensional solution of Cr^{3+} on the surface of the alumina. Co-precipitated catalysts do not exhibit the line. The effects were similar for SiO_2-Cr_2O_3 catalysts. Hall, Leftin et al. investigated the deuterium exchange of several catalyst types on a rising temperature by NMR. The deuterium was intended to distinguish the different kinds of hydrogen held by the solids. Their data showed that the temperature region (the activation energy) for exchange increases in the order: Al_2O_3, Al_2O_3-SiO_2, SiO_2. The magnetic resonance absorption spectra from SiO_2-Al_2O_3 were indistinguishable from SiO_2, qualitatively. There was no evidence to show that any portion of the hydrogen of dehydrated SiO_2-Al_2O_3 is acidic, but possibly 20% of the total hydrogen was acidic AlOH. O'Reilly and Poole interpreted changes in intensity of the signals with metal concentration of adsorbed oxides of chromium, nickel, and cobalt in high-area alumina in terms of changes in the ^{27}Al spin-lattice relaxation times induced by the adsorbed oxides. Clusters of these metal ions on the surface of the alumina were found to be effective in removing the ^{27}Al nuclei near the surface.

Poole and Itzel (1964) investigated the ESR at 125 to 550°K of chromia-alumina mixtures that had been calcined between 500 and 1400°C. The chromic ions present in compositions of low chromia content were paramagnetic; at high-chromia contents the spectra exhibited antiferromagnetic behavior. This is a system analogous to the ferromagnetic state except that neighboring spins are antiparallel instead of parallel, that is, the substance exhibits paramagnetism (a low positive susceptibility) that varies with temperature in a manner similar to ferromagnetism, and passes through a Curie point. Sharp Néel points (magnetic transformation from this system) were obtained for Cr/Al ratios of 2/3, calcined at 1400°C. Samples with Cr/Al ratios of 1/2 gave broad Néel points, which became less well resolved with decreasing chromia content. The spectra of high Cr/Al ratio samples calcined at 900°C or lower consisted of superpositions of a paramagnetic resonance (β_w) and a fairly sharp Néel point (β_n). M. G. Townsend examined the ESR of pink single crystals of alpha alumina doped with 0.02% cobalt, grown by cooling from a PbO-PbF_2 melt. Measurements at 4.2°K with a spectrometer operating at 1-cm wavelength, and the use of phase-

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sensitive detection with 100 kc/sec modulation, indicated the presence of Co^{2+} in only one substitutional site. This is contrary to the measurements of Zverev and Prokhorov, which showed Co^{2+} in two different sites, both those normally occupied by Al^{3+} and vacant octahedral sites present in the lattice. The latter deduced that for every two Co^{2+} substituting for Al^{3+}, a third Co^{2+} was in an interstitial site. Pink crystals with localized green areas were grown by using an alumina melt doped with 0.02% cobalt and 0.02% magnesium as oxides. Their optical spectrum was characteristic of both Co^{3+} and Co^{2+}, indicating that magnesia charge-compensates for Co^{3+}.

Krebs applied ESR to crystalline alpha alumina containing Fe^{3+} and Mn^{2+}. The broadening of the ESR lines was interpreted as a splitting of an unresolved line which is linear in the applied field. A change in the spin Hamiltonian D parameter with the field applied parallel to the c-axis ($\partial D / \partial E$) was 1.00 ± 0.09 for Fe^{3+} and 1.03 ± 0.09 for Mn^{2+} in units of 10^{-5} gauss-cm/v. This effect implies a substitutional replacement of Al^{3+} ions in the lattice. Dixon and Bloembergen observed electrical perturbations of the NMR of ^{27}Al in single-crystal sapphire as splittings of the quadrupole satellite resonance lines in fields as high as 300 kv/cm. The splittings were ascribed to symmetrically opposed changes in the electric-field gradient tensor at crystallographic Al sites which were related to each other by inversion symmetry. By applying the magnetic field in various crystallographic orientations, the magnitudes and relative signs of five independent R-tensor elements which completely describe the shifts were determined.

Pace, Sampson, and Thorp measured the spin-lattice relaxation time in sapphire in the range 1.4 to $56^{\circ}K$ at frequencies as high as 34.6 Gcps. The relaxation times were as much as five milliseconds in this range, and were found to be temperature-dependent, as was also the case for chromia-doped specimens. The relaxation times for ruby were independent of frequency.

10 OPTICAL PROPERTIES OF ALUMINA

10-1 REFRACTIVE INDEX OF ALUMINA

The pure alumina phases, in general, appear as colorless or white powders. Except for artificial corundum, none is commercially available in sufficient single crystal size to be used as components of optical instruments. Refractive index is used as a means of identification of the alumina phases, since it can be applied to crystals of microscopic size by observation of the behavior of the Becke line when the powder is immersed in a liquid of suitable refractive index and dispersion.

Some of the hydrated and calcined alumina phases have good opacifying or hiding properties as pigments, because of their higher than average refractive indices. Other factors, which are characteristic of all powders, are also significant in affecting the pigment properties, however. Maximum reflectance is generally attained at about 0.4 to 0.7 micron particle size, maximum color brilliance with particles of about 5 microns. The alumina trihydrates, at refractive indices of 1.57 to 1.58, have no pronounced opacifying action in the usual suspension media for pigments.

The refractive indices of the different alumina phases at room temperature and for the nominal wavelength 5893 Å are shown in Table 7. Some optical properties of general interest are shown in Table 13.

Synthetic corundum is now available in sizes of two inches or greater for use in windows, lenses, and other optical equipment in which transparence and moderately high refractive index is significant, and for uses at elevated temperatures, or where abrasive or corrosive action may be involved.

Alpha aluminum oxide is anisotropic with variable properties in different crystal directions. It belongs to the rhombohedral (trigonal) division of the hexagonal system. It is convenient to use the hexagonal set of axes: c, a_1, a_2, and a_3, in describing crystal directions. Corundum is uniaxial, indicating that the c-axis is the only direction that does not exhibit double refraction of light. The crystal is negative, the convention indicating that the ordinary index (n_ω) is larger than the extraordinary index (n_ϵ).

Kebler developed a Hartmann-type formula for calculating the refractive index of pure sapphire at 25°C for wavelengths within the range from the C-line (6563 Å) to the Hg-line (3660 Å). The equation: $n_\omega = 1.74453 + 101.0/(\lambda - 1598)$, in which λ is measured in angstroms, fits the data within the experimental error (about 0.00003). Malitson (1962) measured the refractive index of

Table 13
Optical Properties of Alumina

Refractive Index

Sapphire 24°C

$$\frac{\eta_\omega^2}{} = 1 + \frac{1.023798\lambda}{\lambda^2 - 0.00377588} + \frac{1.058264\lambda^2}{\lambda^2 - 0.0122544} + \frac{5.280792\lambda^2}{\lambda^2 - 321.3616} \tag{1}$$

λ	η_ω	λ	η_ω	λ	η_ω	λ	η_ω
0.270	1.83047	0.570	1.76925	0.870	1.75845	2.600	1.72368
0.290	1.81915	0.590	1.76810	0.890	1.75800	2.800	1.71818
0.310	1.81026	0.610	1.76705	0.910	1.75756	3.000	1.71224
0.330	1.80312	0.630	1.76609	0.930	1.75713	3.200	1.70584
0.350	1.79729	0.650	1.76521	0.950	1.75672	3.400	1.69896
0.370	1.79245	0.670	1.76439	0.970	1.75632	3.600	1.69158
0.390	1.78840	0.690	1.76362	0.990	1.75592	3.800	1.68368
0.410	1.78495	0.710	1.76291	1.000	1.75554	4.000	1.67524
0.430	1.78199	0.730	1.76224	1.200	1.75216	4.200	1.66623
0.450	1.77942	0.750	1.76162	1.400	1.74880	4.400	1.65662
0.470	1.77719	0.770	1.76102	1.600	1.74535	4.600	1.64640
0.490	1.77522	0.790	1.76046	1.800	1.74169	4.800	1.63553
0.510	1.77347	0.810	1.75992	2.000	1.73773	5.000	1.62397
0.530	1.77191	0.830	1.75941	2.200	1.73344	5.200	1.61168
0.550	1.77051	0.850	1.75892	2.400	1.72876	5.400	1.59864
						5.600	1.58479

Temperature coefficient of refractive index

0.4 micron	20×10^{-6}/°C
0.4 to 0.7 micron	13×10^{-6}/°C
4 microns	10×10^{-6}/°C

(1) Malitson, 1962

Infrared Spectra of Aluminas -(microns) (2)

Phase	OH-Stretch	OH-Bend	Unassigned	Al-O Stretch	Reference
Alpha Trihydrate	2.765(m),2.842(s), 2.917(vs),2.960(m), 2.975(s)	9.85(vs),10.37(m)	11.0(w),12.1* 12.58(s)	13.48(s)	Frederickson Hannah
Beta Trihydrate	2.830(m), 2.842(m), 2.895(m),2.940(m)	9.85(s),10.25(s)	11.6(m),12.3(m)* 13.9(m)*	12.88(s)	Frederickson Hannah
Alpha Monohydrate	3.065(s),3.247(s)	8.75(m),9.35(s)		13.5(s)	Frederickson Hannah
Beta Monohydrate	3.42(vs),4.27(m), 4.73(m),5.04(m)	9.35(s),10.42(s)		13.89(vs)	Cabannes-Ott
Alpha Alumina			15.58(m),16.61(s) 17.89(m),20.41(w) 22.21(s)	13.16(vs) 12.84-13.89	Hannah Kolesova
Alumina "Gel"		8.5,8.3,9.8	6.9, 7.7 10.7, 12.3	13.5	Imelik (1954)
Anodic Oxide	4.15	8.4-8.7	10.2-10.6		Fichter

m = Medium intensity   s = Strong

vs = Very strong   * = Shoulder

w = Weak

(2) Taken from Alcoa Technical Paper No. 10, Table 10.

sapphire at selected wavelengths, and found that it varies from 1.8336 at 0.2652 micron to 1.5864 at 5.577 microns for the ordinary ray, corrected to 24°C. In the visual region, the thermal coefficient of the index is about 13 X 10^{-6}/°C, and it decreases with increasing wavelength. A three-term Sellmeier dispersion equation was fitted to the experimental data, as shown in Table 13. The dispersive coefficient, $dn/d\lambda$, was computed at regular wavelength intervals, from which the relative "dispersive power," $dn/d\lambda/(1-n)$, was determined. The relative dispersion decreased from a value of about 0.8 at 0.25 micron to about 0.02 near 1.3 microns, and then increased again at higher wavelengths. A plot of the quantity, $(\lambda dn/d\lambda)^{-1}$, against wavelength indicated that optimum resolution is obtained in the wavelength regions below about 0.4 micron and longer than about 2.5 microns.

Loewenstein obtained n_ω = 3.4 ± 4% and n_ϵ = 3.61 ± 4%, in the infrared region, 170 to 500 microns. The extrapolation of Malitson's equation as the wavelength approaches infinity, n_∞ = 8.4, the approximate dielectric constant.

Jaffe (1956) stated that the empirical rule of Gladstone and Dale: $(n - 1)/d = k$, the specific refraction, holds very well. The formula of Lorenz and Lorentz is claimed to be superior. The refractive index and dispersion of light by a dielectric material is explained in terms of electric dipole movements. The dielectric material contains charge carriers that can be displaced to retard light waves. Dielectric polarization is caused by a shift in the electron cloud surrounding the atomic nucleus. In an electric field the charge displacement neutralizes part of the field. The remainder, the bound charge, is neutralized by polarization of the dielectric. The interactions of the dielectric and electromagnetic radiations cause the index of refraction to increase with decreasing wavelength in the visual range (normal dispersion), but to decrease in the region of natural frequency where resonance occurs (anomalous dispersion). The application of a stress (tensile) increases the index of alumina perpendicular to the direction of the stress, and decreases it parallel to the stress direction. The birefringence produced can be applied to measure the stress.

The reciprocal dispersion of sapphire (ν) = $(n_d - 1/(n_f - n_0)$ has a value of 72.2 (Kebler). This is high compared with available optical glasses, and would be important in the fabrication of photographic lens elements. Strain effects in flame-fusion sapphire and hardness cause difficulties in this application.

10-2 TRANSMISSION, EMISSIVITY, AND ABSORPTION OF ALUMINA

The light transmission of sapphire is only slightly poorer than that of fluorite, lithium fluoride, and rock salt, but none

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of these is satisfactory at temperatures above 600 to 800°C because of surface-clouding effects. Klevens and Platt; Bauple, Gilles, Romand, and Vodar; Gaunt; Gilles; and Kebler have contributed to the literature. A sharp cutoff in transmission occurs in the Schumann region of the ultraviolet at about 0.170 to 0.145 micron, with an absorption peak at 0.184 micron. The transmission increases to about 84% at 0.30 micron, and smoothly rises to 93% at 6 microns, thereafter falling rapidly to less than 20% at 7 microns. The loss in transmission in the visual range is mainly Fresnel-type reflection. The loss to this source, determined from the formula: $R = [(n-1)/(n+1)]^2$ for normal incidence of the radiation, is about 8%. Gilles showed that the absorption at the shorter wavelengths increases with increasing temperature.

Early investigators determined the emissivities of polycrystalline powders and massive structures used as thermal insulators. Heilman; Taylor and Edwards; Kilham; and Michaud, in general, have shown that the total emissivity of alumina decreases from about 98% at room temperature to 80% at 400°C, 50% at 750°C, 30% at 1000°C, and 18% at 1600°C. Skaupy and Hoppe observed no absorption in pure sapphire below 1230°C. Polycrystalline alumina had substantial emissivity at elevated temperatures, especially in the blue wavelengths, which was ascribed to emission centers located at crystal boundaries. Skaupy and Liebmann established a relation between the emissivity and decreasing crystal size, and found that the emissivity increased to a critical size, 1 to 2 microns. Two absorption bands were found in the infrared at 1.0 and 5 microns wavelength. At elevated temperatures, the total emissivity was about 10% from which it was concluded that alumina is substantially a "white body." Ruby was found to be very transparent at room temperature, but was almost a black body at high temperatures, having an emissivity of 30% at 1100°C. Michaud noted that the monochromatic emissivity at 0.655 micron was 15% from 1000 to 1600°C.

Kingery and Norton (1955) found that the transmissivity (corrected for Fresnel reflection) of sapphire was independent of temperature to beyond 3 microns wavelength within the temperature range from 30 to 1200°C. The transmissivity was about 99% at 2 microns for a 2 mm thick specimen, dropping gradually to about 97% at 3.6 microns, beyond which point the cutoff was rapid and temperature-dependent. Somewhat similar results were obtained at Alfred University (1957) for the same temperature range, and about the same specimen thickness, but with different test equipment. The values ranged from about 82 to 85% emissivity at 1.0 micron to 84 to 86% at 3.6 microns, with a rapid cutoff, commencing first at the higher temperatures. Gaunt (1951) obtained emissivities of about 75% on sapphire 3 mm thick, substantially unchanged within the infrared region from 1.0 to 4.4 microns. Lowenstein (1961) found that sapphire is highly transparent in

the region 100 to 250 microns, with the transmission dropping off to zero near 110 microns.

Olson and Morris determined room-temperature emissivities on prospective commercial aircraft structural coatings: Rokide A (Norton) on molybdenum and on No. 446 stainless steel, and Norton LA-603 and RA-4213 oxides. Emissivity decreased sharply in the visual wavelengths for all specimens to less than 30% at 0.6 micron; beyond 0.6 micron the coatings on metal increased in two levels to 30% at 1.0 micron, and about 40% at 1.8 microns. The oxides dropped to even lower emissivities, less than 14% at 0.8 micron, and exhibiting a minimum at 1.4 microns.

Sully, Brandes and Waterhouse; Pattison; and Robijn and Angenot also investigated the total emissivity of the pure oxide at elevated temperatures. The total emissivity of pure dense poly-crystalline alumina decreased from about 50% at 325°C to about 25% at 875°C, but increased thereafter to 30% at about 1350°C (Sully; Kingery and Norton 1955). The oxides, RA-4213 and LA-603, also showed increasing emissivity above 875°C (Pattison). The coatings of Rokide on metal also showed decreasing emissivity with increasing temperature in the range from 175 to about 1740°C.

Wade (1959) measured the total hemispheric normal emissivities of refractory oxide coatings of alumina and zirconia. The emissivity values ranged from 0.69 to 0.44 for the alumina coatings. Flame-sprayed coatings showed higher values than those applied by other methods.

10-3 PHOSPHORESCENCE, FLUORESCENCE, AND THERMOLUMINESCENCE

Pure alumina is neither phosphorescent nor fluorescent (de Ment, Kröger). Less than 0.001% of chromic oxide produced a decided fluorescence (Kröger), but it is observed that the threshold for pink color of beads fused in the electric arc is only 0.00035% Cr_2O_3. Thosar ascribed the bright red fluorescence of ruby, stimulated by short wavelengths of light, to Cr^{3+} replacing Al^{3+} in the lattice of alpha aluminum oxide.

Thermoluminescence, induced by irradiation with gamma rays, depends on the amount of hydration and the crystal structure. Rieke and Daniels found that the intensity increased with calcination temperature, and was the highest for synthetic sapphire. The glow curve was resolved as peaks, each of which corresponds to a separate electron-trapping level. The principal peak for tabular alumina (Alcoa T-61) fell at 164°C, with lesser peaks at 103 and 310°C. A peak at 236° was ascribed to sodium impurity. The intensity was quenched quickly in water, which suggests that the trapping centers are surface sites, and that the water is

bound chemically.

Atlas and Firestone applied this method to an investigation of lattice defects in alumina ceramics, as influenced by impurities. The energy depth of each trap was estimated from the glow-peak temperature and the temperature at which the light intensity reached one-half its maximum value. Glow curves were obtained for alumina disks containing less than 100 ppm of impurities, prepared by dissolving 99.999% pure aluminum metal in HCl, precipitating with NH_4OH, and calcining at 1300°C. The high-purity product was doped during milling (in plastic jars with polystyrene balls), was dry-pressed and fired at 1850 to 1960°C in air. The effects of low concentrations of the oxides of silicon, titanium, iron, magnesium, and calcium on the development of peaks were determined, where possible. The impurity ions were found to contribute not only by being instrumental in creating anion and cation vacancies, but also by acting directly as trapping sites for electrons or by capture of positive holes. Trapped electrons appear to be the principal agency for thermoluminescence.

Gabrysh et al. concluded that the glow curves from gamma-ray induced thermoluminescence of sapphire have the form: $I = I_0 [b/(b + t)]^m$, which is a second order decay process. In ruby, principal emission bands have maxima at about 150 and 240°K. Ruby, damaged by gamma-ray irradiation shows an afterglow long after the crystal has reached room temperature.

Przibram (1960) drew attention to the blue fluorescence shown by purified alumina and other minerals excited by 0.365-micron light. The effect is caused by traces of organic matter and is destroyed on heating for a few minutes to redness.

The emission of electrons (exoelectron emission) from metallic surfaces as an after effect of mechanical working or glow discharge has been investigated by Kramer (1949); Haxel, Houtermans, and Seeger; and Seeger, among others. The phenomenon has been interpreted on the basis of removal of a chemisorbed layer of oxygen by the abrasion or discharge, followed by reformation, of the adsorbed oxygen layer. The changes in the freshly formed surfaces can be correlated to the chemical nature, the adsorption properties, and the catalytic activities of the solid. Gouge and Hanle investigated the exoelectron emission from synthetic corundum and ruby. Greenberg and Wright found a very strong exoelectron emission from abraded aluminum irradiated at 0.470 micron. They suggested that metal-excess oxides may be present in the oxide oxygen ion vacancies occupied by 2 electrons, called F' centers. The oxide film on a mechanically polished metal surface would probably contain large numbers of F' centers, and this might be expected to increase the dielectric constant of the film in the region of 0.470 micron. Ramsey measured the optical constants by the method of Drude in the visible region

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and found a considerable increase in the absorption index, k, and a marked lowering in the refractive index in the vicinity of 0.470 micron. Petrescu measured the intensity of exoelectron emission from both scratched metal and crystalline aluminum oxide (which does not require mechanical activation for exoelectron emission). He concluded that crystalline alumina layers of about one micron in thickness completely mask the emission of the metal below, and that there may be several forms of emission that do not verify the hypothesis of the identity of emission centers.

Irradiation of sapphire with light from a low-pressure mercury lamp caused a faint phosphorescence detected by a photomultiplier with S-11 spectral response, for times exceeding one hour. The luminous decay obeyed the expression: $I = k/t^n$, with $n = 1.664$ for t up to 4 minutes, and $n = 0.445$ thereafter (Coop and Hammond).

Alumina and its salts have entered into phosphor compositions, as for example, a mixture of alumina, lithia, and iron oxide, excited by ultraviolet radiation at 0.2537 micron, and emitting at 0.6800 micron with one-half the peak intensity at 0.6520 and 0.7320 micron (S. Jones, 1949). Froelich and Margolis produced a phosphor consisting of aluminum phosphate, activated with 12 to 25% Ce_2O_3 and 0.2 to 15% ThO_2.

Trofimov and Tolkachov followed the phase changes during dehydration of the hydrated alumina by the phosphorescence spectra, with about 1% (mole) $Eu(NO_3)_3$ present as an activator. Band spectra were observed for calcinations below 900°C, and line spectra appeared above 900°C, with wavelengths in the visible spectrum of 0.594, 0.600, 0.620, 0.628, and 0.650 micron, and in the infrared of 0.709, 0.716, and 0.718 micron.

10-4 OPTICAL SPECTRA OF ALUMINA

According to Meggers (1941) each chemical element is characterized by Z totally different atomic spectra, in which Z is the atomic number, 13 for aluminum. The wavelengths of optical spectra are measured in Angstroms (10^{-10} meter), millimicrons (10^{-9} meter), or microns (10^{-6} meter). In the investigation of series spectra, the wavelengths are often converted to wavenumbers or the number of waves per centimeter (cm^{-1}). The first atomic spectrum of aluminum, designated Al I, is characteristic of neutral atoms; the second is ascribed to atoms that have lost one outer electron, and so forth. The total number and types of spectra are fixed by the electron orbits; two (1s) in the innermost shell, two (2s) and six (2p) in the intermediate shell, and two (3s) and one (3p) in the outermost shell. A classification of the different spectra in wavenumbers, including the ground levels (cm^{-1}) and ionization potentials (ev), is given by C. E. Moore (1949). The ionization potentials range from 5.984 ev for Al I at a ground level

of 48,279.16 cm^{-1} to 2085.46 ev for Al XII at a ground level of 16,825,000 cm^{-1}. The binding energy of an electron of given type in any state of a neutral or ionized atom may be defined as that required to remove it along successive terms of a spectral series to its limit. The data permit the calculation of the binding energy (Moore and Russell).

Emission spectroscopy in the visual and ultraviolet range has been applied by many investigators in the qualitative and quantitative analysis of ceramic materials, for example, by the modified excitation method proposed by Ryan and Ruh (1964). The accuracy of such methods has been shown to be sufficient for general analysis in many cases, and the sensitivity (ppm) has been adequate, except perhaps for a few applications, as in semiconductors, involving impurity levels in parts per billion.

Shreve (1952) discussed the application of infrared, ultraviolet, and Raman spectroscopy to the analysis of complex materials. Hunt et al. (1950) described a method for utilizing the infrared spectrometer in the analysis of mineral and ceramic materials. Miller and Wilkins presented a table of infrared spectra and the characteristic frequencies of 33 polyatomic ions. They found that the chief limitation of infrared analysis is the practical necessity of working with powders, which makes it difficult to place the data on a quantitative basis.

Imelik, Petitjean, and Prettre (1954) obtained infrared spectra for aluminum hydroxide gels. Frederickson applied infrared methods to the examination of bauxite ores, and showed that the four distinct alumina hydrate phases: boehmite, gibbsite, bayerite, and diaspore possess hydroxyl groups of sufficiently different absorption patterns in the O-H stretching and deformation regions, to permit their identification. The infrared O-H patterns observed with the pure hydrates were used to identify the phase composition in a variety of bauxitic ores and diaspore clays. Petitjean (1955) investigated the absorption of gibbsite during its thermal dehydration, and Kolesova and Ryskin the absorption of gibbsite and its deuterium analog, $Al(OD)_3$ in the spectral region 2.7 to 23.8 microns. The bands at 9.9, 10.5, and 11.0 microns gradually lost intensity during dehydration and disappeared below the structure $Al_2O_3 \cdot H_2O$. The 9.35 band of boehmite showed first at $Al_2O_3 \cdot 2.5 H_2O$, and the 8.7 band at $Al_2O_3 - H_2O$. Upon heating to the nearly anhydrous condition (500°C), the spectrum became more transparent around 8 microns and more absorptive beyond 11 microns. The spectrum retained the characteristics of boehmite in diminishing intensity from $Al_2O_3 \cdot 0.8 H_2O$ to $Al_2O_3 \cdot 0.2 H_2O$, but at $Al_2O_3 \cdot 0.10 H_2O$ the vestiges of OH bands had disappeared (Orsini and Petitjean). Kolesova and Ryskin concluded that the Al-O bond was partially covalent. The Al-O stretching vibrations for diaspore, boehmite, and the Ga-O bond in GaO·OH correspond to bands at 13.16, 13.33 to 12.82, and 15.62 microns, respectively. Additional references to the infrared absorption of diaspore include: Lecompte; Nakamoto, Margoshes, and Rundle; and Cabannes-Ott. Rundle and

Parasol related the wavelength of the OH absorption to the OH-O distance, which is the length of the hydrogen bond.

Fichter measured an OH-stretch, OH-bend, and two unassigned bands for anodic oxide. L. Harris (1955) determined the infrared transmission of anodic films as thin as 250 A. The films were prepared by anodizing aluminum foil in a 3% aqueous solution of ammonium citrate at 17 to 200 volts. One anodized layer was removed by NaOH and the metal by HCl, leaving the free aluminum oxide film. Even the thinnest films showed marked absorption beyond 11 microns. The index of reflection of all infrared wavelengths decreased with increasing film thickness. The index varied with wavelength, and had a minimum at 9 microns. The absorption coefficient did not vary with thickness but increased to a maximum at 15 microns.

Kolesova (1959) observed in the infrared spectra of alumina, aluminum silicates, and aluminates in which the atoms of aluminum are in the anion shell, a band in the region 12.84 to 13.89, which was attributed to Al-O stretch bonds.

Boreskov et al. (1964) investigated the infrared behavior of ethanol adsorbed on gamma alumina. When the ethanol was adsorbed at 20°C, bands were observed at about 9.43, 9.27, 8.93, and 7.52 microns. The first of these is eliminated by pumping at 170°C, the second and third only at 350°C. When the ethanol was adsorbed at 20°C on theta alumina or on gamma alumina, pretreated with HCl (which blocks the tetrahedral aluminum atoms), and was then pumped at 170°C, bands were observed at about 9.18 and 9.27 microns, respectively, but none at 8.93 microns. The band at 9.43 was ascribed to physically adsorbed molecules, that at 9.27 microns to AlOEt structures, octahedrally coordinated, that at 8.93 microns to AlOEt, tetrahedrally coordinated, and that at 7.52 microns to the CH_3 radicle.

Tanabe and Sugano, and Neuhaus and Richartz examined the absorption spectra of natural ruby and chromia-doped single crystals and alumina powders. Poole and Itzel, and Loh determined the reflection spectra. The Hartmann-Bethe theory of chromogenous complex ions was applied to crystals containing Cr^{3+}. The chromium enters into octahedral or quasioctahedral coordinated lattice positions. The change in color from red to violet to green in such crystals was explained by a contraction or expansion of the (CrX_6) complex, resulting from variable polarization by different adjacent central ions. Spinel and alpha alumina were successively expanded by exchange of Ga for Al, but maintaining the chromium content constant. The room-temperature ultraviolet reflectance spectrum of flux-grown ruby (about 4% Cr_2O_3) at 6 to 14 ev and at an angle of 45 degrees showed an exciton-like peak at 9.1 ev. Alumina has a spectrum very similar to that of magnesia.

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Mandarino observed a strong peak in the absorption of synthetic ruby at 0.55 micron, and also measured the changes in the indices of refraction with compressive strength, applied parallel to the c-axis. Bates and Gibbs measured the absorption coefficient of sapphire doped with various impurities in the region 0.21 to 15 microns. Color centers were found in some crystals. They could also be induced by X-rays and by heating in oxygen above 1300°C.

Krishnan determined the Raman frequencies of sapphire and the luminescence and absorption spectra of ruby. The values found for sapphire and their relative intensities are: 26.66 (8), 23.97 (10), 23.15 (4), 22.25 (2), 17.30 (3), 15.60 (6), and 13.34 (7) microns. Bands appearing in the luminescence and absorption spectra of ruby arise from the combination of the vibration frequencies of the alumina lattice with the electronic transitions of Cr^{3+} ions. The Raman spectrum was confirmed by C. V. Raman in 1951.

The band spectrum for the molecule AlO has been identified (Pearse). Hebert and Tyte measured the relative integrated band intensities of 29 bands in the blue-green region of AlO, the $A^2\Sigma - X^2\Sigma$ system of aluminum oxide. The bands were excited in a low-pressure arc. K. Innes (1958) investigated the conditions under which diatomic aluminum as well as the oxides, AlO, Al_2O, and AlO^+, exist and exhibit electronic spectra. Of this group, only AlO was observed previously. Becart and Mahieu used a Schuler lamp to measure the band spectra in the visible system of the AlO molecule, $X^2\Sigma^+ \rightarrow {}^2\Sigma^+$. A 4-mm thick aluminum cathode was used in oxygen at 2.4 mm pressure. The lamp operated at 25 pulses/sec., at about 1800 volts and 90 milliamperes. After 2 hours exposure, 16 new band tips were identified, belonging either to the principal sequence $\Delta V = 0$, or to adjacent sequences. The intensity of the head of band 6-6 is affected by the presence of the aluminum line 4962.1 A. The visible limit of the spectrum of the sequence $\Delta V = -1$ is near 19,046 cm^{-1} (0.52504 micron).

Becart (1962) developed a formula connecting the frequency of the zero line of a band spectrum with the frequency of the band head, which enabled the determination of the constants of other levels. Applied to the ultraviolet bands of AlO by using the constants derived from the visible bands, the calculated dissociation energy was 5.04 ev, in comparison with 5.2 ev, determined experimentally by DeMaria et al.

Rautenberg and Johnson investigated the excitation mechanism of the continuum and the AlO spectra. The color temperature and the intensity of the continuum were limited by the boiling point of alumina. As applied to photoflash lamps, the light emission results from blackbody radiation of AlO and Al_2O_3 at temperatures of 3800°K or less.

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F. Coheur and P. Coheur used the molecule AlO as an example of a spectral method for determining temperature. It was shown theoretically and experimentally that the spectral method does not necessarily measure the total spherical temperature of the source, but only the localized temperature of certain zones from which the bands of the molecules selected for measurement are emitted. AlO, burning in oxygen, had a temperature of 4225 ± 200°C; in air 4210 ± 300°C; and in a vacuum 4275 ± 300°C. When AlO was replaced by Al_2O_3, $AlCl_3$, or $Al_2(SO_4)_3$, the respective temperatures were 4175 ± 225°C, 3877 ± 250°C, and 3950 ± 300°C.

Mal'tsev and Shevel'kov (1964) have investigated the infrared absorption spectrum of Al_2O at 1500 to 1840°C, and from 5 to 435 microns wavelength. The configuration of Al_2O is linear.

Tarte mentioned potential applications of infrared investigations in the study of isomorphous replacements in complex anionic groups such as $(AlO_6)^-$, as well as in nonisomorphous silicates. Polymorphism in the Al_2O_3 and SiO_2 systems, and the investigation of analogous problems in glass constitution has disclosed important structural information, as for example, in the role of such groups as (AlO_4). Order-disorder conversions, as shown in the special case of $LiAl_5O_8$, and the feldspars may also prove to be useful applications (Laves and Hafner).

Emschwiller et al. applied infrared analysis to the hydrated calcium aluminates to show that $3CaO \cdot Al_2O_3 \cdot 6H_2O$ could not be dehydrated at room temperature. Ease of dehydration or the replacement with heavy water was found to be dependent on crystal structure. Nuclear magnetic resonance was more useful to place the nature of the water.

Trombe and Foëx (1957) applied the high-energy infrared radiation of the sun, 300 watts at 250 to 300 watts/cm^2, collected by a parabolic mirror of 2 meters diameter and 0.85 meter focal length. A filter of manganese glass absorbed visible radiation. The radiation that passed was equivalent to a black body at 2350°C. Alpha aluminum oxide and silica absorbed very little infrared radiation under these conditions, and were heated only slightly.

10-5 COLOR IN ALUMINA

Alum has been used from ancient times as a mordant for fixing native dyes and developing their brilliance. The basic aluminum salts, gelatinous aluminum hydroxide, anodized coatings on aluminum, and partially dehydrated Bayer alumina trihydrate serve as effective carriers for fixing organic dyes strongly as pigments. The intensity of dye fixation is very weak in Bayer hydrated alumina and in hydrothermal boehmite, but it reaches a maximum at activation around 350 to 400°C, and then gradually decreases and practically disappears on conversion to alpha aluminum oxide.

Very stable, fade-resistant organic paint and ink pigments are formed in such structures (Harrison, 1930; Ellis, 1940). These high-surface alumina forms also adsorb and fix the soluble salts of the colorant metals (Fe, Co, Ni, Cr, Ti, V, etc.) by precipitation as hydroxides and oxides on the active surface.

Thermally stable ceramic pigments are produced by heating intimate mixtures of the colorant metal oxides with alumina at temperatures sufficient to obtain color development, apparently by solid solution. As inferred previously, various gem-stone colors are developed by adding the appropriate oxides to the feed in the Verneuil process, or to the nutrient alumina in the solution-grown process.

The threshold of visual detection of coloration of polycrystalline alumina is quite sensitive, as determined on spectrographic beads fused in the electric arc. The sensitivity varies for different oxides, being about 0.02% for Fe_2O_3 and about 0.0035% for Cr_2O_3. The internal reflection from hollow, translucent ware is a more sensitive method of color detection. The red colorants (Cr_2O_3, Fe_2O_3) appear to augment each other's intensities, while cobalt masks their effect by producing gray tints.

Color in sintered alumina and high-alumina porcelains, picked up from specks of contamination introduced during various stages of processing, diffuses spherically from the point of contact. When diffusion is incomplete during firing, the coloration appears with circular boundaries in the ware. A reducing atmosphere at about 1500°C was effective in removing or concealing spotted brown discoloration.

Spinel formation is an effective method for obtaining a range of brilliant colors from the metal oxides, for use as ceramic stains and pigments. Singer (1946) recommended that ceramic stains be prepared by combining a monoxide and a sesquioxide, either one of which may be the coloring agent. Some of the direct colors available with alumina spinels include: $CoAl_2O_4$, dark blue; $CuAl_2O_4$, light green; $FeAl_2O_4$, black; $MnAl_2O_4$, tan; $NiAl_2O_4$, blue; $ZnAl_2O_4$, violet. Partial substitution of these with spinels produced by other common bivalent and trivalent metal oxides increase the color spectrum. Among these are: $BaCr_2O_4$, dark green; $CoCr_2O_4$, blue green; $CuCr_2O_4$, green; $MgCr_2O_4$, yellow green; $NiCr_2O_4$, green; $SrCr_2O_4$, green; $ZnCr_2O_4$, green to brown; $BaFe_2O_4$, gray to brown; $CaFe_2O_4$, gray; $CoFe_2O_4$, black; $CuFe_2O_4$, brown; $MgFe_2O_4$, brown; $NiFe_2O_4$, black; $SrFe_2O_4$, gray; and $ZnFe_2O_4$, gray to brown. Evers found that the coloration of fused spinel containing from 0.1 to 15% Cr_2O_3 was homogeneously green for the low concentrations, but showed points of red ruby at the higher concentrations. Specimens containing 25% Cr_2O_3 had alternating zones of red and green, while spinels containing 50% Cr_2O_3 showed some metallic chromium. Magnesia vaporized more readily than

alumina. Annealing at 950°C caused separation of alumina, generally as ruby. Absorption coefficients showed a maximum at 5893 Å and a minimum at 5016 A.

Steindorff (1947) discussed in detail the various coloring matters which are added to aluminum oxide and spinel to produce different colors. Grum-Grzhimailo and Lyamina applied refractive index and absorption curves as tests of the homogeneity of alumina and spinel colors. Colors containing $3MnO-P_2O_5 \cdot 12Al_2O_3$, in which the P_2O_5 acted as a flux, were yellow when fired at 900°C; their refractive index ranged from 1.650 to 1.667 in the batch; and the absorption curve did not resemble that for Mn^{3+}. When fired at 1000°C, the refractive index ranged from 1.683 to 1.690, and at 1060°C, to 1.735 to 1.760, and resulted in the formation of anisotropic crystals of corundum; the absorption curve had the maximum characteristics of Mn^{3+}. At 1100°C the portions of material having the lower index surrounded the more highly refracting crystals and bound them into aggregates. With increasing temperature, the grain size of the corundum increased, and at 1300°C a maximum amount of lamellar corundum was formed. Colors fired at 1350°C for one hour varied in index from 1.71 to 176, regardless of the chromium content, indicating incomplete reaction, but at 1750°C, the reaction was homogeneous and complete. Similar lack of homogeneity during color formation was demonstrated for magnesium and zinc spinels. The addition of 5% boric acid to samples composed of $Cr_2O_3 \cdot Al_2O_3$ enabled the same development of color at 1350°C as without it would require 1750°. The addition of boric acid to a composition $(0.1\ CoO,\ 0.9\ MgO) \cdot Al_2O_3$ stabilized the refractive index at 1.736.

Fujii et al. described the method of manufacturing "Toshiko" or manganese pink from a mixture of 2 parts manganese phosphate to 8 parts $Al_2O_3 \cdot 3H_2O$. Yamaguchi and Tomiura also investigated the manganese pinks, and Yamaguchi et al. (1954) the following systems: blue, $CoO-MgO-Al_2O_3$; blue, $CoO-NiO-MgO-Al_2O_3$; blue, $NiO \cdot Al_2O_3$; brown, $CuO \cdot Al_2O_3$; green, $CoO \cdot 3MgO \cdot 2Cr_2O_3 \cdot 2Al_2O_3$; pink, $ZnO-Cr_2O_3-Al_2O_3$; brown, $MgO-Cr_2O_3-Al_2O_3$. The brown spinel structure, $CuO \cdot Al_2O_3$, is stable only below 750°C; blue color is obtained at 1100°C. Yamaguchi (1954) recommended the spinel with lower valence aluminum ion, which has 0.8 equivalent reducing power per formula weight, for the preparation of ruby glass and glass transparent to ultraviolet rays.

N.S.G. Rao (1958, 1960) investigated various colors including chrome alumina pink. At a calcination temperature of 1300°C with 3% potassium dichromate, some successful compositions (concentrations in parts) were as follows: dark rose pink, Al_2O_3 20, ZnO 40, and Be_2O_3 40; dark rose pink, Al_2O_3 20, ZnO 40, B_2O_3 20, and SiO_2 17.23; brick red, Al_2O_3 60, CaO 20, and B_2O_3 20. Calcia, added as $CaCO_3$, is not necessary to produce pink but it lowers the firing temperature and deepens the color. A mat blue composition contained: Al_2O_3 64.5, ZnO 32.25, and CoO 3.25, fired at 1200°C. The preparation of various other ratios, fluxed with

borax, was investigated. Vecchi evaluated the use of nickel in the production of colors ranging from bright greens to steel blue.

Sono reported experiments showing the influence of alumina in altering the shade of vanadium colors in the systems $ZrO_2-SiO_2-V_2O_5$ and $SnO_2-SiO_2-V_2O_5$.

The foregoing references are indicative of the role of alumina in the development of a very large number of ceramic colors.

P. Levy (1961) determined the peak energy (E_0) and the full width (U) in ev of the color centers found in alumina both before and after gamma ray and reactor irradiation to induce defect structure. The following values were observed:

Before Irradiation		Irradiation			
		30,000 roentgen X-ray		Reactor	
E_0	U	E_0	U	E_0	U
5.45	0.60	5.45	1.25	6.02	0.60
4.84	0.54	4.28	0.70	5.35	0.40
6.2	0.4	3.08	1.50	4.85	0.54
				4.21	0.80
				3.74	0.88
				2.64	0.64
				2.00	0.44

The curves of color-center concentration vs. irradiation time for the reactor-induced bands at E_0 = 6.02, 5.35, and 4.85 ev could be accurately represented by a saturation exponential plus a linear increase expression. This conforms with a simple theory which assumes that the defects present before irradiation contribute to coloring as well as the radiation-induced defects.

Mie scattering, particularly in the infrared, and absorption cross sections of micron-size alumina spheres has been investigated by Bauer and Carlson and by Plass. In both cases, the sphere diameters ranged from 0.5 to 10 microns, but Bauer and Carlson presented cross sections for absorption and for differential and total scattering for several particle size distributions with mean radii in the region of one micron. For wavelengths below 8 microns, the absorption cross section was generally less than one percent of the scattering cross section. The data were found applicable to the calculation of the emissivity of optically thick rocket plumes. Plass observed that when the particles are small compared with the wavelength, the absorption cross section varies as the radius of the particle, and the scattering cross section as the 4th power of the radius. Unless the radius is several orders of magnitude smaller than the wavelength, the scattering cross section is larger than the absorption cross section. The ratio of forward to backward
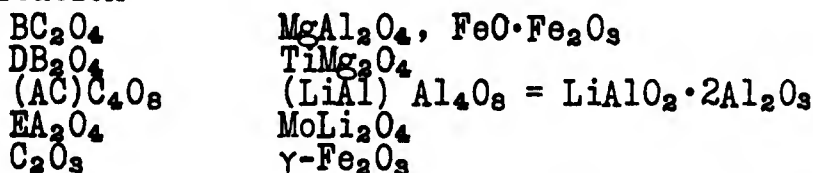
scattering as a function of particle size of the alumina spheres at wavelengths of 4 and 8 microns was derived, as well as the angular distribution of the scattered radiation at 4 microns.

10-6 SPINEL

Alumina reacts with magnesia to produce spinel, $MgAl_2O_4$ or $MgO \cdot Al_2O_3$, the end product of a family of analogous compounds, many of which occur in nature. Spinel is face-centered cubic, with cubic close packing. The unit cell contains 8 molecules of $MgAl_2O_4$. There are 64 tetrahedral and 32 octahedral sites in the oxygen packing, of which only 16 octahedral and 8 tetrahedral sites are occupied by cations. The octahedral sites contain the smaller trivalent cations. Spinel has the unusual structural feature that close-packed oxygen ions fall on the (111) planes. Hornstra showed that dislocations in the spinel structure lie on these planes, and have [110] Burgers vectors; twelve slip modes are possible.

The magnesium ion can be replaced by similarly sized bivalent ions such as Zn, Co, or Ni, without changing the lattice appreciably, and the aluminum can be replaced by trivalent ions, such as Fe and Cr. Univalent, tetravalent, and hexavalent substitutions are also possible for the cations, and sulfur, selenium, and tellurium, theoretically, for the oxygen. All the spinels are isomorphous, and the unit cell constant usually falls in the range 8.0 to 8.5 A.

Examples of the types of spinels are as follows, assuming A, B, C, D, and E to represent metal ions of valence equal to 1, 2, 3, 4, and 6, respectively, and O to signify oxygen or its substitution.

BC_2O_4	$MgAl_2O_4$, $FeO \cdot Fe_2O_3$
DB_2O_4	$TiMg_2O_4$
$(AC)C_4O_8$	$(LiAl) Al_4O_8 = LiAlO_2 \cdot 2Al_2O_3$
EA_2O_4	$MoLi_2O_4$
C_2O_3	γ-Fe_2O_3

Spinels composed of a single metal in two states of oxidation are designated "inner" spinels, as for example, magnetite, $FeO \cdot Fe_2O_3$, and the claimed $AlO \cdot Al_2O_3$ of Filonenko, Lavrov, Andreeva, and Pevzner. The bivalent cations may be replaced by ions of different valence, in which case the spinel is designated "inverse" to distinguish from the "normal" spinels. Inverse spinels include the magnetic iron spinels, the nickel, and manganese (partially). The cobalt spinel is almost completely normal (Greenwald, Pickart, and Grannis), as are the nonmagnetic iron spinels. The complexity of the spinels increases because of their ability to take in solid solution an excess of either the bivalent or trivalent ion; $MgO \cdot Al_2O_3$ picks up as much as 60% Al_2O_3, according to Winchell (1940), but to $MgO \cdot 4Al_2O_3$,

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according to Biltz and Lemke (1930). Magnesia is hardly soluble in MgO·Al₂O₃, but dissolves in other types (to 1.5 MgO·Cr₂O₃). Verwey (1935) related gamma alumina to spinel by assuming 32 oxygen ions in the unit cell, and that all 8 tetrahedral sites are filled by aluminum ion replacement of magnesium ions. Only 13-1/3 of the 16 normal octahedral positions are filled, but the total electric charges are the same as for the spinel. Bacon (1954), and Sinha and Sinha investigated the spinel structure by X-ray. In gamma alumina the vacancies are randomly distributed among the octahedral positions, but there is no ordered structure of vacancies.

Jagodinski and Saalfeld (1958) using the Fourier analysis of X-ray data, and Brun (1960), by measurement of paramagnetic nuclear resonance, found that natural spinel crystals show almost completely the "normal" spinel structure with the aluminum ions in the octahedral positions. Synthetic spinels in MgO:Al₂O₃ ratios of 1:1, 1:2, and 1:3.5 show more disordered distribution from normal. Natural spinels become disordered by heating at 800 to 900°C, but the process could not be observed in the reverse direction, that is, ordering in synthetic spinels. Since all the crystals investigated did not correspond strictly to the space group $Fd_3m(O_h^7)$, it was concluded that spinels are composed of twinned crystallites of lower symmetry. Arnold (1960) interpreted the visible acicular inhomogeneities observed in synthetic spinels as voids caused by a decrease in internal strains during annealing. Stoichiometric spinel (MgO·Al₂O₃) showed decreased absorption in the 3-micron band and a shift of the transmission limit to longer wavelengths. It also had a minimum index of refraction with increases on both the alumina-rich and the magnesia-rich (MgO·0.8 Al₂O₃) sides of the stoichiometry (Wickersheim and Lefever). Rasch developed two-dimensional schematic diagrams of the spinels and corundum.

Rinne (1928) determined the index of refraction of Mg-Al spinel to be 1.718 to 1.728 (n_D). The change in density with change in Al₂O₃ content was as follows:

Al₂O₃ (%)	71.7	81.5	89.4	91.0	92.7
g/ml	3.578	3.604	3.621	3.625	3.624

The molecular weight is 142.27, and the ideal alumina concentration 71.67%. W. C. Allen (1963) presented the following data as representative of the range, the "best" single value, and his own determinations of identifying properties of several spinel types:

Properties of MgO Spinels

Property		MgAl$_2$O$_4$ Spinel	MgCr$_2$O$_4$ Picrochromite	MgFe$_2$O$_4$ Magnesioferrite
Refractive Index	RANGE	1.709-1.723	1.90-2.08	2.34-2.39
	"BEST"	1.713		
	Author	1.715	2.11	
Density (cm/cc)	RANGE	3.53-3.63	4.2-4.43	4.20-4.65
	"BEST"	3.58	4.43	4.51
	(Author,Calc.)	3.573	4.411	4.522
Lattice Parameter, A.U.	RANGE	8.02-8.09	8.29-8.34	8.34-8.40
	"BEST"	8.080	8.33	8.39
	Author	8.085	8.335	8.375
		Normal	Normal	Inverse

Properties of FeO Spinels

Property		FeAl$_2$O$_4$ Hercynite	FeCr$_2$O$_4$ Chromite	Fe$_3$O$_4$ Magnetite
Refractive Index	RANGE	1.79-1.83	2.12-2.16	2.42
	"BEST"	1.790		
Density (gm/cc)	RANGE	4.05-4.39	4.50-5.11	5.01-5.25
	"BEST"	4.32		5.03
Lattice Parameter,	RANGE	8.10-8.19	8.34-8.38	8.37-8.42
	"BEST"	8.114		8.395
		Normal		Inverse

Normal spinel (MgAl$_2$O$_4$) has been successfully fabricated by the usual ceramic processes, such as casting, extrusion, or cold pressing, followed by sintering at about 1650 to 1850°C. Ryshkewitch (1941, 1942, 1948, 1960) recognized the importance of spinel as a pure oxide ceramic material, and drew attention to its chemical stability and refractory properties. Early attempts to realize these properties, particularly in refractory applications, were marred by variability in the properties, coarse grain, and incomplete densification. The structural properties of spinel are largely dependent on the microstructure, which is influenced by the raw materials and the processing conditions (Palmour 1964). Noguchi (1948) prepared the normal spinel by heating cylindrical pressed specimens of the equimolecular mixture of oxides at 1535°C for 30 minutes with 0.01, 0.03, or 0.05% of various mineralizers. Compounds of Li, B, Ti, and V were effective, but not those of Ca, Sr, or Ba. Toropov and Sirozhiddinov found that Y$_2$O$_3$ had the greatest mineralizing action of the rare earths, La$_2$O$_3$, Y$_2$O$_3$, and Nd$_2$O$_3$ on spinel synthesis. The formation was almost complete (97%) after 5 hours at 1300°C for 1 and 3% additions. The additions of 1 and 5% Nd$_2$O$_3$ and of 1% La$_2$O$_3$ required 5 hours at 1500°C, or an effectiveness equivalent to that of H$_3$BO$_3$. Spinel production occurred

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in two steps (1) an intense reaction at the boundaries of the particles up to 1300°C, in which a layer of spinel formed at the surface of separation; (2) above 1300°C a decreasing reaction rate with time and temperature regulated by the denser spinel layer, which decreased the rate of diffusion of the Mg^{2+} and Al^{3+} ions. Diesperova and Bron found that the rate of synthesis of $MgO-Al_2O_3$ commences below 900°C, and finishes at 1500°C when catalyzed by Y_2O_3 or B_2O_3.

Hedvall and Loeffler found that the reaction between CaO and Al_2O_3 occurred at a faster rate when gamma alumina was used instead of dead-burned alumina, and Co_2O_3 instead of CoO. An increased velocity (Hedvall effect) is generally observed when one or more participating components undergo a transformation during the reaction.

The preparation of normal spinel by electrofusion and casting was described by Alais in 1944. The product was characterized by high refractoriness and exceptional dielectric properties. Navias (1961, 1963) described the preparation and some properties of spinel made by the vapor transport of MgO from periclase in hydrogen atmosphere at 1500 to 1900°C. The products diffused into alumina (sapphire) to form a uniform outer layer of spinel on all surfaces. At 1900°C, the spinel layer was 20 mils thick in one hour and 48 mils in 16 hours; at 1600°C, the rate was about 2.6 mils in one hour and 6.1 mils in 16 hours. The calculated activation energy was 100 kcal/mole. The lattice constant, Vickers hardness, and refractive index of the spinel layer varied with depth in a uniform manner, indicating a continuous change in composition from $MgO \cdot Al_2O_3$ to $MgO \cdot 2$ to $3Al_2O_3$. In conversion to spinel, a volume increase of 47% over that of the original sapphire occurred. Clear shapes of spinel were produced from clear sapphire and from translucent polycrystalline alumina. Vapor of alumina diffused into fused periclase blocks to form spinel. In an oxidizing atmosphere, spinel was formed only on the surface of sapphire directly in contact with periclase, in the range 1500 to 1900°C. Altman (1963) observed that gaseous MgO is of little importance in the vapor phase at 2000°K. A negative heat of formation from the oxides is probable, from Knudsen experiments. Rossi and Fulrath (1963) examined the solid-state reaction between MgO and Al_2O_3 in air at 1560°C. Two spinel layers were observed, one thick layer grown contiguous with the sapphire crystal, and a thinner layer grown from the periclase-spinel interface. Often a fracture appeared within the sapphire about parallel to the sapphire-spinel interface. From the ratio of thicknesses of the two layers, the mechanism of counterdiffusion of cations through the oxygen framework was verified. The crystallographic orientation of the parent crystals had no effect on the rate of spinel growth. The orientation of spinel grown from sapphire was always determined from the orientation of the sapphire, as was also the case when epitaxy was observed in periclase-grown spinel. The orientation of spinel

grown from periclase appeared to depend on the mechanism of transport across the periclase-spinel interface.

Bruch (1964) claimed that spinel bodies produced by treating compacted polycrystalline alumina with magnesia vapor carried in hydrogen, or as a directly contacted hot solid body, are free from an internal zone of weakness that splits readily, if all but one side of the alumina body is kept from contact with the MgO, as by masking. Crystal faults, where growths from opposite directions meet, are prevented. At 1900°C, the activation energy is 92 kcal/mole.

Carter (1961) ascribed the solid-state reaction forming $MgAl_2O_4$ in single-crystal and polycrystalline alumina to the counterdiffusion of the Mg^{2+} and Al^{3+} ions through the relatively rigid oxygen lattice. Inert markers were used in the experiments, but Carter demonstrated that pores could serve equally well as markers.

Budnikov and Zlochevskaya (1958) found that the use of salt solutions instead of magnesite, and fine dispersions of alumina (0.9 to 2 m^2/g) gave uniform production of spinel at temperatures above 1400°C. At lower temperatures, spinel formation practically ceased within two hours.

Kriegel, Palmour, and Choi (1964) investigated the effect of intimacy of mixing on the mechanical properties of synthetic normal spinel. One sample was prepared by direct solid-state reaction of a mixture of low-soda alumina (Alcoa A-14) and magnesium carbonate, that had been wet-milled for 4 hours in a 96% Al_2O_3 ball mill prior to conversion at 1450 to 1470°C, held for 2 hours. The ultimate crystal size was less than 2 microns. Marked recrystallization growth occurred at high temperatures (1800 to 1850°C). Total impurities were less than 0.5%, mainly CaO, Fe_2O_3, and SiO_2. A second sample was prepared by coprecipitating a stoichiometric mixture of aluminum and magnesium chlorides with NH_4OH. The gelatinous precipitate, which formed, was partially dehydrated slowly under infrared lamps, and the temperature was slowly increased to 850 to 860°C, and held for 24 hours. The ultimate particle size was about 0.04 micron, and total impurities less than 0.1%. The latter material was very labile, since calcination at slightly higher temperature induced marked crystal growth. Marked broadening of the X-ray peaks was also indicative of the high reactivity.

Choi, Palmour, and Kriegel (1962) investigated the properties of hot-pressed polycrystalline spinel ($MgO \cdot Al_2O_3$). The specimens were hot-pressed in a graphite die at 1227 to 1750°C, at 1000 to 3000 psi for 5 to 320 minutes holding time. For maximum strength, it was necessary to develop fine grain size (2 to 15 microns) and nearly the theoretical density (greater than 99.5%). The maximum average transverse strength was about 34,000 psi, obtained by maturing either at about 5 minutes at 1620°C (short time, high

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temperature), or at about 300 minutes at 1500°C (long time, intermediate temperature). The maximum modulus of elasticity was about 3.5 X 10⁷ psi, obtained for hot-pressing at 8000 psi over a wide range of temperature and time. Palmour, Choi, Barnes, McBrayer, and Kriegel obtained nearly the theoretical density by additions of graphite, from 0.001 to 10% (wt). The strength and modulus of elasticity were maximum for specimens matured at 1450°C and at 2000 psi. They concluded that spinel is a little harder, stronger, and less brittle than comparable reoxidized materials. Graphite additions above 0.1% reduce strength, decrease micro-hardness, and increase brittleness.

Chung, Terwilliger, Crandall, and Lawrence (1964) measured the elastic moduli of magnesium aluminate spinel of varying molar ratios of MgO to Al₂O₃. Budnikov and Zlochevskaya (1964) investigated the properties of the pseudobinary system, mullite-spinel. Compositions prepared from mixtures of spinel and mullite were characterized by a eutectic, melting at 1800 ± 20°C and containing 50% (mole) spinel. At 1450 to 1500°C, the mullite component decomposed to corundum and a liquid from which corundum crystallized. By passing this temperature region rapidly, mullite could be preserved in the initial crystallization of spinel. Compositions prepared by heating mixtures of the component oxides that had been prefired for 8 hours at 1480°C, developed highly defective, fine crystalline spinel at 900°C. At 1200 to 1300°C sapphirine and cordierite appeared. These decomposed into spinel, mullite, and a liquid phase. Above 1550°C, the mullite decomposed into corundum and a liquid.

The refractory properties of spinel are further discussed in the section on refractories.

Smoke (1954) demonstrated the low-loss, ceramic dielectric properties of compositions in which MgO·Al₂O₃ spinel was the principal phase. The addition of from 10 to 20% silica to these compositions resulted in strong, dense bodies. When clay binders were used, the bodies matured at 1450 to 1540°C; when talc was substituted for part of the composition, the maturing temperature was lowered to 1315°C.

Yamaguchi (1953) observed for various mixtures of MgO, CoO, NiO, CuO, ZnO, and MnO with Al₂O₃, heated between 900 and 1700°C, that spinel was most readily formed in the NiO-Al₂O₃ system, was formed with difficulty in the MnO-Al₂O₃ system, and was not obtained in the CdO-Al₂O₃ or CaO-Al₂O₃ systems. MgO, CoO, and ZnO were intermediate in reaction. Pattison, Keely, and Maynor obtained synthesis of NiO·Al₂O₃ and CoO·Al₂O₃ in solid-state reactions when calcining mixtures of the hydrated oxides at 1200°C, but did not achieve conversion when alpha aluminum oxide was used.

Unicrystalline precious stones or shapes, such as rods, filaments, and filament guides, prepared by the flame-fusion process from spinel, can be deformed and bent to shape, after heating until the form becomes plastic (Linde, 1948).

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10-7 CHROMIA-ALUMINA SYSTEM LASER APPLICATIONS

Ceramics in the Al_2O_3-Cr_2O_3 system have become important because of several applications having quite different properties. Among these are fused cast refractories of significantly improved corrosion resistance to molten glasses, ruby jewels and abrasives of enhanced hardness compared with sapphire (Skaupy 1947), and ruby lasers.

Neuhaus stated that the incorporation of coloring, transition-element ions, especially of Cr^{3+}, into sapphire provides information on the structure, such as the determination of atomic positions, expansion and contraction effects, and the existence of unmixing phases. The change from red to violet to green of Cr^{3+} is caused by specific shifts in wavelength of the characteristic maxima of absorption in the Cr^{3+} spectrum. Dils, Martin, and Huggins analyzed ruby boules in a plane normal to the growth direction by the electron probe microanalysis technique. The chromium content of boules whose overall chromium contend ranged from 0.03 to 0.5%, fluctuated markedly, with a general decrease from the center towards the periphery. A microscopic heterogeneity of considerable magnitude but on a very fine scale was also found. Saalfeld (1964) observed a considerable distortion of the oxygen lattice by the introduction of Cr^{3+} ions, although the structure was ordered and strain-free. Janowski and Conrad (1964) used a technique of polishing in H_3PO_4, followed by etching in $KHSO_4$ to reveal dislocations on the various crystallographic planes of crystals to be used as ruby lasers from four sources. Dislocations and subboundaries were revealed on the (0001) and (11$\bar{2}$0) planes. Less distinct pits developed on the (0$\bar{1}$11) planes and none were observed on the (1$\bar{1}$00) planes. The average dislocation density on the basal plane was (1.5 to 3) X 10^6/cm^2 and about 5 X 10^5/cm^2 on the (11$\bar{2}$0) plane. Wander in the c-axis for a typical sapphire crystal 1.25 inches long varied as much as 1 degree 35 minutes, as determined by Laue back-reflection. Slight etching of a mechanically polished crystal revealed numerous polishing scratches, suggesting a plastic-flow layer.

The general function of "maser" devices is molecular amplification by stimulated emission of radiation. Observations by Forrester, Parkins, and Gerjuoy (1947) on the possibility of observing beat frequencies in photoelectric emission generated by two separate light sources, and by Schawlow and Townes (1958) on the potentialities of masers foreshadowed the developments of "lasers." Makhov, Kikuchi, Lambe, and Terhune (1958) "pumped" a 0.1% chromia ruby crystal by a klystron tube at 2.4 X 10^{10} cps in a 4230-gauss field at 4.2°K, and it radiated at 0.9 X 10^{10} cps, short electromagnetic radiation.

Maiman (1960) was the first to make a laser, a device capable of generating and amplifying coherent infrared and visual light by stimulated emission of radiation. His laser consisted of a

ruby rod placed in the axis of a helix-shaped xenon tube. The ends of the rod were plane-polished and silvered - one more heavily than the other. Light from the xenon tube entered the crystal through the sidewall, and nearly coherent flashes of concentrated light energy were emitted from the rod.

Lewis (1963) discussed the significance of coherent light, spectral purity, and laser operation. The waves of coherent light are in phase over the width of the beam and of uniform wavelength. The propagation as a parallel beam spreading only through the diffraction angle (less than one minute of arc) has suggested the use for communication through long distances, particularly in outer space. A beam to the moon is calculated to be spread less than one mile in diameter (Bell Telephone Laboratories, March 1961). At any one frequency, a laser crystal may emit billions of times as much energy as is emitted by a comparable area of the sun's surface.

More effective methods for pumping the energy have since been devised. Schawlow; Luck; Devlin, McKenna, May, and Schawlow; Holland; Rechsteiner; Olt; Nelson and Boyle; and Humphreys contributed to the information on laser systems. Threshold pumping power was reduced and power output was increased by cladding the ruby laser in a sapphire shell, and by growth on a sapphire base. Output energies of the order of 300 joules at an efficiency around 1% have been obtained for ruby lasers.

Murray, Lamorte, and Vogel discussed such factors as crystal growth development, the preparation of scatter-free crystals, crystal annealing, the valency of the dopant, the preparation of laser rods and the reflecting surface, and laser crystal testing. Nelson and Remeika found that flux-grown ruby lasers (as from lead oxide-boron oxide flux) were superior to flame-fusion (Verneuil) crystals for laser uses. Kisliuk and Krupke investigated the biquadratic exchange energy in ruby. Birnbaum and Stocker showed that in the operation of solid-state lasers (ruby) near the threshold, many axial modes are present, even when a train of regularly spaced damped spikes appears in the output of the laser.

Hoskins (1959) observed a relaxation time of about 10^{-2} second for the inverted state of the Cr^{3+} ion in an adiabatic, rapid passage of the spin transition, $\Delta m = 1$ at about $4.1°K$. Kushida and Silver (1963) induced a nuclear spin, $\Delta m = \pm 2$ transitions, using a double resonance technique in the application of a radiofrequency electrical field orthogonal to the trigonal axis of the ruby crystal. The line observed for the quadrupole transitions was more than twice as broad as the dipolar lines, and with a distinct asymmetry.

The ability to focus coherent laser beams has suggested many

applications involving the application of high concentrations of radiant energy to burn, melt or drill holes in refractory ceramic materials, including the diamond.

Laser techniques for welding both ceramic and nonceramic materials have been developed, and the repair of retinal detachment in the eye (coagulation) has been suggested. In the latter case, coagulation by the use of conventional light optics is presently favored (Cibis; Kühn and Weinhold).

Bonem used the laser beam to evaporate aluminum oxide, tantalum metal, etc., in the preparation of thin films. No boat is required, and the film purity is claimed to equal that of the specimen before evaporation.

11 RADIATION AND ALUMINA

The effects of radiation on the properties of alumina are of interest because of the present and potential uses of ceramic materials around nuclear reactors. Some investigators who have drawn attention to these applications include: Lambertson (1951); Murray; White (1953); Warde; McCreight and Sowman; Sargent; Livey; and Wisnyi and Taylor (1960). The requirements extend from crucibles used in the laboratory processing of metal components to applications within the reactor itself, the fuels, moderators, controls, structural materials, and shielding. Aside from the conventional use of refractories in nuclear power plants, the uses of ceramics in the storage of nuclear wastes, and as pumps and container material in heat exchange systems are also of interest. One of the objectives of using ceramic materials in nuclear applications was to raise the operating temperatures into a more efficient range.

Dickinson presented a classification of the radioactive isotopes, and their potential uses in industry. The types of nuclear radiation include:
Neutrons (n), at 1837 X the electron mass, but without a charge, and unstable. These include fast neutrons (nf) having a speed greater than 10^4 ev, and thermal neutrons (ns) having a speed of 0.025 ev or less.
Protons (p), the basic nuclear charge, 4.8 X 10^{-10} esu, and having a mass 1835 X the electron mass.
Deuterons (d), neutron-proton units.
Alpha particles (α), helium nuclei.
Fission products (F/p), fragments of fissioned sources.
Electrons (e), beta rays (β), unit mass 9.1085 X 10^{-28} g.
Electromagnetic radiation (photons), including gamma rays (γ) and X-rays (about 10^{-7} cm or less).

The radiation damage in ceramics caused by each of the types of radiation is about as follows:
nf causes scattering of ions in the crystal lattice.
ns induces nucleon reactions (neutron lattice).
p, d, α cause nuclear reactions, lattice displacement.
F/p causes displacement and severe ionization.
β causes ionization by recoil electrons, a minor effect.
γ causes secondary ionization.

In general, irradiation by high-energy radiation particles usually causes lattice defects in ceramics with the least damage to simple ionic crystal structures. Anisotropic structures and highly covalent crystals are particularly sensitive. Most radiation-induced defects can be annealed by heating at 600 to 1200°C. Less damage was incurred by graphite (and probably other ceramic types) at higher temperatures. Gamma-induced defects are usually annealed at 200 to 400°C. Howie (1961) listed three types of radiation damage (1) ionization and electronic

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excitation, (2) transmutation, and (3) knock-on damage.

The neutron flux (nv), neutrons/cm², and the integrated neutron flux (nvt), neutrons/cm² X time (sec), are measured in terms of "barns," in which one barn = 10^{-24} cm²/nucleus. A unit commonly used is megawatt days per central ton, (MWD/ct = 3 X 10^{17} nvt).

When either single-crystal or polycrystalline alpha aluminum oxide was subjected to 2 X 10^{20} nvt of radiation, no change was observed in the X-ray pattern or in thermal conductivity (Johnson, 1957). A color change, probably an F-center phenomenon, was observed.

Nuclear radiation data reported by Way (1950) for aluminum is as follows: absorption (σ_a) 0.23 barn; scattering (σ_s), 1.5 barns; average loss in natural logarithm of energy in a collision (ξ), 0.070; slowing down power ($N\sigma_s\xi$), 0.0056; moderating ratio (σ_s/σ_a)ξ, 0.47. N = the number of nuclei per cubic centimeter.

Antal and Goland found that fast-neutron irradiation of sapphire at temperatures below 40°C resulted in little damage, but some volume expansion. The defects were only about one-fortieth the predicted number, believed to have been caused in part by Al-O vacancy pairs. Annealing at 400 to 1250°C produced no decrease in the damage, or in neutron scattering and discoloration beyond 1250°C. Annealing at 1800°C did not remove the coloring, but the density returned to its pre-irradiation value. Levy concluded, in the case of glasses, that each of three optical absorption bands produced by gamma radiation was associated with a specific oxide component of the glass. The effects on the absorption spectrum of additions of alumina to the glass, suggested that the aluminum atom replaces the silicon atom in the glass network.

Berman, Bleiberg, and Yeniscavich determined that alumina and zircon show little change in properties when exposed to 10^{18} to 10^{19} nvt of thermal neutrons. When, however, a source of fission fragments is provided in the form of a UO₂ dispersant, the grain boundaries and the peaks of the X-ray diffraction pattern disappear on irradiation. The alumina was observed to increase about 30% in volume concurrent with the destruction of its crystal lattice. Apparently only a small proportion of the atoms were displaced by elastic collisions or other applicable mechanisms, but more probably indirectly through anisotropic effects which distorted the lattice and made it unstable. Several ceramic materials having the cubic structure exhibited better stability against fission fragment recoil. Berman, Foster et al. (1960) measured the thermal conductivity both of single-crystal synthetic sapphire and of polycrystalline specimens at 2 to 100°K, before and after gamma ray and reactor

irradiations. The reactor irradiation introduced two types of defects that influenced the thermal resistivity. The gamma radiation also induced an extra thermal resistivity at low temperatures which seemed to depend on the initial crystal imperfections.

Compton and Arnold claimed that lattice defects cannot be generated in alpha-alumina by low-energy ionization processes; fast electrons with energy less than 0.37 Mev cannot generate the lattice defects responsible for the optical absorption band appearing at 0.205 micron. Three Gaussian-shaped optical absorption bands were induced in calcium-boron-aluminum (cabal) glasses by gamma rays, with their maxima at 0.550, 0.350, and 0.250 micron (2.3, 3.5, and 5.0 ev). The intensity of the 0.350 micron band increased with increasing Al_2O_3 content in the glass (Bishay).

McChesney and Johnson (1964) observed the effect of fast-neutron irradiation on the dielectric constant (k') and the dissipation factor (tan δ) of polycrystalline alumina (Coors AD-995) at one Mc/sec. Irradiation to 6 X 10^{17} and 2 to 5 X 10^{19} fast neutrons/cm² at 95°C and 47°C, respectively, caused a slight decrease in k' with the treatment. The dissipation factor rose sharply for doses of this range, but decreased for higher doses.

C. G. Young (1962) investigated the radiation effects in alpha alumina by electron-spin resonance. Y. R. Young (1957) measured the energy distribution of electrons penetrating thin specimens of sintered alumina. For a given bombarding energy, the average loss per unit thickness remained almost constant over the entire depth of penetration, but this loss factor decreased slowly as the bombarding energy increased. The effects of radiation on the physical properties of alumina and other refractory single oxides are given in detail in Effects of Radiation on Materials and Components (Editors Kircher, J. F. and Bowman, R.E.) Reinhold Publishing Corporation, New York 1964.

McCreight found that a composition containing 1 part BeO to 1 part Al_2O_3 had remarkable resistance to corrosion by sodium metal at 500°C, only 0.0003 mg/cm²/month. This was considered as a container material in reactant cooling. Gangler (1954) showed that single component ceramic materials such as Al_2O_3 were far superior to most metals in resisting attack by such heat-transfer agents as molten lead-bismuth alloys. Hahn and VanderWall found that lead chloride ($PbCl_2$) rapidly dissolves zirconium and uranium-zirconium alloys at 510°C, allowing consideration of alumina as a container material.

Primak and associates, Kreidl and associates, and Lukesh reported the damage to glasses, silica, and silicon carbide. In some cases devitrification, metal precipitation, and expansion as great as 3.7% occurred in nuclear irradiation.

Gift (1957) described the use of a bed of 0.5-in. silvered alundum Raschig rings in a homogeneous reactor (HRT). During operation, a steam-gas mixture entering the bed was dried by a steam coil preceding the bed. The purpose of the bed was to remove iodine, a poisoner of the recombiner catalyst. During shutdown, it was necessary to remove decay heat for about 10 hours by a combination of steam flow and internal cooling of the bed by water-jacketed annuli. Richt examined by metallographic methods $Cr-Al_2O_3$ cermet specimens that had been previously irradiated to about 10^{20} nvt (thermal). The cermets showed no evidence of structural changes alone, but when fueled with UO_2 and irradiated to 2.53×10^{20} nvt at 1000°C, changes were observed.

Elleman et al. measured the height of the expansion step at the boundary between irradiated and unirradiated regions when fission fragments were recoiled into flat alumina specimens. Expansion normal to the exposed surface was independent of crystal orientation for specimens of sapphire cut along three different axes. Expansion was not a linear function of fission-fragment concentration. Radiation expansion coefficients, calculated from the expansion normal to the surface were at least three times larger than those calculated from the bending moment of thin fission-fragment-irradiated disks. It was concluded that fission-fragment-induced expansion is not isotropic, but that the stresses are preferentially relieved by expansion normal to the free surface.

Smalley, Riley, and Duckworth investigated the preparation of an alumina-clad uranium nuclear fuel. A special, high-purity, sinterable alumina powder was applied to unsintered uranium oxide pellets by a spraying-tumbling method followed by isostatic pressing and sintering in hydrogen. Crack-free, spheroidal pellets (1000 to 2000 microns diameter) with a sintered alumina coating (300 to 500 microns) of near theoretical density were sufficiently impervious to prevent oxidation of the uranium for at least 100 hours at 1200°C. No measurable release of fission products was observed at 927°C in vacuum for seven days after exposure to 6.0×10^{12} nv for one hour at room temperature.

Whittemore (1963) claimed a method comprising surrounding a refractory metal core including a radioactive material with a ceramic sheath, molded around the core, and firing the composite to an impervious integral nuclear fuel element. Oel discussed ceramic materials for breeders, moderators, reflectors, control rods, shielding, and construction elements for thermoelectric power generation.

The radioactive wastes from nuclear power generation comprise such materials as salts of cesium, strontium, and ruthenium, which require from 600 to 1000 years half-life. A

potential method for segregating these salts comprises reacting them in silica-alumina gels to form zeolites or preferably non-base-exchange silicates. The waste materials have a nominal thermal energy of about 5 watts/gal. (Warde 1955).

Fleshman conducted tests to determine the leaching effect of rainwater on buried radiation-contaminated alumina. When the acid-leached alumina was treated with caustic soda before burial, the uranium contamination was converted into an insoluble diuranate which was absorbed by the alumina. Bridoux used sintered aluminum powder (SAP) as a canning material, but found (1) diffusion of fission products into the SAP, (2) the appearance of cracks from prolonged heating, and (3) poor ductility of the SAP, particularly in tubes that receive no support from the fuel. At 400 to 500°C, however, the creep strength of SAP is comparable to that of beryllium and is hence acceptable.

Dalmai et al. found that the catalytic activity of activated gibbsite (as measured by the decomposition of formic acid) is increased when the gibbsite has been irradiated with gamma rays or neutrons. Tsitsishvili and Sidamonidze similarly found that fast neutron and gamma radiation increased the catalytic effect of aluminum hydroxide and gamma alumina in the adsorption of water and benzene at 25°C, and in the dehydrogenation of iso-propyl alcohol. The phase composition is unaffected.

Schwab and Conrad found that irradiation of alumina with reactor neutrons affected the rate of conversion of para hydrogen. Bogoyavlenskii and Dobrotvorskii stated that the incorporation of Na_2 [185]WO_4 into the anodic film on aluminum (duralumin) in the course of formation caused the specific surface radioactivity, i, of the alumina film formed to increase proportional to the duration of anodization t, with the anodic current density, D_a, and with the specific radioactivity of the solution, X. Empirically, $i = a \log t + b$, and $\log i = -1.85 - 0.67/D_a$. When the temperature was increased from 20 to 25°C, i decreased very rapidly, and finally, asymtotically, to zero at 35°C.

Gorodishcher and Mashneva removed [32]P from drinking water by adsorption in aluminum hydroxide gel from concentrations from 7×10^{-8} to 8×10^{-7} curies/liter. The activity of the clarified water was reduced to the maximum permissible dose of $(0.82 \text{ to } 2) \times 10^{-8}$ curies/liter.

The chemical properties of alumina may be separated arbitrarily into two general classifications (1) hydrothermal and (2) thermal. Phase Diagrams for Ceramists, Levin, Robbins, and McMurdie (1964) contains 132 phase diagrams involving Al_2O_3 as a component, of which 17 also contain H_2O. Early very complete references to the chemical properties of alumina include: Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry (1924), and Gmelin, Aluminum Vol II (1934). More recent accounts can be found in Chemical Background of the Aluminum Industry, J. G. Pearson (1955); Encyclopedia of Chemistry, Clark and Hawley (1957); Encyclopedia of Chemical Technology, Kirk and Othmer (1947, 1957); Progress in Inorganic Chemistry, Vol I (1959); and Handbook of High Temperature Materials: No. 2, Properties Index, Samsonov (1964).

Chemical reactions of alumina of general ceramic interest include the resistance to attack of sintered alumina by various reagents, particularly at high temperatures. High-temperature chemistry includes those chemical phenomena which occur above 1000°C. Such temperatures are attained by combustion, by electrical heating, or by chemical explosions and nuclear reactions (Margrave, 1962). The high-alumina regions of the phase diagrams are of particular interest in interpreting the influence of additives on the sintering behavior and refractory properties of polycrystalline alumina. Equilibrium is probably more nearly realized in these cases than is usually expected in the practical application of the phase diagrams in general (W.R. Foster, 1951). Of the ten large-scale phase diagrams selected for publication by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation (1960), five include Al_2O_3 as a component, namely: $CaO-Al_2O_3-SiO_2$, $MgO-Al_2O_3-SiO_2$, $Na_2O-Al_2O_3-SiO_2$, $K_2O-Al_2O_3-SiO_2$, and $FeO-Al_2O_3-SiO_2$.

Wygant and Kingery (1952) discussed the stability of ceramic oxides in terms of the equilibrium oxygen pressure, in the case of $a-Al_2O_3$ about 10^{-184} atm. The stability at 298°K (the free energy of formation per gram atom of oxygen) = -125,600 cal. The order of increasing stability for some refractory oxides on this basis is as follows: $1/2\ ZrO_2$, $1/3\ Al_2O_3$, BaO, MgO, BeO, CaO, $1/3\ Y_2O_3$, $1/3\ La_2O_3$, and $1/2\ ThO_2$. From heat content, entropy, and heat capacity data, they concluded, for example, that sintered alumina would not be a suitable container material for molten calcium metal at 1200°K. Contrariwise, Jaeger and Krasemann (1952) found by actual experiment that calcium, strontium, and barium are inert in contact with sintered alumina to their boiling points. Tripp and King (1955) prepared graphs of the variation in free energy of the various ceramic oxides of interest, in order to simplify the use of such information. Fiegel, Mohanty, and Healy (1962) have investigated the equilibrium of

the refractory metal oxides. Gulbransen and Wysong (1949) measured the rate of formation of amorphous alumina from purest aluminum and oxygen at about 8 micrograms/cm²hr at 500°C, or a thickness increase of 400 Å/hr. The activation energy was 22.8 kcal/mole, and the entropy of activation was -26 cal/mole deg.

12-1 WET CHEMICAL REACTIONS OF SINTERED ALUMINA

Impermeable polycrystalline alpha alumina has marked resistance to wet chemical corrosion. As a rule, the lower phases of alumina and the hydrous aluminas show increasing chemical reactivity as they decrease in density. Early experiments on the resistance of sintered alumina to attack were intended to demonstrate its suitability as a container, crucibles, etc., for thermal reactions (Winzer, 1932). Concentrated H_2SO_4, HCl, HNO_3, H_3PO_4, and 20% NaOH dissolved no more than 0.02% of a 30 X 35 mm crucible within six hours, as indicated by loss in weight of the crucible. This is not necessarily indicative of chemical inertness, as for example, phosphoric acid readily reacts even with coarsely crystalline tabular alumina to form slowly soluble phosphate bonds at temperatures below the boiling point of the acid.

Finely divided alpha alumina is rapidly dissolved by HF, hot concentrated H_2SO_4, mixtures of these acids, ammonium fluoride, molten alkali bisulfates or pyrosulfates, and by concentrated HCl, especially when under pressure. All these reagents have been used to dissolve alumina in analytical procedures. Sintered alumina dissolves in concentrated H_2SO_4 faster than some high-alumina porcelains containing clay binders (85% Al_2O_3). Karpacheva and Rozen found that the densest sintered alumina reacts with water, even at temperatures as low as 200°C. With heavy water, $H_2{}^{18}O$, the following reaction rates, as percent reaction within 80 minutes, were observed:

Temp °C	200	400	600	900
Rate (%/80 min)	20	30	50	97

Hot-water solutions of the free alkali hydroxides and carbonates cause perceptible reaction, the rate being correspondingly faster at higher temperatures and under pressure.

Jaeger and Krasemann (1952) extended the earlier work of Winzer on the resistance to corrosion of sintered alumina crucibles. In many instances, the weight loss estimates were based on multiple tests. Crucibles lost little weight on successive heating, but in many cases after treatment with acid, especially with 1:1 hydrochloric acid, they shattered on subsequent heating as a result of intercrystalline attack. In general, attack by the alkali oxides was very aggressive, but sodium oxide could be contained in alumina at 1350°C. The order of decreasing attack for alkaline melts was Na_2O, $Na_2S_2O_7$, Na_2O_2+KOH, Na_2CO_3+KNO_3, Na_2CO_3+S, NaOH, Na_2CO_3, K_2CO_3, and $NaKCO_3$. Ashed precipitates

showing an adherence to sintered alumina include SiO_2, Al_2O_3, $BaSO_4$, CaO, BeO, SnO_2, ZnO, and graphite. Little adherence was shown by Fe_2O_3, Cr_2O_3, or $CaSO_4$. The sulfides, MnS and CuS were strongly fluxed, and also $Mg_2P_2O_7$.

12-2 REACTION OF THE CHEMICAL ELEMENTS WITH ALUMINA

Ryshkewitch (1960, p 177) discussed the chemical properties of sintered alumina, particularly in its applications as a high-temperature container material for various chemical reactions. Norton and Kingery (1952), Norton, Kingery, Economos, and Humenik (1953), and Reed (1954) have investigated high-temperature metal-ceramic reactions. Lyon (1954) assembled the available data on the corrosion of alumina and other prospective materials by low-boiling metals and alloys that might be suitable for high-temperature heat exchange systems. Gangler determined the corrosion resistance of 18 ceramic compositions and cermets to molten lead-bismuth alloys.

Some reactions of interest between the various chemical elements and sintered alumina are shown in the following references. These are discussed in alphabetical order, in general, for convenience of reference.

Alkali Metals

Ryshkewitch (1960) stated that molten lithium attacks alumina aggressively, potassium to a lesser degree, and sodium the least. Reed claimed that the corrosion resistance of sintered alumina to both liquid and vaporized sodium is good at 900°C. A commercial sintered alumina article disintegrated within 168 hours at 940°C, however. A synthetic sapphire cylinder (1/4 in. diameter by 1 in. length) lost about 1% in weight in 168 hours at 900°C but remained clear. Kelman, Wilkinson, and Yaggee found that sodium-potassium did not attack below 500°, but caused corrosion at 600°C. The behavior of vaporized alkali metals on oxides and other dielectric materials has been of interest for thermoelectric converters. Wagner and Coriell (1959) tested Al_2O_3, BN, ZrO_2, MgO, HfO_2, ThO_2, CaO, and NbC to exposure to cesium vapor at temperatures as high as 1475°C. Only fused alumina remained unaffected by the test. It was concluded that cesium probably reacts with impurities in the contacting material, but the effect could be observed only when the surface areas available for reaction are relatively large, as is the case with sintered specimens. C. E. Adams (1959) investigated the condensation of rubidium vapor onto hot oxide surfaces and found that rubidium effectively condensed at high temperatures only on oxides with which it could form stable complex compounds. Cowan and Stoddard (1964) stated that glasses could not be used in thermionic converter seals because of alkali metal (cesium) corrosion. Small additions of yttria (from 0.05 to 2% Y_2O_3) in sintered alumina provides a bonding strength with tungsten of 4

to 10 kpsi at 1600 to 1800°C metallizing temperature. The
yttrium garnet provides the grain boundary phase between the alu-
mina and tungsten.

Alkaline Earth Metals

Jaeger and Krasemann (1952) observed no reaction of calcium,
barium, or strontium to their boiling points (about 1150°C).
This is likely, since BaO and SrO can be reduced to the metals
(thermite reaction) by metallic aluminum at 1100°C in a vacuum
(Gvelisiani and Pazukhin). Magnesium also shows no attack to its
boiling point (1110°C).

Aluminum

Aluminum reacts at 1100°C to form Al_2O, and at 1600°C to
form AlO (Hoch and Johnston).

Antimony, Arsenic

Jaeger and Krasemann claimed no attack.

Beryllium

Beryllium (m.p. 1500°C) shows no attack below 1600°C. A
slight darkening of the alumina, caused by formation of an inter-
facial layer of chrysoberyl occurred at 1800°C (Economos and
Kingery).

Bismuth

The corrosion resistance is good to 1400°C (Reed).

Carbon

Carbon reduces Al_2O_3 to the carbide, Al_4C above 1700°C
(Jaeger and Krasemann), above 1450°C (Komarek et al.).

Chlorine

Chlorine does not attack, except in the presence of carbon
(Singer and Thurnauer).

Chromium

Chromium wets alumina at 1650°C in a reducing atmosphere
(Blackburn, Shevlin, and Lowers).

Cobalt

Cobalt neither wets nor reacts with sintered alumina to
above its melting point (1480°C) in a reducing atmosphere
(Sieverts and Moritz; Tumanov et al.).

Fluorine

Winzer claimed attack at 1700°C.

Gallium

Alumina is inert to gallium to 1000°C (Kelman et al.).

Hydrogen

No reduction occurs at the melting point of Al_2O_3. Surface darkening is produced (Jaeger and Krasemann).

Iron

Iron can be melted in sintered alumina under reducing conditions, but wets at about 1600°C (Blackburn et al.).

Lead

No reaction occurs at the melting point. In lead-bismuth eutectic alloy (44.5% Pb), Gangler found 0.000 mils/year disintegration at 1090°C.

Lithium (see alkali metals)

Manganese

There is no attack to above the melting point (1260°C) in a reducing atmosphere. Manganese is more active than iron, cobalt, or nickel, but can be distilled to give a spectrographically pure product in sintered alumina (Sieverts and Moritz).

Mercury

Kelman et al. found no reaction with mercury at 300°C.

Molybdenum

Alumina is not reduced by molybdenum even above the melting point of the alumina. Discoloration may occur at 2100°C in a dry, inert atmosphere (He).

Nickel

No attack occurs in dry inert atmosphere. Nickel can be melted in sintered alumina in hydrogen atmosphere (Economos and Kingery). Wetting occurs at 1800°C.

Nitrogen

Nitrogen does not attack (Jaeger and Krasemann).

Palladium, Platinum

Both metals can be handled in the molten condition in sintered alumina (Jaeger and Krasemann).

Phosphorus

No attack was observed at moderate temperature (Jaeger).

Sulfur, Selenium, Tellurium

These elements do not attack alumina.

Tin

No reaction occurred in molten tin at 1000°C.

Titanium, Zirconium

No reaction occurred in an inert atmosphere below 1800°C, at which temperature black discoloration of the grains and corrosion occurred (Economos and Kingery).

Tungsten

Jaeger and Krasemann observed no reaction between tungsten and sintered alumina. Wallace et al. (1961) investigated the reactions in a Knudsen cell-oven operable at 2500°C in conjunction with a Nier-type mass spectrometer. Jaccodine (1960) observed a growth of nodules or hillocks of alumina in the investigation of heater-cathode breakdown of alumina-coated heaters operated at 1200°C and 180 volts dc.

Uranium

Jaeger and Krasemann found no reaction to 1200°C.

Titanium + Aluminum-Hardened Nickel-Base Alloy

Decker, Rowe, and Freeman found that trace amounts of zirconium or boron picked up from zirconia or magnesia crucibles reduced cracking of the hardened nickel-base alloys during hot-working and increased their rupture strength and ductility. It was desirable to compensate for this effect when making heats in sintered alumina crucibles.

12-3 METAL OXIDE SYSTEMS

Several metal oxide phase diagrams in which Al_2O_3 is one component are described briefly in this section. The arrangement, as far as practical, is the same as has been used by Levin, Robbins, and McMurdie in classifying Phase Diagrams for

(1964). The order of writing the oxides of a compound or the components of a system is according to increasing valence, and alphabetical order. The diagrams are also arranged on the same basis, and with increasing complexity and number of components.

FeO-Al$_2$O$_3$

The development of oxidation-resistant iron-aluminum alloys has led to an interest in cermets composed of these alloys and aluminum oxide (1958). The pseudobinary system FeO-Al$_2$O$_3$ was described by McIntosh, Rait, and Hay (1937). The hypothetical phase 3FeO·Al$_2$O$_3$, suggested by them, does not exist (Fischer and Hoffmann). A eutectic exists between wüstite (FeO) and hercynite (FeAl$_2$O$_4$) at 1330°C, and a questioned eutectic between the spinel (FeAl$_2$O$_4$) and Al$_2$O$_3$ at 1750°C. Limited solid solution (~6%) occurs between the spinel and Al$_2$O$_3$ at 1750°C. The FeO dissolves about 3% Al$_2$O$_3$ in solid solution. Two compounds were identified, 3FeO·Al$_2$O$_3$ and FeO·Al$_2$O$_3$.

Fe$_2$O$_3$-Al$_2$O$_3$

Investigation of the system Fe$_2$O$_3$-Al$_2$O$_3$ by Muan and Gee (1956) and Muan (1958) revealed that the phase Fe$_2$O$_3$·Al$_2$O$_3$ is unstable relative to the phase assemblage hematite solid solution plus corundum solid solution below 1318°C. Limited solid solution exists between the phase Fe$_2$O$_3$·Al$_2$O$_3$ and corundum at about 1500°C at one atmosphere of oxygen, decreasing with decreasing oxygen pressure.

FeO-Al$_2$O$_3$-Fe$_2$O$_3$

Richards and White (1954), Atlas and Sumida (1958), and Turnock and Lindsley investigated the spinel regions of this system. Complete solid solution between FeAl$_2$O$_4$ and Fe$_3$O$_4$ spinels was observed. The alumina dissolves up to 12% (wt) Fe$_2$O$_3$ in neutral (argon) or low-oxygen atmospheres at 1370 to 1380°C, but up to 18% at one atm. oxygen. Hoffman and Fischer observed a decrease in the lattice constants of the spinel structures, dependent on firing temperature: 8.164 to 8.187 Å at 650 to 800°C, 8.150 Å at 1500°C, and 8.100 Å at 1800°C. This was ascribed to evaporation of up to 2.5% FeO at 1800°C and to disordering of the "normal" spinel structure, in which some Fe^{2+} ions occupy octahedral lattice sites and some Al^{3+} ions occupy tetrahedral positions. The wüstite varies in composition from 23.10 to 25.60% oxygen, and dissolves up to about 0.5 to 1% Al^{3+}. The compound Fe$_2$O$_3$·Al$_2$O$_3$ has the kappa alumina structure, and requires above 1320°C to prepare. Oxygen dissociation occurs below one solidus (spinel-Fe$_2$O$_3$-Al$_2$O$_3$) and another in which melting occurs without significant oxygen loss (Fe-spinel-Al$_2$O$_3$-Al). Turnock and Eugster (1962) observed the change in cell edge a_0 from 8.391 (magnetite) to 8.15 (hercynite) by the equation: $a_0 = 8.391 - 0.00190X - 0.5 X^2 10^{-5}$, in which X is the mole percent FeAl$_2$O$_4$ in solid

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solution. Hercynite is a rare mineral because it requires a relatively low oxygen pressure, and an extremely Fe-Al-rich environment.

$Al_2O_3-Cr_2O_3-Fe_2O_3$

Muan and Somiya found only the hexagonal corundum structure below 1318°C at one atm. pressure in the subsolidus phase relations of the system $Al_2O_3-Cr_2O_3-Fe_2O_3$. Between 1318 and 1410°C in air, and between 1318 and 1495°C at one atm. oxygen pressure, the monoclinic phase $Fe_2O_3 \cdot Al_2O_3$ with some Cr_2O_3 in solid solution was present. Above 1380°C in air and 1445°C at one atm. oxygen, a complex spinel solid solution developed.

$Cu_2O-Al_2O_3$

The compound, $Cu(AlO_2)_2$ forms at about 800°C, presumably by a solid-state reaction, and it is stable to about 1000°C in air. It then converts to $CuAlO_2$, stable to about 1260°C in air (Misra and Chaklader, 1963).

$Li_2O-Al_2O_3$

Hatch (1943) reported that the compound $Li_2O \cdot Al_2O_3$ is uniaxial negative with $\eta\omega = 1.624$, $\eta_\epsilon = 1.606$. A second phase, $LiAl_5O_8$, or $Li_2O \cdot 5Al_2O_3$, is the spinel, previously described as zeta alumina. This latter fluoresces when activated with Fe_2O_3, whereas corundum and $Li_2O \cdot Al_2O_3$ do not. It shows an order-disorder transition between 1200 and 1300°C. The compound $Li_2O \cdot Al_2O_3$ melts at 1610°C, as determined in a rapidly heated strip furnace (Hummel, Sastry, and Wotrinz, 1958; Strickler and Roy, 1961). Vaporization of Li_2O proceeds at an appreciable rate at 1400°C, as indicated by the fluorescence.

$BaO-Al_2O_3$ and $BaO-CaO-Al_2O_3$

Purt (1960) shows eutectics for the system $BaO-Al_2O_3$ at 1875°C (16% BaO), 1620°C (38% BaO), 1480°C (76.5% BaO), and 1425°C (84% BaO). Solid compounds include: $BaO \cdot 6Al_2O_3$ (m.p. 1915°C), $BaO \cdot Al_2O_3$ (m.p. 1815°C), and $3BaO \cdot Al_2O_3$ (m.p. 1425°C). Wallmark and Westgren found that $BaO \cdot Al_2O_3$ has a hexagonal unit cell, a = 5.209, c = 8.761 Å, containing two molecules in the space group $D_6^6 = C6_32$. The phase $BaO \cdot 6Al_2O_3$ is also hexagonal, a = 5.577, c = 22.67 Å and isomorphous with beta alumina containing other metal oxides. Avgustinik and Mchedlov-Petrosyan and Smirnov et al. (1949) observed that the conversion of a 1:1 mixture of $BaSO_4$ and Al_2O_3 proceeds noticeably above 1200°C, is accelerated greatly at 1300°C, but does not reach completion at 1400°C. The reaction is impeded by the large energy of separation, which was 170, 240, and 260 kcal/mole for 1:1, 2:1, and 3:1 mixtures, respectively. The addition of 5% CaF_2 promoted the reaction at these temperatures.

Peppler and Newman (1951) determined the heats of formation of various barium aluminate phases from the heats of solution in HCl.

Calvet, Thibon, and Dozoul (1964) claimed to have produced $2BaO \cdot Al_2O_3$ by precipitating stoichiometric proportions of the two chlorides in ammoniacal $(NH_4)_2CO_3$ solution, and heating at 1200 to 1300°C. $2BaO \cdot Al_2O_3 \cdot 4$ to $5H_2O$ was formed by boiling aluminum shavings in $Ba(OH)_2$ solution.

Massazza (1963) observed that the neutron absorption cross-section of hydraulic cements containing BaO is 3 times that of CaO, 6 times that of Al_2O_3, and 9 times that of SiO_2. The ternary diagram of the solid phases of the $BaO-CaO-Al_2O_3$ system was arbitrarily subdivided into 6 adjacent zones corresponding to aluminates of calcium or barium. The first zone contains Al_2O_3, $CaO \cdot 6Al_2O_3$, $BaO \cdot 6Al_2O_3$, and some solid solutions; the second zone contains $BaO \cdot 6Al_2O_3$, $CaO \cdot 6Al_2O_3$, and $CaO \cdot 2Al_2O_3$, and some solid solutions; the third zone contains $BaO \cdot 6Al_2O_3$, $CaO \cdot 2Al_2O_3$, $CaO \cdot Al_2O_3$, and $BaO \cdot Al_2O_3$, and limited solid solutions; the fourth zone contains $CaO \cdot Al_2O_3$, $BaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, the latter compound in equilibrium only at 1400°C. The fifth zone contains $BaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $3CaO \cdot Al_2O_3$; and the sixth zone $BaO \cdot Al_2O_3$, $3CaO \cdot Al_2O_3$, CaO, and $3BaO \cdot Al_2O_3$. The ternary diagram generally corresponds to an isothermal section at 1400°C.

$BeO-Al_2O_3$

Lang, Fillmore, and Maxwell (1952), and Galakhov (1957) described the system $BeO-Al_2O_3$. The system has three eutectics: about $BeO:4Al_2O_3$ (94.2 wt % Al_2O_3), melting at 1890°C; about $2BeO:3Al_2O_3$ (85.9% Al_2O_3), melting at 1850°C; and 75 wt % Al_2O_3, melting at 1835°C. The system also contains two congruently melting compounds: $BeO \cdot 3Al_2O_3$ (92.4 wt % Al_2O_3), melting at 1910°C, and chrysoberyl, $BeO \cdot Al_2O_3$ (80.3% Al_2O_3), melting at 1870°C. In the alumina-rich end of the diagram, Al_2O_3 is in equilibrium with liquid to its melting point.

$CaO-Al_2O_3$

The system $CaO-Al_2O_3$ might be taken as an example of the direct application of a phase diagram to the production of a commercial product, high-purity calcium aluminate cement. When this product is prepared from low-iron, low-silica Bayer alumina and native limestone of available purity, the product has substantially the same thermal behavior as is predicted by the ideal phase diagram.

Lea and Desch (1956) described the generally accepted form of the phase diagram of the $CaO-Al_2O_3$ system. Filonenko and Lavrov (1950), and Wisnyi (1954), among others, have reappraised the solidus and liquidus curves in the high-alumina portion of

the system, the latter by synthesizing homogeneous single crystals of CaO·Al$_2$O$_3$, CaO·2Al$_2$O$_3$, and CaO·6Al$_2$O$_3$ (Filonenko's phase). Boyco and Wisnyi obtained the following data:

CaO·2Al$_2$O$_3$ Melting point 1745° ± 15°C, congruent; crystals monoclinic; unit cell a = 12.889, b = 8.879, c = 15.454, β = 107.4, type C 2/c; density 2.880 g/ml (calculated); refractive index a = 1.6178, β = 1.6184, γ = 1.6516, biaxial positive.

CaO·6Al$_2$O$_3$ Melting point 1820° ± 15°C incongruent (30% a-Al$_2$O$_3$, 70% liquid); crystals hexagonal; unit cell a = 5.566, c = 22.010, type C$_6$ 3/m; density 3.731 g/ml; refractive index ω = 1.763, ϵ = 1.754, uniaxial negative.

Buessem and Eitel (1936) found by X-ray appraisal that the previously so-called 5CaO·3Al$_2$O$_3$ is actually 12CaO·7Al$_2$O$_3$, having a calculated density of 2.69 g/ml, a unit cell cube edge of 11.95, and a probable space group T$_9^6$. Auriol, Hauser, and Wurm (1961) suggested 3CaO·16Al$_2$O$_3$ as the formula of the alumina-richest phase. The approximate melting points of the phases in the system are: 3CaO·Al$_2$O$_3$ 1535°C, 12CaO·7Al$_2$O$_3$ 1455°C, CaO·Al$_2$O$_3$ 1608°C, CaO·2Al$_2$O$_3$ 1770°C, and CaO·6Al$_2$O$_3$ 1860°C. Ampian (1964) reviewed the published optical, microscopic, and X-ray data for 3CaO·Al$_2$O$_3$, CaO·Al$_2$O$_3$, and 12CaO·7Al$_2$O$_3$. Polymorphism has not been observed for these compounds.

Roth and Wolf obtained the following heats of formation for two phases: 12CaO·7Al$_2$O$_3$, -11.1 kcal at 20°C; 3CaO·Al$_2$O$_3$, 3.9 kcal at 20°C. Babushkin and Mchedlov-Petrosyan prepared equations and a chart for determining the variations in free energy as a function of temperature for ten possible reactions in the system.

Brcic et al. (1962) found that only 5CaO·3Al$_2$O$_3$ is formed at 400 to 600°C when a-Al$_2$O$_3$, boehmite or bayerite is reacted with CaO-Ca(NO$_3$)$_2$. Uchikawa, Tsumagari, and Koike stated that 3CaO·Al$_2$O$_3$ is the first compound formed regardless of the proportions of the mix, when CaCO$_3$ and a-Al$_2$O$_3$ are heated at 800 to 1000°C. Andouze claimed that an orthorhombic form of 5CaO·Al$_2$O$_3$ exists (stable above 950°C); CaO·Al$_2$O$_3$ begins to form at 900°C; and a cubic form has the composition 7CaO·12Al$_2$O$_3$. Calcium aluminates form mainly by diffusion of CaO into Al$_2$O$_3$. Except for the phase 2CaO·Al$_2$O$_3$, all the calcium aluminate phases cited in the literature could be prepared by reaction of CaO and Al$_2$O$_3$ at 900 to 1600°C.

CdAl$_2$O$_4$, CdAl$_2$S$_4$, CdAl$_2$Se$_4$, HgAl$_2$S$_4$, HgAl$_2$Se$_4$, ZnAl$_2$Tr$_4$, CdAl$_2$Te$_4$

Hahn, Frank et al. (1955) stated that only CdAl$_2$O$_4$ of the compounds in this group has the spinel structure on heating mixtures of the appropriate oxides. The others usually form in the tetragonal system. No compound with Hg$_2$O is possible. Only the compounds CuAlO$_2$ and CuGaO$_2$ could be prepared by reaction of Cu$_2$O with Al(OH)$_3$ or Ga$_2$O$_3$ at higher temperatures. Both compounds crystallize in the hexagonal (rhombohedral) system, space group

D_{3d}^5 - R $\bar{3}$ m. No compounds with Ag_2O could be prepared.

$MgO \cdot Al_2O_3 - Al_2O_3$

Kanolt determined the melting point of MgO at 2800°C, re-determined by McNally, Peters, and Ribbe (1961) at 2825°C. Rankin and Merwin (1916) melted spinel ($MgAl_2O_4$) at 2135°C, and the eutectic (about 45 wt % MgO, 55% Al_2O_3) at 2030°C. These have been redetermined by Alper, McNally, Ribbe, and Doman (1962) at 2105°C and 1995°C, respectively, using Alcoa A-14 (99.8% Al_2O_3) as the alumina source, and Mallinckrodt magnesia (99.85% MgO). They also confirmed that the maximum solid solution of aluminum ions in periclase (MgO) is about 9.5% Al^{3+} (82 wt % MgO, 18% Al_2O_3). The maximum solid solution of magnesium ions in spinel is about 6% Mg^{2+} (39% MgO, 61% Al_2O_3). The periclase and spinel solid solutions were found to exist stably at temperatures above about 1500°C.

Geller, Yavorsky et al. obtained 80 to 90% spinel by reacting the intimately mixed oxides at 1650°C, but did not obtain complete sintering at 1900°C. They found the T_e value (temperature determinant of resistivity) to be 1170°C. Roy, Roy, and Osborn (1953) found that the subsolidus reactions are greatly accelerated in the presence of an aqueous phase at high pressures.

$MnO - Al_2O_3$

The system $MnO - Al_2O_3$ has a single eutectic containing about 25% Al_2O_3 (approximately 4 $MnO \cdot Al_2O_3$) and melting at 1520°C. The compound $MnAl_2O_4$, a spinel, is stable in the region 1520 to 1560°C (Hay, White, and McIntosh (1934-35).

$Mn_2O_3 - Al_2O_3$

Ranganathan, MacKean, and Muan found three isobaric (atmospheric pressure) invariant situations as follows: tetragonal Mn_3O_4 solid solution (91% Mn_2O_3, 9% Al_2O_3), Mn_2O_3 solid solution (85% Mn_2O_3, 15% Al_2O_3), corundum, and gas (p oxygen = 0.21 atm.), coexisting in equilibrium at 881°C; tetragonal Mn_3O_4 solid solution (84% Mn_2O_3), 16% Al_2O_3), spinel solid solution (62% Mn_2O_3, 38% Al_2O_3), corundum, and gas in equilibrium at 990°C; and spinel solid solution (27% Mn_2O_3, 73% Al_2O_3), corundum, liquid (37% Mn_2O_3, 63% Al_2O_3), and gas, coexisting at 1740°C.

$PbO - Al_2O_3$

Geller and Bunting (1943) investigated the lead-rich end of the binary, $PbO - Al_2O_3$, and concluded that the compound $PbO \cdot Al_2O_3$ exists (m.p. 865°C), unstable at temperatures above 970°C.

SrO-Al₂O₃

Massazza (1959) found the compounds β-4SrO·Al₂O₃ (stable between 1125 and 1575C), 3SrO·Al₂O₃ (m.p. 1660°C), SrO·Al₂O₃ (m.p. 1790°C), SrO·2Al₂O₃ (m.p. ~1850°C), and SrO·6Al₂O₃ (m.p. ~1920°C). Eutectics at 1630°C, 1505°C, 1760°C, and 1780°C conform with compositions containing about 27%, 32%, 56%, and 74% Al₂O₃, respectively. Toropov (1939) and Carlson (1955) determined the characteristics of the different crystalline phases. Wet-process 3SrO·Al₂O₃·6H₂O is isomophous with 3CaO·Al₂O₃·6H₂O, and a complete series of solid solutions exists between the two. The unit cell edge is 13.04 Å, and the index of refraction 1.588. The compound decomposes about 454°C (420 atm. vapor pressure) to 5SrO·4Al₂O₃, which decomposes on further heating to SrO·Al₂O₃ and 3SrO·Al₂O₃. Boyko and Wisnyi (1958) determined the melting point of SrO·2Al₂O₃ at 1770 ± 15°C.

ZnO-Al₂O₃

Bunting (1932) found the melting point of compositions in the ZnO-Al₂O₃ system to be constant at about 1950°C from about 20 to 60 mole % Al₂O₃. A minimum occurs at about 1710°C (82 mole % Al₂O₃). Huttig, Wörl, and Weitzer observed that the first reaction stage starts with the diffusion of the lattice unit of higher mobility on the surface of the lattice unit of lower mobility, enveloping completely the grains of the latter component.

Al₂O₃-B₂O₃

Kim and Hummel (1961, 1962) presented a tentative phase diagram for the Al₂O₃-B₂O₃ system, showing the compounds 2Al₂O₃·-B₂O₃ and 9Al₂O₃·2B₂O₃ (H. Scholze, 1956; Gielisse, Rockett et al.). The first melted at 1030°C incongruently, and the second at about 1440°C. The naturally occurring compound, jeremejevite (Al₂O₃·B₂O₃) was not observed.

Al₂O₃-Bi₂O₃

Levin and Roth (1964) divided the subsolidus region in the Bi₂O₃ end of the binary system to about 14 mol.% Al₂O₃ into approximately equal fields of monoclinic Bi₂O₃ + body-centered cubic phase, and body-centered cubic phase + Bi₂O₃·2Al₂O₃. The two regions are separated by a narrow band of 15 Bi₂O:Al₂O₃. The monoclinic Bi₂O₃ transforms to cubic Bi₂O₃ at about 730°C; the body-centered cubic phase transforms to cubic Bi₂O₃ at about 770°C. A eutectic, containing about 3 mol.% Al₂O₃, melts at 810°C.

Al₂O₃-Cr₂O₃

Bunting (1931) found that both Al₂O₃ and Cr₂O₃ are completely miscible in the liquid and solid states, and do not form

compounds. The melting point of Cr_2O_3 was redetermined to be $2275 \pm 25°C$. Chromium is trivalent in all mixed crystals. Thilo and coworkers found that the density increased sharply in the red color region with increasing chromia concentration to 8% and thereafter decreased. The lattice remained constant, however, in this region. Upon heating at 1300°C in hydrogen, chromium vaporized until 8% Cr_2O_3 was reached and held constant for more than 40 hours of heating. A similar relation was found to hold for the spinel $MgAl_2O_4$ combined with $MgO-Cr_2O_3$ spinels up to 15 mole % chromia spinel. The supposed discontinuity observed by Thilo et al. was thought to disprove Vegard's law that the lattice parameters of binary systems which form a continuous series of solid solutions are linearly related to the atomic percentage of one of the components (Zen; Spriggs and Bender; Sarver). Fang (1963) cited evidence to disprove the discontinuity near 8 mole % Cr_2O_3. Knapp (1953) used the $Al_2O_3-Cr_2O_3$ system as an example of a method of using free energy data in the construction of phase diagrams. The method described involves an assumption of ideal solution behavior, and is limited in application to systems in which the ideal solutions are approximated.

$Al_2O_3-Ga_2O_3$

At temperatures below 810°C, a compound, $GaAlO_3$, and a series of $(Al,Ga)_2O_3$ structures are stable. Above 810°C, continuous or nearly continuous solid solution characterizes both the $a-Al_2O_3$ and $\beta-Ga_2O_3$ components (Wartenberg and Reusch, 1932). Two regions of solid solutions: $a-Al_2O_3$ to 30 mol % Ga_2O_3, and $\beta-Ga_2O_3$ with up to 65 mol.% Al_2O_3. The melting point of Ga_2O_3 in air is 1795°C (Schneider and Waring), 1725°C (Hill, Roy, and Osborn).

$Al_2O_3-R_2O_3$ R = La, Nd, Sm, Eu, Gd, Dy, Ho, Y , Er, Tm, Yb, Lu, In, or Sc

Schneider, Roth, and Waring (1961) predicted the subsolidus for R_2O_3 types in this group, according to the following notation: A = A-type rare earth oxide, B = B-type rare earth oxide, C = C-type rare earth oxide; G = garnet; beta = beta alumina; P = perovskite; R = unknown, of rhombohedral symmetry; and alpha = alpha alumina; all concentrations shown as molecular ratios of R_2O_3 to Al_2O_3.

La_2O_3 Below 440°C, A+P (rhomb) for ratios 1:0 to 1:1, and P (rhomb) + beta for ratios 0.1: 0.9. Above 440°C to 1800°C, A+P (cubic) for ratios 1:0 to 1:1, and P (cubic) + beta for 0.1: 0.9. Beyond 0.1: 0.9, a mixture of beta and alpha.

Nd_2O_3 At all temperatures to 1700°C, A+P for ratios 1:0 to 1:1, and P + alpha for ratios 1:1 to 0:1.

Sm_2O_3 Below 800°C, B+P (orth) for ratios 1:0 to 1:1, and

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P (orth) + alpha for ratios 1:1 to 0:1. Above 800°C to 1700°C, B+P (rhomb) for ratios 1:0 to 1:1, and P (rhomb) + alpha for 1:1 to 0:1.

Eu_2O_3 At all temperatures to 1700°C, B+P for ratios from 1:0 to 1:1, and P + alpha for 1:1 to 0:1.

Gd_2O_3 At all temperatures to 1650°C, B + $2Gd_2O_3 \cdot Al_2O_3$ for ratios 1:0 to 2:1, $2Gd_2O_3 \cdot Al_2O_3$ for ratios 2:1 to 1:1, and P + alpha for ratios 1:1 to 0:1.

Dy_2O_3 At all temperatures to 1800°C, C + $2Dy_2O_3 \cdot Al_2O_3$ for ratios 1:0 to 2:1, $2Dy_2O_3 \cdot Al_2O_3$ + P for ratios 2:1 to 1:1, P+G for ratios 1:1 to 3:5, and G + alpha for ratios 3:5 to 0:1.

Ho_2O_3 At all temperatures to 1900°C, G + $2Ho_2O_3 \cdot Al_2O_3$ for ratios 1:0 to 2:1, $2Ho_2O_3 \cdot Al_2O_3$ + P for ratios 2:1 to 3:5, and G + alpha for ratios 3:5 to 0:1.

Y_2O_3 At all temperatures to about 1950°C, C + $2Y_2O_3 \cdot Al_2O_3$ for ratios from 1:0 to 2:1, $Y_2O_3 \cdot Al_2O_3$ + G below 1800°C for ratios 2:1 to 3:5, P + $2Y_2O_3 \cdot Al_2O_3$ for ratios 2:1 to 1:1 and P + G for ratios 1:1 to 3:5 both above 1800°C, and G + alpha for the complete temperature field from 3:5 to 0:1.

Er_2O_3 At temperatures to about 1700°C, C + $2Er_2O_3 \cdot Al_2O_3$ from 1:0 to 2:1, $2Er_2O_3 \cdot Al_2O_3$ + P from 2:1 to 1:1, P+G from 1:1 to 3:5, and G + alpha from 3:5 to 0:1.

Tm_2O_3 At temperatures to about 1900°C, C + $2Tm_2O_3 \cdot Al_2O_3$ from 1:0 to 2:1, $2Tm_2O_3 \cdot Al_2O_3$ + G from 2:1 to 3:5, and G + alpha from 3:5 to 0:1.

Yb_2O_3 At temperatures to 1900°C, C + $2Yb_2O_3 \cdot Al_2O_3$ from 1:0 to 2:1, $Yb_2O_3 \cdot Al_2O_3$ + G (ss) from 2:1 to nearly 3:5, a narrow region of G (ss), and G + alpha from 3:5 to 0:1.

Lu_2O_3 At temperatures to about 1850°C, C+G (ss) from 1:0 to nearly 3:5, G (ss) in the narrow region to 3:5, and G + alpha beyond 3:5.

In_2O_3 At temperatures to 1650°C, C (ss) in narrow range from 1:0 to 9:1, and C (ss) + alpha for remaining field.

Sc_2O_3 At temperatures to about 1800°C, C(ss) from 1:0 to about 0.87:0.13, C (ss) + R from 0.87:13 to 0.63:0.37, R (ss) from 0.63:0.37 to 0.4:0.6, and R (ss) + alpha from 0.4:0.6 to 0:1.

$Al_2O_3-Y_2O_3$

Warshaw and Roy (1959) state that three compounds exist in this system: $Y_2O_3 \cdot Al_2O_3$, $3Y_2O_3 \cdot 5Al_2O_3$, and $2Y_2O_3 \cdot Al_2O_3$, but only the latter two are stable. The compound $3Y_2O_3 \cdot 5Al_2O_3$ melts at 1970°C, and $2Y_2O_3 \cdot Al_2O_3$ at 2050°C. Pure Y_2O_3 in air melts at 2410°C (Int. 1948), as determined by Ruff and Lauschke. The compound, $3Y_2O_3 \cdot 5Al_2O_3$ is a garnet-type structure, which has drawn attention following the discovery of ferrimagnetism in the garnet structures. Keith and Roy (1954) investigated the crystal chemistry of the ABO_3 compounds, in particular 1:1 and 3:5 rare earth aluminates, ferrites, gallates, etc., as perovskites, garnets, and ilminitic structures. Under hydrothermal conditions, small euhedral dodecahedrons were prepared from $YAlO_3$ compositions. Aleshin et al. (1959) investigated solid solution in the garnet structure and neutron damage studies were made.

Curtis (1957) found that the cubic structure of Y_2O_3 is stable to 1800°C in air, as indicated by petrographic X-ray, and DTA analysis. The lattice parameter changed by less than 0.007 Å on heating to 1800°C. The mean specific heat of Y_2O_3 to 1600°C was 0.13 cal/g°C. The coefficient of linear expansion to 1400°C was 9.3×10^{-6} in./in.°C. Compacts of Y_2O_3 required 1800°C to vitrify. In equimolecular binary mixtures heated in the powdered state at 1500°C, Y_2O_3 formed compounds with Al_2O_3 or with Fe_2O_3, and solid solutions with ZrO_2 or HfO_2.

$Al_2O_3-Dy_2O_3$

Ploetz et al. (1960) observed three compounds in the system $Dy_2O_3-Al_2O_3$. These appeared predominantly in the molecular ratios 1:2, 1:1, and 3:1. The compound $Dy_2O_3 \cdot 2Al_2O_3$ was considered to be a body-centered cube with cell edge of 12.040 Å, melting point 1820°C, index of refraction 1.815, coefficient of linear thermal expansion 8.3×10^{-6}/°C from 30 to 1000°C. The values for the end members are 8.5×10^{-6} for Al_2O_3 and 8.3×10^{-6} for Dy_2O_3. The melting point of Dy_2O_3 is 2340°C (Int. 1948).

$Al_2O_3-SiO_2$

Many investigators, particularly Bowen and Greig, have contributed to the knowledge of this most important binary system. Aramaki and Roy (1962) have added revisions along the mullite-corundum boundary. From their version, a eutectic between SiO_2 and mullite $(3Al_2O_3 \cdot 2SiO_2)$ appears at about 5.0 mol.% Al_2O_3 and at 1595°C. With increasing Al_2O_3 content the liquidus curve shows a nearly continuous rise with increasing Al_2O_3 content, pointing up the remarkable improvement in aluminosilica refractories with increasing alumina content. A second eutectic, between mullite and corundum, is located at about 67 mol.% Al_2O_3 and 1840°C. Mullite melts congruently at about 1850°C. The extent of equilibrium solid solution in mullite at the solidus temperature extends from about 60 mol.% Al_2O_3 $(3Al_2O_3 \cdot 2SiO_2)$ to

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about 53 mol. % Al_2O_3. Solid solutions beyond this up to about 67 mol. % Al_2O_3 are metastable. No evidence was found for stable solubility of the excess SiO_2 beyond the compound $3Al_2O_3 \cdot 2SiO_2$ at pressures below 3 kbars. There is substantially no evidence of an equilibrium solubility toward sillimanite.

In the version of J. H. Welch (1960) the primary phase in the mullite region is approximately $2Al_2O_3 \cdot SiO_2$. It melts incongruently to corundum and a liquid. A peritectic point appears at about 1880°C and 75% Al_2O_3. At progressively lower temperatures $2Al_2O_3 \cdot SiO_2$ takes increasing amounts of SiO_2 into solid solution. The composition $3Al_2O_3 \cdot 2SiO_2$ was not expected as an equilibrium phase above the solidus temperature in this system.

DeVries (1964) found that kyanite melts incongruently above about 1500°C at 25 kbars to Al_2O_3 plus liquid. The pressure-temperature curves are substantially identical whether starting with 1:1 Al_2O_3-SiO_2 gel or with kyanite, but differ considerably from the results with andalusite and sillimanite. The "equilibrium" curve (based on the andalusite-sillimanite data) agrees with the expression: $P = 33.8 \times 10^{-3}T - 26.4$, in which P is kbars, T is °C.

Al_2O_3-SnO_2

Barczak and Insley (1962) found only a simple eutectic near 98 wt % SnO_2 at 1620°C. The melting point of SnO_2 was determined to be 1630°C, comparing favorably with the earlier datum of Ruff, Seiferheld, and Suda, 1637°C (Int. 1948).

Al_2O_3-Ti_2O_3

Belon and Forestier (1964) claimed a eutectic having the composition, 55% Al_2O_3, 45% Ti_2O_3, with a limited solubility of Ti_2O_3 in Al_2O_3 to about 12.5 mol. %. Horibe and Kuwabara (1964) found that the system oxidized by heating to $Al_2O_3 \cdot Ti_2O_{3.1}$. The lowest melting point was obtained at 1720°C for a composition containing 30% Al_2O_3. The solubility found for Ti_2O_3 in Al_2O_3 was 1.6, 2.7, and 1.7 mol. % at 1600, 1710, and 1840°C, respectively.

Al_2O_3-TiO_2

Lang, Fillmore, and Maxwell (1952) observed a eutectic melting at 1840°C between α-Al_2O_3 and $\alpha Al_2O_3 \cdot TiO_2$ at about 39% TiO_2. The compound α-$Al_2O_3 \cdot TiO_2$ melts at 1860°C. A second eutectic, melting at 1705°C, appears at about 81% TiO_2. The melting point of TiO_2 was found to be 1845°C. Brauer and Littke found that the melting point of TiO_2 varied with the atmospheric pressure and the oxygen content of the atmosphere from 1840°C at O_2 at 300 torr., A at 400 torr., to 1870°C for O_2 at 1140 torr. The compound, $Al_2O_3 \cdot TiO_2$ (tieilite) is

isomorphous with rhombic $Fe_2O_3 \cdot TiO_2$ (pseudo-brookite). The
lattice constants are a = 9.60, b = 9.63, and c = 3.60 A; the
density, calculated, 3.61 and measured, 3.62 g/ml; the refrac-
tive indices are γ, 2.04, α, 1.98 (Yamaguchi, 1944). Patzak (1964)
established the presence of tieilite in highly calcined Demerara
bauxites by X-ray and chemical analysis. It is synthesized by
heating equimolar mixtures of Al_2O_3 and TiO_2 at 1400°C for 24
hours.

$Al_2O_3-Cr_2O_3-TiO_2$

Hamelin found that rutile is the stable phase of TiO_2 at
least to 1600°C. The solid solution $Al_2O_3-Cr_2O_3$ occupies a
large portion of the ternary. Small quantities of Al_2O_3 allow
the presence of the high-temperature solid solution of Cr_2O_3
and TiO_2 to exist at lower temperature than is possible in the
binary.

$Al_2O_3-UO_2$

Dykstra (1960) states that no solid solution between Al_2O_3
and any uranium oxide has been found. In the system Al-U-O,
the available phases are UO_2, U_4O_8, U_3O_8, UO_3, UAl_2, UAl_3, UAl_4,
and Al_2O_3, all of which are known in the corresponding binaries.
Lang, Knudsen, Fillmore, and Roth (1956) show the lowest melt-
ing point at about 1915°C (75 mol.% Al_2O_3). Lambertson and
Mueller obtained 2878°C as the melting point of UO_2.

$Al_2O_3-Nb_2O_5$

H. J. Goldschmidt (1960), and Müller and Nicholson reported
that $AlNbO_4$ is the only compound in the system $Al_2O_3-Nb_2O_5$.
Goldschmidt stated that Nb_2O_5 dissolves in solid solution about
15% Al_2O_3. This is denied by Layden (1963), who claims that
two distinct phases exist, $Al_2O_3 \cdot 9Nb_2O_5$ and $Al_2O_3 \cdot 25Nb_2O_5$,
melting points about 1430°C and 1460°C, respectively. Müller
and Nicholson determined the melting point of $AlNbO_4$ as 1550°C.
Dyer and White (1964) determined the variations in permittivity
and resistance with temperature to 500°C of $A_2O_3-B_2O_5$ compounds,
in which A_2O_3 is a Group III or rare earth oxide, and B_2O_5 is
niobia or tantala. Cathodo-luminescence was shown by all com-
pounds of the composition ABO_4. The effects are independent
of both the structure type and the presence of activators.
Coates and Kay found that all ABO_4 compounds in these systems
are monoclinic.

$Al_2O_3-P_2O_5$

There is marked commercial interest in aluminum phosphate
as a high-temperature refractory binder for alumina and alumino-
silica refractories. While the development of such bonds is
usually by wet reaction, as by heating tabular alumina, coated
with about 8% by weight of concentrated H_3PO_4, at about 200°C to

mature the bond, temperatures of around 400 to 600°C are required to insolubilize the bond, and the refractory may subsequently be subjected to high use temperatures in service. Reactions of interest are in the Al_2O_3-rich field of the diagram, and under both oxidizing and reducing conditions.

Stone, Egan, and Lehr investigated that part of the binary system $Al_2O_3 \cdot 3P_2O_5$-$Al_2O_3 \cdot P_2O_5$ which melted below 1600°C, that is, the region from 23 to 30 wt % Al_2O_3. No compound corresponding to $2Al_2O_3 \cdot 3P_2O_5$ was found. A eutectic was found at 1212°C and 28% Al_2O_3. $Al_2O_3 \cdot 3P_2O_5$ retained a superficial appearance of stability, even when heated to 2000°C, but the residue was a mixture of a glass and crystals of $Al_2O_3 \cdot P_2O_5$. The melting point was estimated to be 1490°C. The weight loss per hour (P_2O_5 volatilization) varied from about 0.1% at 800°C to about 0.8% at 1100°C.

Beck (1949) showed the analogy between the crystallographic inversions of the aluminum orthophosphate polymorphs and those of silica. A crystalline form of anhydrous $Al_2O_3 \cdot P_2O_5$, probably the β-tridymite form, resulted when $Al_2O_3 \cdot P_2O_5 \cdot 4H_2O$ was heated to about 90°C. The α-tridymite form was obtained at 300°C, and the cristobalite form at about 1000°C. $Al_2O_3 \cdot P_2O_5$ apparently lost some P_2O_5 at 1450°C during 40 hours, or at 1600°C for about 5 hours (about 0.7%/hr at 1600°C).

Al_2O_3-Ta_2O_5

King, Schultz, Durbin, and Duckworth found compounds in the region from about 15 to 30 mol.% Ta_2O_5 which were stable to about 1700°C, consisting of Al_2O_3 plus phase Z (solid solution) plus a variable solid solution. In the region from 30 to 50 mol.% Ta_2O_5, phase Z exists alone as a solid solution, melting at about 1700°C. In the region from 50 to 80 mol.% Ta_2O_5, phase Z plus Ta_2O_5 plus a variable solid solution remain stable to about 1700°C.

Al_2O_3-V_2O_5

Burdese investigated the systems of V_2O_5 and the sesquioxides of chromium, iron, and aluminum. The mixtures were prepared by sintering at 500°C for 200 hours, using gamma alumina as the aluminous component. Burdese found 685°C as the melting point of V_2O_5 in CO_2 atmosphere. The preferred value is 675°C (C. McDaniel, 1963). Each system formed only one compound, incongruently melting, at 695°C in the case of $AlVO_4$. A eutectic at about 30 mol.% Al_2O_3 melted at 640°C.

Al_2O_3-Bi_2O_3

Levin and Roth (1964) show only one eutectic at about 3 mol.% Al_2O_3, 97 mol.% Bi_2O_3, melting at about 810°C. Levin and McDaniel (1962) found the melting point of Bi_2O_3 to be 825°C.

$Al_2O_3-Ce_2O_3$

Leonov and Keler heated mixtures of ceria and alumina in varying molar ratios at 1000 to 1750°C in a reducing atmosphere to make $CeAlO_3$ and $Ce_2O_3 \cdot 11Al_2O_3$. $CeAlO_3$ has the same structure as perovskite. Its melting point was 2075°C in hydrogen. It undergoes polymorphic transition at about 90° from rhombic to rhombohedral and at 980°, to cubic in conformity with other rare earth aluminates having the perovskite structure. The density is 6.17 g/ml, and the refractive index 2.02. Heating the compound in air produces Al_2O_3 and CeO_2. $Ce_2O_3 \cdot 11Al_2O_3$ has the same structure as beta alumina. It melts at 1950°C in hydrogen, and has a density of 4.07 g/ml and a refractive index of 1.80. Both aluminates decompose when heated in air above 800°C, but are stable in reducing atmospheres. The beta phase resists the action of acids (including HF).

$Al_2O_3-CeO_2$

Ceria forms no compounds with alumina, according to Wartenberg and Eckhardt. A minimum in the liquidus occurs at about 1790°C for the mixture containing about 30 mol. % CeO_2, but with increasing content of ceria, the refractoriness under oxidizing conditions increases and attains a melting point of 2600°C for the pure CeO_2. Trombé (1949) fused ceria at 2800°C.

$K_2O-CaO-Al_2O_3$

Brownmiller (1935) described five binary compounds, which have been mentioned previously in the binary systems. The system also contains a quadruple point which is not a eutectic, $CaO-3CaO \cdot Al_2O_3$, melting point 1535°C. There are two ternary eutectics: $3CaO \cdot Al_2O_3-K_2O \cdot Al_2O_3-5CaO \cdot 3Al_2O_3$ ($12CaO \cdot 7Al_2O_3$), melting point 1425°C, and $CaO \cdot Al_2O_3-5CaO \cdot 3Al_2O_3$ ($12CaO \cdot 7Al_2O_3$)-$K_2O \cdot Al_2O_3$, melting point 1430°C. There is one quintuple point, which is not a eutectic, $CaO-3CaO \cdot Al_2O_3-K_2O \cdot Al_2O_3$, melting point 1485°C.

Suzukawa (1956) reported the phase $K_2O \cdot 8CaO \cdot 3Al_2O_3$.

$K_2O-Al_2O_3-SiO_2$

Schairer and Bowen (1955) found six binary systems in the primary system $K_2O-Al_2O_3-SiO_2$: leucite-silica; leucite-corundum; K disilicate-leucite; $KAlSiO_4$-leucite; K disilicate - $KAlSiO_4$; $KAlSiO_4$-corundum. Four ternary compounds were found in the ternary system: $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ (feldspar) - $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ (leucite) - $KAlSiO_4$. Schairer and Bowen failed to observe a field for beta alumina, perhaps influenced by the supposition that it is monotropic (metastable) with respect to corundum (Rankin and Merwin). They found a eutectic in the subsystem, $Al_2O_3-K_2O \cdot Al_2O_3 \cdot 2SiO_2$ at about 8 wt % Al_2O_3, 92% $K_2O \cdot Al_2O_3 \cdot 2SiO_2$, melting point 1680°C. Another eutectic in the subsystem,

Al_2O_3-leucite, melted at 1588°C, at about 8% Al_2O_3, 92% $K_2O\cdot Al_2O_3\cdot4SiO_2$.

DePablo-Galan and Foster, on the basis of quenching tests, found a wedge-shaped field for $Na_2O\cdot11Al_2O_3$, adjacent to the field of corundum plus liquid in the Na_2O-Al_2O_3-SiO_2 system. A similar field should, however, correspond in the K_2O-Al_2O_3-SiO_2 system, and in other systems, to conform with all the types of beta alumina.

Li_2O-Al_2O_3-B_2O_3

Kim and Hummel (1962) isolated two ternary compounds, $2Li_2O\cdot Al_2O_3\cdot B_2O_3$ and $2Li_2O\cdot2Al_2O_3\cdot3B_2O_3$. The 2:1:1 compound melted at 870° ± 20°C (by differential thermal analysis) but the exact nature of the melting behavior was not determined. The 2:2:3 compound melted at 790° ± 20°C to $Li_2O\cdot5Al_2O_3$ and liquid.

Li_2O-Al_2O_3-Fe_2O_3

Strickler and Roy (1961) investigated the subsolidus equilibrium of a portion of this system in the temperature range 500 to 1400°C, because of the application of spinels in square-loop ferromagnetic electrical devices, as well as in refractories. The $LiFe_5O_8$-$LiAl_5O_8$ join shows complete solid solution above 1180°C. Below this temperature, the solid solution exsolves into two spinel phases. At 600°C, approximately 15 mol.% of each compound is soluble in the other.

Li_2O-Al_2O_3-SiO_2

Hatch (1943) showed that four aluminum compounds are of possible significance in this system: eucryptite ($Li_2O\cdot Al_2O_3\cdot2SiO_2$), beta spodumene ($Li_2O\cdot Al_2O_3\cdot4SiO_2$), "lithium orthoclase" ($Li_2O\cdot Al_2O_3\cdot6SiO_2$), and petalite ($Li_2O\cdot Al_2O_3\cdot8SiO_2$). In the binary system $Li_2O\cdot SiO_2$-eucryptite, no solid solution or binary compound exists. A eutectic occurs at 1070°C and 57% eucryptite (Murthy and Hummel, 1954). Eucryptite exists in two forms: α-eucryptite is rhombohedral, as found in nature, with positive indices ϵ 1.587, ω 1.572; and β-eucryptite, the stable form above 972°C. It is hexagonal, negative, and with ϵ 1.517, ω 1.521. Winkler found the cell dimensions to be a = 5.27 A and c = 11.25 A. The space group is $C6_2 2$. It dissociates about 1400°C to a liquid and a crystalline phase, thought to be the spinel $LiAl_5O_8$. The petalite is present in the subsolidus below about 700°C, and the lithium orthoclase, if it exists, probably in a narrow region slightly higher.

The binary $Li_2O\cdot SiO_2$-spodumene is similar to the preceding system. The eutectic occurs at 1026°C and at the composition 54.6 beta spodumene (Roy and Osborn, 1949). In the ternary system $Li_2O\cdot SiO_2$-beta spodumene-SiO_2, there are two eutectics and

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a maximum. The first eutectic is at 980°C, the second at 985°C.
A. Moldvai (1958) also investigated conditions of formation of
the lithium aluminosilicates.

$Li_2O-Al_2O_3-TiO_2$

Kim and Hummel (1960) investigated the solid-state reactions
mainly for that portion of the ternary system bounded by
$Li_2O \cdot Al_2O_3$, $Li_2O \cdot TiO_2$, Al_2O_3, and TiO_2. A ternary compound
$Li_2O \cdot Al_2O_3 \cdot 4TiO_2$ was obtained by heat treating the mixed com-
ponents for 36 hours at 1250°C. It is stable between 1090 and
1343°C. No compound was found corresponding to $LiAlTiO_4$. The
lower limit of stability of the compound $Al_2O_3 \cdot TiO_2$ is 1237°C.

$Na_2O-CaO-Al_2O_3$

Brownmiller and Bogue (1932) found in the region low in
Na_2O two ternaries, $2Na_2O \cdot 3CaO \cdot 5Al_2O_3$, melting point 1630°C, and
$Na_2O \cdot 8CaO \cdot 3Al_2O_3$, which dissociates to CaO and liquid at 1508°C.
Three quintuple eutectics were found:
(a) $3CaO \cdot 5Al_2O_3-CaO \cdot Al_2O_3-2Na_2O \cdot 3CaO \cdot 5Al_2O_3$-liquid-vapor
(b) $5CaO \cdot 3Al_2O_3 \cdot CaO \cdot Al_2O_3-2Na_2O \cdot 3CaO \cdot 5Al_2O_3$-liquid-vapor
(c) $5CaO \cdot 3Al_2O_3-Na_2O \cdot 8CaO \cdot 3Al_2O_3-2Na_2O \cdot 3CaO \cdot 5Al_2O_3$-liquid-vapor
The compositions and melting points of these eutectics are as
follows:

	(a)	(b)	(c)
Melting point °C	1465	1430	1420
Composition (Wt %)			
Na_2O	6.0	4.0	5.0
CaO	27.5	38.0	46.0
Al_2O_3	66.5	58.0	49.0

$Na_2O-Al_2O_3-SiO_2$

Schairer and Bowen (1956) found that seven binary systems
comprise the phase diagram $Na_2O-Al_2O_3-SiO_2$: albite-silica;
albite-corundum; nepheline (carnegieite)-albite; sodium disil-
icate-nepheline; carnegieite-corundum; and carnegieite-sodium
aluminate ($Na_2O \cdot Al_2O_3$). There are only two ternary compounds:
albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) and $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$. In the sub-
system Al_2O_3-carnegieite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), a eutectic contain-
ing about 7.7 wt % Al_2O_3 and 92.3% carnegieite was found, which
melted at 1475°C. In the subsystem Al_2O_3-albite, a eutectic
containing only 1.5% Al_2O_3 and 98.5% albite melted at 1108°C.
No field of sodium beta alumina was found.

$BaO-Al_2O_3-SiO_2$

Toropov, Galakhov, and Bondar found 13 fields of stability.
Besides the compounds found in the binary systems, the following
phases were observed: the ternary solid solution ($2BaO \cdot 3SiO_2$-
$BaO \cdot 2SiO_2-BaO \cdot Al_2O_3 \cdot 2SiO_2$); celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$); and a

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solid solution of an incongruent compound of the composition ($3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$) which had not been previously observed. The diagram has 11 binary eutectics and 13 invariant points, of which 4 are eutectics.

Schwiete investigated the system with the aid of infrared spectroscopy, X-ray, and dynamic differential thermal methods. An economic method for producing celsian was devised. Planz and Muller-Hesse observed that the thermal synthesis of $3BaO \cdot Al_2O_3$ and $BaO \cdot 6Al_2O_3$ from the oxides is always through $BaO \cdot Al_2O_3$. In the pure system Al_2O_3-SiO_2, mullite is not formed below 1000°C, but mullite and cristobalite form appreciably at 1000°C in the presence of 8 mol. % Na_2WO_4.

$BeO-MgO-Al_2O_3$

Geller, Yavorsky, Steierman, and Creamer investigated various combinations of beryllium oxide and alumina with the oxides MgO, ThO_2, and ZrO_2. The system $BeO-MgO-Al_2O_3$ has a probable compound conforming to $BeO \cdot MgO \cdot 2Al_2O_3$. A eutectic melting at 1640°C conformed to 44.4% MgO, 27.5% BeO, and 28.1% Al_2O_3, approximately $4BeO \cdot 4MgO \cdot Al_2O_3$.

$BeO-Al_2O_3-ThO_2$

Geller, Yavorsky et al. (1946) found a eutectic in the Al_2O_3-ThO_2 system melting at 1910°C, for a composition containing 60.7 wt % Al_2O_3. The lowest fusing ternary found was approximately $4BeO \cdot 2Al_2O_3 \cdot ThO_2$, and melted at 1795°C. The optimum temperature for vitrification was 1600 to 1700°C.

$BeO-Al_2O_3-ZrO_2$

Geller, Yavorsky et al. (1946) found that zirconia is less refractory by about 50°C than thoria in thermal reactions with alumina. In the binary system Al_2O_3-ZrO_2, a eutectic melting at 1885°C corresponded approximately with ZrO_2 55% and Al_2O_3 45% (wt). The lowest ternary conformed approximately with $2BeO \cdot Al_2O_3 \cdot ZrO_2$, and melted at 1750°C.

$CaO-MgO-Al_2O_3$

Rankin and Merwin (1916) found that the presence of calcia markedly lowers the refractoriness of alumina, although its own melting point is about 2620°C. Ternary eutectics occur for compositions: 46.0 wt % CaO, 6.3% MgO, and 47.7% Al_2O_3 (1345°C), and 41.5% CaO, 6.7% MgO, and 51.8% Al_2O_3 (1345°C).

Repenko examined the region of nonrefractory composition of this system. The addition of calcium aluminates to periclase lowers the refractoriness of the subsystems $CaO \cdot Al_2O_3$, $MgO-3CaO \cdot Al_2O_3$, $MgO-12CaO \cdot 7Al_2O_3$, and $MgO-CaO \cdot Al_2O_3$. Kalyanram and Bell measured the sulfur equilibrium in a gas mixture of $CO-CO_2-SO_2$

and the melt as a means of evaluating the activity of lime in
melts in the system CaO-MgO-Al₂O₃ at 1500°C. By the application
of thermodynamic data to the phase diagram, isoactivity lines
for alumina could be drawn.

Majumdar (1964) speculated on the composition of two re-
cently discovered ternary compounds in this system. The stable
compound, for which a small primary-phase field has been located,
has the structure $25CaO \cdot 8MgO \cdot 17Al_2O_3$, or perhaps $3CaO \cdot MgO \cdot 2Al_2O_3$.
The other compound is metastable, and its formula is unknown,
perhaps $7CaO \cdot MgO \cdot 5Al_2O_3$. It resembles an unknown quaternary
phase found in high-alumina cement. Each compound has a unique
constant for the unit cell dimension.

$CaO-Al_2O_3-Cr_2O_3$

Vasenin (1940) found only a series of solid solutions with-
out maxima or minima in the system, $CaO \cdot Al_2O_3-CaO \cdot Cr_2O_3$. Ford
and Rees (1958) observed that $CaO \cdot Al_2O_3$, $CaO \cdot Fe_2O_3$, and $\beta-CaO \cdot -
Cr_2O_3$ are all orthorhombic and isomorphous. $CaO \cdot Al_2O_3$ dis-
solves in $\beta-CaO \cdot Cr_2O_3$ to about 15 wt %, stable to about 1400°C,
and remaining at room temperature. Heating the ratio $4CaO \cdot Al_2O_3 \cdot -
CaO \cdot Cr_2O_3$ in air below 1400°C forms a complex oxidation product,
$10CaO \cdot 8Al_2O_3 \cdot 2CrO_2 \cdot Cr_2O_3$, which dissociates into $CaO \cdot Al_2O_3$ and
$\alpha-CaO \cdot Cr_2O_3$ on heating to 1500°C.

$CaO-Al_2O_3-Fe_2O_3$

Hansen, Brownmiller, and Bogue (1928); Tavasci; and Toropov
and Boikova have investigated this system. Tavasci began his
study with the components, $CaO \cdot Al_2O_3$, Al_2O_3, Fe_2O_3, and $CaO \cdot -
Fe_2O_3$. Toropov et al. considered the system as a continuous
series of solid solutions of $2CaO \cdot Fe_2O_3$ in $5CaO \cdot 3Al_2O_3(12CaO \cdot -
7Al_2O_3)$. They found the maximum solubility of alumina in a com-
position containing 17.5 wt % Fe_2O_3, of the formula $8CaO \cdot 3Al_2O_3 \cdot -
Fe_2O_3$. Newkirk and Thwaite (1958) mention three eutectics (1)
CaO, $3CaO \cdot Al_2O_3$, SS, (1389°C); (2) $3CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, SS,
(1336°C); and (3) $12CaO \cdot Al_2O_3$, $CaO \cdot Al_2O_3$, SS, (1335°C). Ternary
compounds include: $6CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (1435°C), $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
(1412°C), and $6CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (1395°C).

$CaO-Al_2O_3-SiO_2$

Thermal reactions in the system $CaO-Al_2O_3-SiO_2$ are of mark-
ed interest because they include the reactions of compositions
corresponding to portland cements, ordinary impure calcium
aluminate cements, and slags produced in many ferrous and non-
ferrous metal operations. The system is also important in the
production of alumina for metal production by such sintering
methods as the previously mentioned Pedersen process.

The system was first defined in detail by Day, Shepherd,
and Wright (1906), but has been since amended by many others,

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among whom are Bowen and Greig (1924), Toropov and Galakhov (1953), Filonenko and Lavrov (1950), and Aramaki and Roy (1959). The compounds of particular interest in alumina ceramics, and their melting points, which have not been previously mentioned in the binary systems, include the ternary compounds gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) 1593°C, and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) 1553°C. Eutectics occur between the anorthite-tridymite (SiO_2)-mullite fields (1368°C melting point), between the tridymite, anorthite, and pseudo-wollastonite ($CaO \cdot SiO_2$) fields (1170°C melting point), between the pseudowollastonite, rankinite ($3CaO \cdot 2SiO_2$), and gehlenite fields (1310°C melting point), and between the $2CaO \cdot SiO_2$, $12CaO \cdot 7Al_2O_3$, and $CaO \cdot Al_2O_3$ fields (melting point 1335°C).

Gentile and Foster (1963) confirmed the validity of $CaO \cdot 6Al_2O_3$ as a stable phase, but in a smaller primary field than that suggested earlier. The anorthite-corundum-calcium hex-aluminate invariant point was relocated at 28.0 wt % CaO, 39.7% Al_2O_3, and 32.3% SiO_2 and at 1405°C.

Kay and Taylor determined the activities of silica in the $CaO-Al_2O_3-SiO_2$ system at 1450, 1500, and 1550°C through the determination of equilibrium pressure for the reaction: $SiO_2 + 3C = SiC + 2CO$. Newman and Wells found that small amounts of Al_2O_3 (1 to 10%) had substantially no effect on the inversion temperature of $\alpha-CaO \cdot SiO_2$ to $\beta-CaO \cdot SiO_2$. Lime and alumina at 1550°C were obtained by the Gibbs-Duhem relation. Free energies of formation of mullite, gehlenite, and anorthite were calculated.

$CaO-Al_2O_3-P_2O_5$

Stone, Egan, and Lehr (1956) determined the primary fields of crystallization of the system $CaO-Al_2O_3-P_2O_5$ at temperatures from 900 to 1600°C by the quenching method. They believed the scope of available native phosphate rock extended beyond ferti-lizer applications to other uses including refractories. The thermochemistry of phosphate bonds for alumina and alumino-silica refractories is also of interest. Three ternary eutectics were claimed as follows:

Fields bordering eutectics	Temp °C	Composition (wt %)		
		CaO	Al₂O₃	P₂O₅
$CaO \cdot P_2O_5-Al_2O_3 \cdot 3P_2O_5-Al_2O_3 \cdot P_2O_5$	905	20.4	7.2	72.4
$2CaO \cdot P_2O_5-CaO \cdot P_2O_5-Al_2O_3 \cdot P_2O_5$	920	25	6	69
$3CaO \cdot P_2O_5-2CaO \cdot P_2O_5-Al_2O_3 \cdot P_2O_5$	1260	41	6	53

On the basis of previous investigations, St. Pierre (1956) suggested changes in the diagram of Stone et al. respecting the binary at the conjunction of the fields $CaO \cdot Al_2O_3$, $3CaO \cdot P_2O_5$, and $Al_2O_3 \cdot P_2O_5$, which was located outside the appropriate com-patibility triangle; also, the join $Al_2O_3-3CaO \cdot P_2O_5$ is a true binary system.

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FeO-MgO-Al₂O₃

FeO-MgO-Al$_2$O$_3$

Kwestroo found a broad spinel area in the temperature region 1250 to 1400°C in the system FeO-MgO-Al$_2$O$_3$, which increases with increasing temperature. The substitution of Al^{3+} ions for Fe^{3+} ions in the spinel phase lowers the value of the magnetic saturation and the Curie temperature.

FeO-MnO-Al$_2$O$_3$

Hay, McIntosh, Rait, and White found a trough extending from the binary MnO·Al$_2$O$_3$ (24% Al$_2$O$_3$, m.p. 1520°C) to the eutectic of the FeO-Al$_2$O$_3$ binary (5% Al$_2$O$_3$, m.p. 1305°C). The intersection of the trough with the peritectic plane of the FeO-MnO binary (20% Al$_2$O$_3$, 40% MnO, 40% FeO) is an invariant point. No ternary eutectic exists.

FeO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$

The ternary diagram FeO-Al$_2$O$_3$-SiO$_2$ of Bowen and Schairer (1932) amended by Bowen and Greig (1924), Aramaki and Roy (1959), and others, has been revised by Osborn and Muan (1960, Fig. 696, Phase Diagrams for Ceramists. The system FeO-Al$_2$O$_3$-SiO$_2$, under strongly reducing conditions (p oxygen about 10^{-13} atm), contains fields for the crystalline phases: wüstite (FeO), fayalite (2FeO·SiO$_2$), the two forms of SiO$_2$, tridymite and cristobalite, hercynite (FeAl$_2$O$_4$ spinel) in solid solution, mullite, corundum, and the two ternaries, iron cordierite (2FeO·-2Al$_2$O$_3$·5SiO$_2$) and 3FeO·Al$_2$O$_3$·3SiO$_2$ (Schairer and Yagi; Muan, 1957).

Under more strongly oxidizing conditions (p oxygen 0.21 atm) as in normal air, the system changes to FeO·Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$. The fields for wüstite and fayalite disappear; the fields for tridymite are greatly reduced; and liquidus temperatures in general increase. Nowotny and Funk found the miscibility of Al$_2$O$_3$ in Fe$_2$O$_3$ (as crystalline solution at 1700°C) is 38 mol.% Al$_2$O$_3$, and that of Fe$_2$O$_3$ in corundum is 24 mol.%; the corresponding solubilities at 1000°C are 28 and 24 mol.%, respectively. In the ternary system, Al$_2$O$_3$-Fe$_2$O$_3$-SiO$_2$, fused at 1700°C under oxygen pressure of 110 atm., no ternary compounds were formed. Only mullite, corundum, and hematite crystalline solutions were identified. There are five quaternary liquidus invariant points in the system. Three of these are located as follows: at 1438°C, mullite (ss), hematite (ss), spinel (ss), Fe$_2$O$_3$·Al$_2$O$_3$ (ss), a liquid of composition 20 wt % SiO$_2$, 24% Al$_2$O$_3$, 15% FeO, 41% Fe$_2$O$_3$, and a gas phase with a partial oxygen pressure of 0.9 atm. At 1450°C, the phases in equilibrium are: mullite (ss), spinel (ss), Fe$_2$O$_3$·Al$_2$O$_3$ (ss), corundum (ss), a liquid composed of 20 wt % SiO$_2$, 25% Al$_2$O$_3$, 17% FeO, 38% Fe$_2$O$_3$, and a gas phase with a partial oxygen pressure of 0.4 atm. The third invariant point is characterized by the coexistence at 1380°C of tridymite, mullite (ss), hematite (ss), spinel (ss), a liquid of composition 40 wt %

SiO_2, 19% Al_2O_3, 16% FeO, 25% Fe_2O_3, and a gas phase with a partial oxygen pressure of about 0.2 atm. The remaining two quaternary liquidus invariant points are near the plane, FeO-Al_2O_3-SiO_2. Tridymite, mullite, spinel (ss), iron cordierite, liquid and gas coexist at about 1180°C; tridymite, spinel (ss), iron cordierite, fayalite, liquid, and gas are in equilibrium at 1050°C.

MgO-Al_2O_3-Cr_2O_3

Wilde and Rees found that a complete series of solid solutions is formed between $MgO \cdot Al_2O_3$ and $MgO \cdot Cr_2O_3$. The series is not completely regular; no ternary compounds are formed. In the Al_2O_3 corner of the diagram, high refractoriness is retained (melting points 1950 to 2000°C).

MgO-Al_2O_3-Fe_2O_3

Cocco (1958) observed a narrow region indicating the presence of a quaternary solid solution under equilibrium conditions at 1600°C. This was identified only qualitatively.

MgO-Al_2O_3-SiO_2

Osborn and Muan (1960) show ten fields of crystalline phases, of which five are aluminous: corundum, mullite, cordierite, spinel, and sapphirine. W. R. Foster (1950) prepared sapphirine ($4MgO \cdot 5Al_2O_3 \cdot 2SiO_2$) by repeated sintering of the constituent oxides to this formula at atmospheric pressure. It melts incongruently near 1475°C. Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) represents a field of interest to electronic insulator manufacturers.

MgO-Al_2O_3-TiO_2

Berezhnoĭ and Gul'ko (1955, A) found two solid solutions, spinellide ($MgAl_2O_4$-Mg_2TiO_4) and anosovite (Al_2TiO_5-$MgTi_2O_5$). Corundum and geikielite react to give ($MgAl_2O_4$-Mg_2TiO_4) (ss) and (Al_2TiO_5-$MgTi_2O_5$) (ss). Two eutectics were assumed: (1) corundum, spinel, and aluminum titanate (MgO 10 wt %, Al_2O_3 68%, TiO_2 22%, m.p. 1730°C) and (2) geikielite, spinel (ss), and anosovite (ss) (MgO 30 wt %, Al_2O_3 15% TiO_2 55%, m.p. 1570°C). Small additions of TiO_2 and especially of $MgTi_2O_5$, lower the porosity and the refractoriness of corundum.

MgO-Al_2O_3-ZrO_2

ZrO_2 and $MgAl_2O_4$ form a simple pseudobinary system with a eutectic, m.p. 1860°C, 52 wt % ZrO_2. Two ternary eutectics are formed by the melt and the following solid phases: (1) Al_2O_3-ZrO_2-$MgAl_2O_4$, m.p. 1830°C (MgO 7 wt %, Al_2O_3 43%, ZrO_2 50%), and (2) MgO-ZrO_2-$MgAl_2O_4$, m.p. 1840°C, (MgO 20 wt %, Al_2O_3 20%, ZrO_2 60%). The solid solutions contain no more than a few percent

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of the third oxide. At 2000°C, the relative magnitude of the
fields of compositions containing not more than 10% of the melt
is about 7.5% (Berezhnoi and Kordyuk).

MgO-Al₂O₃-La₂O₃

The system MgAl₂O₄-LaAlO₃ consists of a simple eutectic
type, with no intermediate compounds or solid solutions. The
eutectic composition is 62 mol. % MgAl₂O₄, 38 LaAlO₃, melting at
1830°C (Toropov and Sirazhiddinov).

MnO-Al₂O₃-SiO₂

Snow (1943) identified the phases rhodonite (MnO·SiO₂),
tephroite (2MnO·SiO₂), spessartite (3MnO·Al₂O₃·3SiO₂), galaxite
(MnO·Al₂O₃), and 2MnO·2Al₂O₃·5SiO₂. The spessartite probably
melts congruently at 1200°C; the 2MnO·2Al₂O₃·5SiO₂ melts incon-
gruently to form mullite plus liquid at an upper reaction limit
of 1200°C. One eutectic and four peritectic quintuple points
were described: the eutectic involves the phases spessartite,
tridymite, and 2MnO·2Al₂O₃·5SiO₂, melting point 1140°C. Galakhov
(1957) found that the boundary between the mullite and corundum
fields coincides with the position of the eutectic point for the
binary Al₂O₃-SiO₂ system.

PbO-Al₂O₃-SiO₂

Geller and Bunting measured the isofracts (compositions of
the same refractive index) of glasses in the high-lead oxide
region of the phase diagram, ranging from n_d 2.24 for glasses
containing 4.5% PbO. Regions in which the hypothetical com-
pounds 4PbO·Al₂O₃·2SiO₂, 8PbO·Al₂O₃·4SiO₂, and 6PbO·Al₂O₃·6SiO₂
fall, were found to contain eutectics having melting points of
764, 695, 694, and 695°C.

In the high-alumina portion of the diagram, the addition of
small amounts of the lead silicates produced no marked effect on
the strength of sintered alumina (unpublished report Alcoa
Research Laboratories).

SrO-Al₂O₃-SiO₂

Watts (1951) found a eutectic conforming to 30 wt % SrO,
10% Al₂O₃, and 60% SiO₂, showing pyrometric cone deformation at
1155 to 1165°C. Dear (1957) divided the system into 15 compati-
bility triangles from the 28 Alkemade lines, to form 3 binary
strontium silicate compounds, 4 binary strontium aluminates
(5SrO·Al₂O₃, 3SrO·Al₂O₃, SrO·Al₂O₃, and SrO·6Al₂O₃), mullite,
and 3 ternary compounds (SrO·Al₂O₃·2SiO₂, 2SrO·Al₂O₃·SiO₂, and
6SrO·9Al₂O₃·2SiO₂).

ZnO-Al₂O₃-SiO₂

No ternary compounds exist in the system ZnO-Al_2O_3-SiO_2, but two ternary eutectics occur: (1) ZnO 40 mol.%, Al_2O_3 8%, SiO_2 52%, melting at 1305°C, with Zn_2SiO_4 and $ZnO \cdot Al_2O_3$ as the solid phases, and (2) ZnO 71.3 mol.%, Al_2O_3 13.3%, SiO_2 18.5%, melting at 1440°C with $ZnO \cdot Zn_2SiO_4$ and $ZnO \cdot Al_2O_3$ as the solid phases. Four quadruple points exist, which are not eutectics (Bunting, 1932).

Al₂O₃-B₂O₃-SiO₂

Gielisse, Rockett, Shevlin, and Foster (1962) reported preliminary information showing the existence of two phases: $2Al_2O_3 \cdot B_2O_3$, melting point 1035°C, and $9Al_2O_3 \cdot 2B_2O_3$, melting point 1950°C. Attempts to synthesize $Al_2O_3 \cdot B_2O_3$ were unsuccessful. Kim and Hummel (Fig. 764, Phase Diagrams for Ceramists, 1964) reported tentative liquidus curves between $9Al_2O_3 \cdot 2B_2O_3$ and $3Al_2O_3 \cdot 2SiO_2$. Dietzel and Scholze (1955) determined the isofracts of glasses in the high-silica portion of the phase diagram. The refractive index varied from 1.46 to 1.50 for liquidus temperatures from 1400 to 1760°C.

Al₂O₃-SiO₂-TiO₂

Agamawi and White (1952), and Galakhov (1958) established the main features of the system Al_2O_3-SiO_2-TiO_2 as consisting of a meeting of the primary fields, mullite, cristobalite, and $Al_2O_3 \cdot TiO_2$ at a reaction point having the composition, 79.4 wt % SiO_2, 8.2% Al_2O_3, and 12.4% TiO_2 at 1480°C; a ternary eutectic at which cristobalite, TiO_2 (rutile), $Al_2O_3 \cdot TiO_2$, and liquid coexist in equilibrium, occurs at 79 wt % SiO_2, 7.5% Al_2O_3, and 13.5% TiO_2, and at a temperature of 1470°C.

Al₂O₃-SiO₂-ZrO₂

Corundum is the principal phase in the mixtures with a ratio of Al_2O_3 to SiO_2 exceeding 4:1. Baddeleyite (ZrO_2) is the principal phase in regions around mullite in which the zirconia content exceeds 30%, and in regions adjoining the corundum field in which the zirconia exceeds 35%. The nonvariant point of crystallization in the system occurs at about 1800°C, and contains 53 wt % Al_2O_3, 17% SiO_2, and 30% ZrO_2 (Budnikov and Litvakoskii).

Al₂O₃-TiO₂-ZrO₂

Berezhnoi and Gul'ko (1955B) determined the melting isotherms and the primary phases of the system. A eutectic appears at 1620°C (51% ZrO_2) in the subsystem Al_2TiO_5-ZrO_2; the two components do not form solid solutions. In the ternary system Al_2O_3-TiO_2-ZrO_2, two eutectics and a triple point were located, having the following values:

	Eutectic 1	Eutectic 2	Triple point
Melting point °C	1610	1580	1590
Composition:			
Al_2O_3	42	18	22
TiO_2	14	60	35
ZrO_2	44	22	43

Solid solutions appear to be formed on the TiO_2-ZrO_2 side of the diagram. None of the liquidus is below 1580°C, which is stated to make this ternary superior to BeO-Al_2O_3-TiO_2 as a refractory.

K_2O-Na_2O-Al_2O_3-SiO_2

Schairer (1950) described the subsystem SiO_2-$KAlSiO_4$-$NaAlSiO_4$. The system contains fields for cristobalite, tridymite, mixed sodium-potassium feldspar solid solutions, sodium-potassium nephelines, leucite, $NaAlSiO_4$, and $KAlSiO_4$. A eutectic appears between the feldspar, nepheline, and leucite fields, melting at 1063°C.

Li_2O-MgO-Al_2O_3-SiO_2

Prokopowicz and Hummel determined the liquidus and sub-solidus relationships for compositions lying on the 65 and 75% SiO_2 planes in the quaternary tetrahedron. In the 75% SiO_2 plane the primary fields are lithium metasilicate, lithium disilicate, cristobalite, tridymite, protoenstatite, β-spodumene, and mullite. Protoenstatite, ($MgSiO_3$), and clinoenstatite are the basis of steatite porcelains. Cordierite ($2MgO \cdot Al_2O_3 \cdot 5SiO_2$) and β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) are the bases of low-expansion, thermal-shock-resistant ceramics. In the 65% SiO_2 plane the primary fields are lithium metasilicate, forsterite (Mg_2SiO_4), protoenstatite, tridymite, cordierite, β-spodumene and mullite. Invariant points in the bounding systems are represented by six eutectics: tridymite, lithium disilicate, β-spodumene, liquid (melting point 980°C); lithium disilicate, lithium metasilicate, β-spodumene, liquid (melting point 975°C); mullite, tridymite, β-spodumene, liquid (melting point 1356°C); tridymite, enstatite, lithium disilicate, liquid (melting point 930°C); lithium disilicate, lithium metasilicate, enstatite, liquid (melting point 935°C); and protoenstatite, cordierite, tridymite, liquid (melting point 1360°C). A quaternary invariant eutectic appears between enstatite, lithium metasilicate, lithium disilicate, β-spodumene, and liquid (melting point 850 to 880°C).

CaO-FeO-Al_2O_3-SiO_2

The combination of phases useful in interpreting the fusibility of coal ash slags was investigated by Schairer (1942). Five joins were examined, characterized as follows: (1) FeO-Al_2O_3-anorthite, (2) FeO-SiO_2-anorthite, (3) FeO-$CaO \cdot SiO_2$-anorthite, (4) FeO-$CaO \cdot SiO_2$-gehlenite, and (5) FeO-gehlenite-anorthite. In the binary Al_2O_3-SiO_2, all compositions between mullite and

alumina are completely crystalline at all temperatures below 1810°C. All compositions between mullite and silica are completely crystalline only below the binary at 1595°C. In the system anorthite-Al_2O_3-SiO_2, all compositions within the area anorthite-mullite-Al_2O_3 are completely crystalline at all temperatures below 1512°C. All compositions within the area anorthite-mullite-silica are completely crystalline only below 1345°C. In the system FeO-Al_2O_3-SiO_2, all compositions within the area mullite-hercynite-Al_2O_3 are completely crystalline at all temperatures below 1380°C. All compositions within the area mullite-hercynite-silica are completely crystallized at all temperatures below 1205°C. All compositions within the area hercynite-SiO_2-fayalite (2FeO·SiO_2) are completely crystalline only at temperatures below 1073°C.

The addition of either or both CaO or FeO causes a marked reduction in the refractoriness of the system.

Li_2O-Al_2O_3-Fe_2O_3

Strickler and Roy (1961) described two joins in the ternary, Li_2O-Al_2O_3-Fe_2O_3. The first is relatively unimportant, and contains only $LiFeO_2$ and $LiAlO_2$ in equilibrium. The second, $LiFe_5O_8$-$LiAl_5O_8$, consists of a spinel solid solution that exsolves below 1180°C into two spinels, one alumina-rich and the other iron-rich. The diagram shows an exsolution dome, fairly symmetrical about the 50 mole percent composition, and increasing in width with decreasing temperature. At 600°C, there still remains about 13 mole percent $LiAl_5O_8$ soluble in $LiFe_5O_8$ and about 15 mole percent $LiFe_5O_8$ soluble in the $LiAl_5O_8$.

CaF_2-Al_2O_3

V. P. Pascal (1913), and Kuo and Yen (1964) described the system CaF_2-Al_2O_3. The latter found only the simple binary system with the eutectic point at 7 mol.% Al_2O_3, melting at about 1290°C. Neither the solid solutions of CaF_2 in Al_2O_3 and Al_2O_3 in CaF_2 claimed by Pascal, nor the compounds CaF_2·Al_2O_3 and CaF_2·$5Al_2O_3$, claimed by Guenther et al., were found to exist by Kuo et al. The CaF_2 melts at 1360°C. At 1275°C, the most probable reaction is: $CaF_2 + 2Al_2O_3 + H_2O = CaO·2Al_2O_3 + 2HF$, less likely, (1) $3CaF_2 + 7Al_2O_3 = 3CaO·2Al_2O_3 + 2AlF_3$, and (2) $2AlF_3 + 3H_2O = Al_2O_3 + 6HF$.

$3NaF·AlF_3$-Al_2O_3

C. M. Hall (1889) discovered that cryolite and other combinations of aluminum fluoride with the fluorides of sodium, potassium, lithium, and calcium, dissolve alumina in substantial quantities, and that the melt is electrolytic. This is the basis of the Hall process for producing metallic aluminum. Lorentz, Jabs, and Eitel; Fedotieff and Ilyinskii, Zintl and

Morawietz, and more recently, P. A. Foster; Fenerty and Hollingshead; and Bretsznajder (1964) have investigated the system. No compounds appeared in the system and no solid solubility was found on either side of the eutectic. The eutectic fell at 10.5 wt % Al_2O_3 at 961°C. The melting point of cryolite was 1004°C. The most probable reaction mechanism for the solution of alumina in cryolite is $3F^- + Al_2O_3 = 3/2 AlO_2^- + 1/2 AlF_6^{3-}$. The deviation from linearity of the plot, $-\log a_C$ vs. $1/T$, at high alumina contents was ascribed to dimerization of the AlO^- ions to give $Al_2O_3^{2-}$ ions (Foster and Frank, 1960).

Bretsznajder et al. (1964) found that the rate of solubility of the aluminum oxide prepared from bauxites of different origin is essentially the same. Blozevic determined the rates of fall and of dissolution of alumina grain in molten cryolite. For the usual reduction plant, the greatest part of the alumina charge to the reduction pot should consist of grains between 50 and 100 microns (270 to 140-mesh). The smaller grains dissolve completely near the top of the molten electrolyte, but the larger grains form a sludge on the bottom.

Fenerty and Hollingshead (1960) determined the liquidus curves by means of cooling curves and visual examination of the cooling melt. The binary systems of cryolite with aluminum fluoride and calcium fluoride gave respectively, a peritectic point at 30 wt % AlF_3 (739°C), a eutectic point at 40% AlF_3 (694°C), and another eutectic at 26% CaF_2 (945°C). In the system, cryolite-alumina-calcium fluoride, the ternary eutectic point was at 2.9% Al_2O_3, and 21% CaF_2 (933°C).

$PbF_2-Al_2O_3$, $PbF_2-ZnAl_2O_4$

Single crystals provide convenient lattices for fundamental optical and magnetic investigations and for practical uses, as for example lasers. Crystal growth from saturated solutions in molten salts has often provided crystals with less defect structure than is the case when the crystals are grown by the flame fusion technique. White (1961) reported the growth of large sapphire crystals (3 grams) from molten PbF_2 solutions. The crystals were in the form of truncated trigonal trapezohedra, and contained about 0.05 wt % of both lead and fluorine.

Giess (1964) determined the solubility of Al_2O_3 (corundum) and $ZnAl_2O_4$ (gahnite spinel) in their respective molten PbF_2 solutions by sealed-tube quenching between 900 and 1200°C, and by differential thermal analysis below 900°C. The solubility (wt ratio Al_2O_3/PbF_2) of Al_2O_3 at 1200°C was 0.151 and at 900°C was 0.093. For $ZnAl_2O_4$, the solubilities were 0.108 at 1200°C, and 0.048 at 900°C. Neither system is a true binary, because small amounts of Pb_2OF_2 were shown by X-ray diffraction.

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Al-O-C

Kroll and Schlechten (1948) claimed that none of the refractory oxides is stable in contact with carbon in vacuum above 1380°C. Thermodynamic calculations and experience show that all the major oxides in bauxite (except Zr_2O_3), and including Fe_2O_3, SiO_2, TiO_2, and V_2O_3, are reduced by carbothermic smelting before alumina is reduced (Stroup). In practice, the oxides do not behave as simply as predicted, partly because of the formation of carbides, intermediates, and volatile subcompounds. Aluminum oxide does not reduce directly to aluminum mixed with carbon monoxide in the presence of carbon at 2100°C, one atmosphere pressure, as might be inferred from the free energies of formation. At about 2030°C, Foster, Long, and Hunter (1956) demonstrated the existence of two oxycarbides, as well as some metallic aluminum, presumably by the following reactions:

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO \text{ (Prescott and Hincke, 1927)}$$
$$4Al_2O_3 + Al_4C_3 = 3Al_4O_4C$$
$$Al_4O_4C + Al_4C_3 = 4Al_2OC$$
$$Al_4C_3 = 4Al + 3C$$
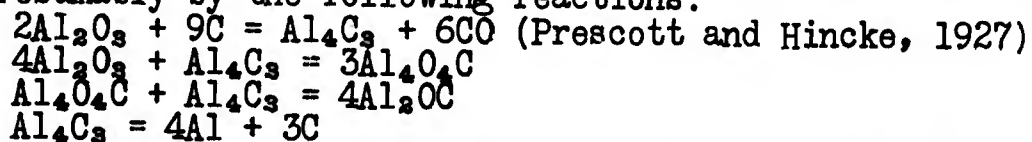
Bauer and Brunner (1934) found that the melting point of alumina dropped from 2040°C to 2016°C for the eutectic in the system Al-O-C containing about 12% Al by weight. With further addition to 25% Al, corresponding to the formula, Al_8O_9, the temperature rose to 2050°C, but further increase to 25% Al caused a linear decrease in the melting point. Filonenko, Lavrov, Andreeva, and Pevzner claimed that a spinel, Al_3O_4 (or $AlO \cdot Al_2O_3$) was formed at about 1615°C in the presence of petroleum coke. At 1680 to 1860°C, the Al_3O_4 converted to Al_4O_4C in the presence of about 15% carbon, and to Al_2OC in the presence of about 26% carbon. Cox and Pidgeon (1963) proposed the following sequence of reactions:

$$Al_2O_3 + 3C = Al_2OC + 2CO$$
$$2Al_2O_3 + 3C = Al_4O_4C + 2CO$$
$$Al_4O_4C + 6C = Al_4C_3 + 4CO$$
$$Al_4O_4C + Al_4C_3 = 8Al + 4CO$$
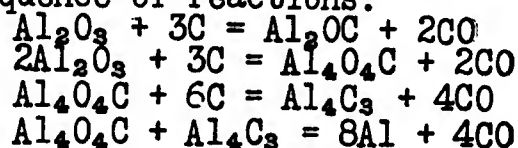
Miller, Foster, and Baker (1958) claimed that the fourth equation of Cox and Pidgeon is the aluminum-producing step, attained by starting with an 85:15 ratio (Al_2O_3:C). The temperature is then raised to about 2000 to 2050°C.

Komarek, Coucoulas, and Klinger obtained the normal carbide at 1307 to 1450°C, presumably by the reaction: $2Al_2O_3(s) + 9C(s) = Al_4C_3(s) + 6CO(g)$. Kohlmeyer and Lundquist (1949) found that 2400°C was required for complete conversion to Al_4C_3, the product appearing as yellow lamellae below 2200°C. Above 2200°C, lamellar graphite was formed by evaporation of aluminum during dissociation of the carbide. Motzfeldt claimed that the loss in weight was always much greater than corresponds with the

reactions:

$$2Al_2O_3 + 3C = Al_4O_4C + 2CO$$
$$Al_4O_4C + 3C = 2Al_2OC + 2CO$$

Considerable amounts of AlO_2 and Al were evolved, probably by the equations:

$$Al_2O_3 + 2C = Al_2O + 2CO$$
$$Al_2O_3 + 3C = 2Al + 3CO$$

Roth, Wolf, and Fritz (1940) calculated the heat of formation of Al_4C_3 to be 50 ± 3 kcal/mole, based on their determination of the molar heat of formation of alpha alumina at 22°C to be 402.9 ± 0.3 kcal.

Juza and Bünsen (1958) investigated the reaction of calcium sulfide, silica, and alumina with calcium carbide melts up to 2900°C, and found that Al_2O_3 reacts with molten CaC_2 (formed by reaction of CaS and C at 2800°C) to form Al_4C_3.

$Na_2O-Al_2O_3-H_2O$

The Bayer process for alumina production is based on the difference in solubility of hydrated alumina in NaOH solutions between approximately 170 and 40°C. Solubilities and densities of Bayer trihydrate, bayerite, and hydrothermal boehmite (coarse), determined by M. Tosterud in Alcoa Research Laboratories, were reported by Russell, Edwards, and Taylor. The data still show good concordance in comparison with those of other investigators. The solubility of gibbsite in sodium hydroxide is complicated by its conversion to much less soluble hydrothermal boehmite at a transition temperature probably below 70°C, but at a rate too slow for practical consideration. Precipitation at 90°C yields substantially alpha trihydrate. At 150°C about 6 hours is required to obtain substantial conversion to boehmite in 124 g NaOH/liter, at 170°C, 0.75 hour.

The solubilities of Bayer trihydrate and boehmite in carbonate-free sodium hydroxide from Tosterud's work, somewhat condensed, are shown in Table 14. The approximate densities of the solutions saturated with Bayer trihydrate (at least for concentrations to 200 g Na_2O) can be expressed by the formula:
$$d = 1.002 + (0.00109 + 5.9 \times 10^{-6}T) \times (g\ Na_2O/liter).$$
The equation for solutions saturated with hydrothermal boehmite follow the expression:
$$d = 1.0002 + (0.00114 + 3.1 \times 10^{-6}T) \times (g\ Na_2O/liter).$$
T is in °C, and d is grams/ml. Panasko and Yashunin (1964) developed a formula for alkali aluminate solutions in which $d = 1 + 0.0144\ C_{Na} + 0.0090\ C_{Al}$. C_{Na} and C_{Al} are the percentages of Na_2O and Al_2O_3, respectively.

Russell et al. found that the equations representing the solubility of these phases are as follows (T in °K):

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for α-trihydrate, log K_3 = (-7340/4.574T) + 4.11
for α-monohydrate, log K_1 = (-4760/4.574T) + 2.22
for β-trihydrate, log K_3 = (-5240/4.574T) + 3.01

In commercial Bayer operations, the sodium aluminate solutions contain in addition to NaOH, varying amounts of Na_2CO_3 and organic matter. Both the solubility of alumina and the stability of the supersaturated solution are generally increased into higher levels of concentration than for the pure sodium aluminate solutions.

Table 14
Solubilities of Hydrated Aluminas in NaOH Solutions

Temp °C	Conc. NaOH as Na_2O g/liter	Concentration Al_2O_3(g/liter) Bayer Tri-hydrate	Hydro-thermal Boehmite	Temp °C	Conc. NaOH as Na_2O g/liter	Concentration Al_2O_3(g/liter) Bayer Tri-hydrate	Hydro-thermal Boehmite
100	62.0	46.0	17.0	150	62.0	74.0	38.5
	77.5	59.0	22.0		77.5	95.0	49.5
	93.0	73.0	27.0		93.0	116.5	61.0
	108.6	89.0	31.7		108.6	138.0	73.0
	132.0	106.0	36.5		132.0	161.5	85.0
120	62.0	60.5	24.5	170	62.0	80.0	45.0
	77.5	78.0	31.0		77.5	104.0	58.0
	93.0	96.0	37.5		93.0	128.0	72.0
	108.6	115.0	45.0		108.6	152.0	86.5
	132.0	135.0	52.5		132.0	175.5	101.5

Ba(OH)₂-Al₂O₃-H₂O

Carlson, Chaconas, and Wells investigated the wet reactions of barium hydroxide and alumina. All the barium aluminate compositions investigated, ($BaO·Al_2O_3·4H_2O$, $2BaO·Al_2O_3·5H_2O$, $BaO·Al_2O_3·7H_2O$, and $7BaO·6Al_2O_3·36H_2O$), hydrolyze in water at 30°C to release gibbsite ($α-Al_2O_3·3H_2O$). The probably stable solid phases are $Ba(OH)_2·8H_2O$ and $2BaO·Al_2O_3·5H_2O$. $BaO·Al_2O_3·2H_2O$ and $BaO·Al_2O_3·H_2O$ were prepared hydrothermally (Carlson and Wells, 1948).

CaO-Al₂O₃-H₂O

The use of calcium aluminate cements in the production of cast or molded refractories has gained wide acceptance in recent years. This is particularly true of the high-purity cements having low iron oxide and silica contents. The phases $CaO·Al_2O_3$, $CaO·2Al_2O_3$, and quick-setting $12CaO·7Al_2O_3$ are the phases usually predominating in the cement clinker, and it is the

hydration products of these compounds that provide the main hydraulic setting properties of the high-purity calcium aluminate cements (Robson, 1962). The phase $3CaO \cdot Al_2O_3$ is not a normal constituent of calcined calcium aluminate, but in the cubic hydrated form $3CaO \cdot Al_2O_3 \cdot 6H_2O$, together with gibbsite and $Ca(OH)_2$, is the only stable calcium aluminate that forms at atmospheric pressure and between 21 and 90°C in the system $CaO-Al_2O_3-H_2O$ (Wells, Clarke, and McMurdie).

$CaO \cdot Al_2O_3 \cdot 10H_2O$, $2CaO \cdot Al_2O_3 \cdot 8H_2O$, and $4CaO \cdot Al_2O_3 \cdot 13H_2O$, and $3CaO \cdot Al_2O_3 \cdot 10$ to $12H_2O$ (if it exists at all) have been claimed to be metastable "hexagonal" hydrates that transform into cubic hydrate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (Wells and Carlson, 1956; Carlson, 1957; Radczewski et al., 1939; Buttler et al., 1959; Cirilli, 1939). Near 1°C, the condition apparently reverses and metastable $3CaO \cdot Al_2O_3 \cdot 6H_2O$ transforms to one or other of the hexagonal hydrates. Curves of metastable equilibrium were established for $CaO \cdot Al_2O_3 \cdot 10H_2O$ and $2CaO \cdot Al_2O_3 \cdot 8H_2O$ (Carlson, 1958). The supposed phase $3CaO \cdot Al_2O_3 \cdot 12H_2O$ was found to be substantially the same as $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot xH_2O$ by X-ray diffraction (Schippa and Turriziani, 1957). It was confirmed by Carlson and Berman (1960) that the carbonated forms, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ and $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 32H_2O$, exist. The former occurs as thin hexagonal plates having refractive indices of 1.532 and 1.554, and with unit cell dimensions $a = 8.716$ and $c = 7.565$. On continued exposure to atmospheric CO_2, it decomposes to $CaCO_3$ and $Al(OH)_3$. These compounds may be analogous to the Dawsonitic alumina gels produced in the presence of alkali bicarbonates at temperatures near 0°C. Simon and Scheibe (1961) claimed a new form of aluminum hydroxide by dropping $Al(NO_3)_3$ slowly into ice-cold 40% aqueous NH_4OH. After filtering, CO_2 is added to precipitate a form having a lattice structure that deviates from the previously known forms of $Al(OH)_3$.

Crowley (1964) stated that very pure starting materials must be used to establish the correct phase relations in the $CaO-Al_2O_3-H_2O$ system from 4 to 260°C. Luminescent-grade $CaCO_3$ must be used, since otherwise, foreign ions promote the forming of $2CaO \cdot Al_2O_3 \cdot 8H_2O$. The hydrate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ was claimed to be stable to 215°C, and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ from 215 to 250°C (Peppler and Wells, 1954). Weiss, Grandjean, and Pavin (1964) identified $3CaO \cdot Al_2O_3 \cdot 6H_2O$ as cubic, with $a = 12.573 \pm 0.005$ A.

Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is a well established product of hydration of portland cement. It forms complete solid solutions with the corresponding ferrite, $3CaO \cdot Fe_2O_3 \cdot 6H_2O$, and also with grossularite garnet, $3CaO \cdot Al_2O_3 \cdot 3SiO_2$, and with andradite garnet, $3CaO \cdot Fe_2O_3 \cdot 3SiO_2$ (Flint et al., 1941). Mori and Tagai found, also, a gel-like solid solution between $4CaO \cdot Al_2O_3 \cdot 13H_2O$ and $4CaO \cdot Fe_2O_3 \cdot 14H_2O$.

CaO-CaSO$_4$-Al$_2$O$_3$-H$_2$O

F. E. Jones (1944) investigated equilibria at 25°C involving gelatinous and crystallized aluminum hydroxide in the formation of calcium sulfoaluminates in hydrated portland cement. He concluded that 3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O (Candlot-Michaelis salt) is initially formed in an alkali- and iron-free cement, but it changes partly or completely to a solid solution. Portland concretes are attacked by sulfate waters. The C-M salt at 20°C metastably formed limiting compounds between 3CaO·CaSO$_4$·12H$_2$O and 3CaO·Ca(OH)$_2$·12H$_2$O. Portland cement decomposes in waters containing more than 4 to 8 mg of CaSO$_4$/liter during the formation of the C-M salt (D'Ans and Eick).

12-4 SLAGGING EFFECTS

An important application of the phase diagrams for ceramists is in the interpretation of slag reactions and the corrosion of refractory linings. In many cases, alumina is a major component involved either in the slag or the refractory.

Early investigators were concerned about the melting and softening of refractories as a viscosity problem (Hartmann, 1938), and the influence of fluidity and solvent action of slags on the destruction of refractories at high temperatures (Endell, Fehling, and Kley, 1939). McGill and McDowell determined the chemical reactions and their temperatures for different refractory materials in contact at high temperatures. The chemical reactions contributed by atmospheres, as for example, the destruction of refractory brick by carbon monoxide disintegration (Hogberg and Heden, 1954), and methods for combating the effect have been recurring ceramic problems. The significance of wetting as a factor in corrosion, and its appraisal by various methods, as for example, the sessile drop method, has been demonstrated (Dinescu, 1962). Marked wettability was shown by Al$_2$O$_3$ and BeO in comparison with V$_2$O$_5$ and ZrO$_2$ for molten lead glass. Physical effects, such as volume changes in slagging reactions, have shown that high-alumina refractories expand markedly in contact with portland cement (Hyslop, 1959). Reich and Panda characterized the slagging resistance of mixtures of sintered alumina and K$_2$SO$_4$ and other slagging combinations by the use of a hot-stage microscope. High liquidus temperatures could be associated with low values for the softening point, the "hemisphere" point, and the flow point of a small pellet observed on the hot stage.

12-4-1 Ash Slags

Coal ash, and petroleum ash, particularly from some South American oils of high vanadium content, are destructive to aluminosilicate refractories. While the ash content of

petroleum is extremely small, varying from less than 0.001 to
about 0.05% in the crude product, this component is nonvolatile
and concentrates in the residual fractions of heavy fuel oil.
Jones and Hardy found that alkaline earth and alkali oxides
(particularly sodium oxide) lower the fusion point of refrac-
tories, but are not as destructive as vanadium. McLaren and
Richardson (1959) described experiments in which cone de-
formations showed that compositions containing alumina in the
mullite concentration were unaffected by vanadium pentoxide up
to 1700°C.

Foster, Leipold, and Shevlin applied a simple phase equi-
librium approach to oil-ash corrosion by devising a compat-
ibility diagram for the system $Na_2O-SO_3-V_2O_5$. Volatilization
experiments and phase identification by microscopic and X-ray
methods confirmed the validity of the diagram. Tho diagram was
found to be consistent with most of the previous recorded ex-
perience. It was noted that Na_2SO_4 and V_2O_5 are not compat-
ible with each other in either the molten or the crystalline
state. They react upon heating to form $NaVO_3$, as well as
several complex vanadates, but they do not form Na_3VO_4 or
$Na_4V_2O_7$. The complex vanadates cause the most severe attack
of any of the possible corrodents. Vanadium pentoxide, previ-
ously credited with a major role in oil-ash attack, is absent
from all but a few fuel-oil ashes, leaving only $NaVO_3$ as the
simple compound which might cause slagging. Sulfur trioxide
is a potentially severe corrosion factor.

One method that has been suggested to counteract the ef-
fect of ash slagging of refractory linings in power-plant
installations is to incorporate nonvolatile additives to the
oil, which change the nature of the ash to less fusible,
powdery consistency, as for example, finely divided alumina.

12-4-2   Slags Containing Sulfates

Ellingham (1944) considered the reducibility of oxides
and sulfides and the value of the slags produced. Gow devised
experimental tests on the reaction of sodium sulfate, either
vaporized or in the liquid state, on aluminous refractories.
The progress of the reaction was followed by the change in
weight, the determination of SO_3 by precipitation, and the de-
termination of Na_2O by the flame photometer. In comparing the
effect of sodium sulfate on a commercial-grade, high-alumina
brick (88% Al_2O_3, 11% SiO_2) and fused crystalline alumina
(99.5% Al_2O_3), it was found that the dissociation of the sodium
sulfate was accelerated more by the presence of SiO_2, probably
as the compound mullite than by the crystalline corundum. It
was deduced that the ultimate product in the commercial brick
was nephelite, $NaAlSiO_4$, but in the fused alumina, sodium
aluminate, $NaAlO_2$. The rate of deposition of sodium sulfate in
the brick was doubled by exposure in a vacuum (150 microns Hg)

at 1200°C, and was increased by one-third in the fused alumina, as compared with the rate in air at atmospheric pressure. Lambertson (1952) measured the loss in weight, checked by the water extraction of unreacted salt, and showed that liquid sodium sulfate reacts with mullite more rapidly than with alumina. Nephelite was the principal reaction product. The resistance of high-alumina firebrick to soda attack could be improved by a refractory coating, particularly by one composed of alumina, nephelite, and sodium aluminate. On the other hand, Steinhoff claimed that sillimanite rings made from kyanite with very little free Al_2O_3 proved to be most resistant to attack by sodium sulfate vapor in laboratory ring tests simulating the normal operating conditions of recuperator tubes. The degree of attack increased rapidly with increasing alumina content. In 99% Al_2O_3 rings, a small amount of alkali induced the formation of beta alumina and cracking of the forms. The formation of feldspathic compounds could be avoided by glazing the inside of the tubes or by using acid refractories.

Bovensiepen, Wolf, and Schwarz claimed that actual service behavior of one year in glass-tank operation and laboratory slagging tests reveals the mechanism of corrosion of refractory brick by sodium silicate-sodium sulfate melts. The sulfate is reduced to sulfide, which reacts with part of the remaining sulfate to form sulfite, SO_2 and free Na_2O. The Na_2O and sulfides diffuse into the refractory and decompose mullite and silica to form $Na_8Al_6Si_6O_{24} \cdot SO_4$ and SiS. The resistance to corrosion of a refractory therefore increases with an increase in the Al_2O_3 content and with a decrease in the SiO_2 content. Hyslop and McLeod found that the loss in weight resulting from reacting a mixture of sodium sulfite and a metal oxide for one hour at 1050°C depended upon the acidity of the oxide. Plotting the weight losses against the atomic numbers of the elements involved gives curves that agree with known chemical properties. In the case of the oxides SiO_2, Al_2O_3, ZnO, Cr_2O_3, Fe_2O_3, and CaO, they agree with the order of mobility or diffusion of these oxides in solid-state reactions.

12-4-3 Steel Furnace Slags

Hartmann and Schulz (1937) stressed the importance of the viscosity of the slags formed in the production of steel. Röntgen, Winterhager, and Kammel measured the viscosities of synthetic slags in the systems FeO- Al_2O_3-SiO_2 and FeO-SiO_2. The constitutions of the slags are similar in both the solid and the liquid state, and the solid-stage bonding forces are still present and active in the liquid state. Mikiashvili et al. measured the viscosity of molten slags of the system Mn-Al_2O_3-SiO_2 corresponding in composition to the products of deoxidation of steel in the regions of the lowest melting temperature. The viscosity of homogeneous liquid slags

increased with increasing SiO_2 content. The viscosity of heterogeneous liquid slags at 1400 to 1590°C increased with decreasing SiO_2 content, and was dependent on the proportion of solid phase present. The lowest viscosity (0.5 to 10 poises) was observed for melts with $MnO:Al_2O_3 = 6$ and 20 to 30% SiO_2. With decreasing $Mn:Al_2O_3$ ratio, the viscosity of the melts increased. The most fluid melts contained 22% Al_2O_3.

Muan (1958) applied phase equilibrium data for the system $FeO-Fe_2O_3-Al_2O_3-SiO_2$ in evaluating the reactions between the iron oxides and aluminosilica refractories under various idealized conditions which approach those occurring in actual practice. The extent of attack and the nature of the reactions changed with different levels of oxygen pressure. At the highest oxygen level considered (1 atm), much iron oxide was present in the Al_2O_3-containing crystalline phases because of the similarity in size of Fe^{3+} and Al^{3+}. Under strongly reducing conditions, the amount of this substitution was trivial. Three different brick compositions were considered for evaluation: fireclay (46 wt % Al_2O_3, 54 SiO_2), mullite (70 Al_2O_3, 30 SiO_2), and high-alumina (90 Al_2O_3, 10 SiO_2). From isothermal planes taken at temperature levels of the phase diagram between 1200 and 1470°C, it was possible to evaluate the performance of the refractories as a function of $Al_2O_3:SiO_2$ ratios of the brick and oxygen partial pressures. The temperature at which a liquid phase developed in the refractory upon reaction with iron oxide decreased as the partial pressure of oxygen was reduced. At temperatures above 1390°C, one atm oxygen, and 1380°C in air, iron oxide, absorbed in excess of 7 wt % Fe_2O_3, caused a liquid phase to develop in the fireclay brick. In mullite brick, about 60% iron oxide absorption was tolerated without liquid formation at 1390 to 1440°C. In the high-alumina brick, no liquid appeared below 1470°C at one atm oxygen, and 1460°C in air.

Under strongly reducing conditions, the refractoriness was much lower than under oxidizing conditions. In the range 1088 to 1205°C, a liquid phase developed in all three brick compositions after 35 to 25% wt % iron oxide had been absorbed. Above 1380°C, in the strongly reducing atmosphere, all three refractories failed rapidly by liquid formation.

Hyslop (1953) found the following order of decreasing stability against reduction, iron oxide-chromite growth reaction, and slagging, for heating effects to 1600°C in the presence of carbon: alpha alumina, magnesia spinel, magnesite, magnesia-chromite, chrome-magnesite, and silica. Minowa and associates found that the reaction between molten steel and high-alumina refractory crucibles under various oxygen pressures (produced by changing the ratio of hydrogen and water vapor) caused the following changes: at p oxygen 1.9×10^{-9} atm, the iron spinel, hercynite ($FeAl_2O_4$), was found, and it increased

with increasing oxygen pressure; at p oxygen 3.74×10^{-9} atm, limonite ($Fe_2O_3 \cdot xH_2O$) was present, and its rate of production increased with increasing H_2O in mixed gas; when the iron was melted in air, hematite (Fe_2O_3) increased and limonite decreased. When molten iron and a refractory oxide contact each other, carbon in the iron reacts with the oxide to liberate carbon monoxide. The apparent activation energy of the reaction was calculated as follows: 50.8 kcal/mole for SiO_2-C, 59.0 kcal/mole for Al_2O_3 (zero porosity)-C, and 48.0 kcal/mole for Al_2O_3 (30% porosity)-C. When a mixed powder of graphite and either SiO_2 or Al_2O_3 was heated in a high vacuum, an increase in pressure for the carbon monoxide reaction occurred at 1170°C for the graphite-SiO_2 couple, and at 1300°C for the graphite-Al_2O_3 couple.

Bachman and Eusner (1959) claimed an improved high-alumina refractory, especially resistant to ferruginous slags, with lower porosity and greater resistance to spalling, characterized as an aggregate of separate particles of calcined fireclay dispersed in a matrix of mullite prepared from either high-purity alumina or high-grade bauxite. The brick, fired for 4 hours at 1510°C (2750°F), had a net Al_2O_3 content of 58%, an apparent porosity of 12.1%, a bulk density of 2.51 g/ml, a 0.0% load deformation under a load of 25 psi for 1.5 hours at 1510°C, 0.0% spalling loss, and a modulus of rupture of 3000 psi. Slagging tests showed only 0.50 in. as compared with 1.0 in. for a 70% Al_2O_3 brick .

McCune, Greaney et al.(1957) found in laboratory tests that Al_2O_3-SiO_2 linings in the low-temperature region of a blast furnace where 3 to 10% K_2O is the principal contaminant, failed by peeling. Superduty fireclay brick and 70% alumina brick treated with KCl-K_2CO_3 mixtures resisted the effect at 870°C. The probable cause of peeling was the formation of leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$).

Changes in steel making since 1957 involve the introduction of oxygen through lances to blast furnaces to speed up the process (from one heat every eight hours to one in 45 minutes) and the present shift to basic oxygen furnaces (BOF). Silica brick and aluminosilica brick, formerly adequate for these applications temperaturewise, are being replaced by more refractory, wear-resistant types. Tar-bonded magnesite and dolomite, and alumina (about 25,000 tons in 1964) have supplied replacements in the steel industry (Chemical Week, May 15, 1965, page 116).

Kozin, Krivchenko et al. (1963) claimed that the decisive factor in the life of oxygen converter linings is the content of Si in the iron and of SiO_2 in the ore. Increased consumption of fluorspar shortens the life of the lining. The intensive working of melts, and the reduction in blast time

increases the life of refractories in acid converters.

Kienow, Artelt, Naefe, and Steinhoff found that vapor-
ization of magnesia in the presence of iron is caused by dis-
sociation; this accounts for the condensation of periclase as
a rectangular lattice.

12-4-4 Glass Furnace Reactions

Stanworth and Turner (1937) found that small amounts of
calcined Bayer alumina (up to 5%) of a mixture of the molec-
ular composition $Na_2CO_3 \cdot CaCO_3 \cdot 6SiO_2$ has no measurable effect
on the rate of decomposition at 700°C, or on the amount of
reacted silica formed. The alumina reacts with sodium
carbonate at this temperature but not with calcium carbonate
or silica, even at 800°C. Abou-El-Azm arranged the oxides in
their order of decreasing rate of reaction with silica as
follows: K_2O, Na_2O, Li_2O, PbO, B_2O_3, BaO, CaO, ZnO, MgO,
TiO_2, Al_2O_3, and ZrO_2. The anionic element or group was also
found influential, the order of decreasing reactivity being:
fluorides, nitrates, carbonates, chlorides, sulfates.

Baudewyns (1938) discussed the attack of refractory
materials used in glassmaking. Hyslop et al. (1947) ob-
served in bench tests that the order of decreasing acceptance
of refractories for soda-lime glass is: chrome-magnesite,
magnesite, alumina, 42% alumina firebrick, kyanite, chrome,
forsterite, 76% alumina firebrick, fusion-cast mullite, 95%
silica, zircon, and clay tank block; the order for lead glass
is: alumina, 42% alumina firebrick, chrome-magnesite, magnesite,
kyanite, forsterite, zircon, fusion-cast mullite, 25% silica,
76% alumina firebrick, clay tank block, and chrome; and for
borosilicate glass: alumina, zircon, 76% alumina firebrick,
fusion-cast mullite, kyanite, clay tank block, 95% silica,
chrome-magnesite, magnesite, chrome, and forsterite.

Day and Ambrosone compared the solubility of single-
crystal sapphire with Corhart ZAC refractory in contact with
common lime glass at 1400 to 1550°C. The corrosion resistance
of the sapphire at the metal line was found to be less than
that of the commercial refractory. Busby and Eccles (1962) ob-
served a wide variation in the rate of corrosion of single-
crystal corundum immersed in four commercial glass melts
(soda-lime-silica, barium crown, borosilicate, and lead) at
1400 and 1500°C. The location above or below the glass level
affected the rate. At least two corroding methods were in-
volved: (1) a surface tension effect at the glass line, and
(2) a density-diffusion effect below the glass level. McCallum
and Barrett found that with lime-alumina-silica slags, an
increase in temperature of 10°C had a much more pronounced ef-
fect on the dissolution rate of single-crystal corundum than had

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an increase in the lime content of the slag from 35 to 55%. The variation in the rate of dissolution with basic oxide content was greater with sodium silicate slags. The dissolution of corundum by these slags is probably an anion-controlled diffusion process. Solomin and Galdina found the material most resistant to lime-soda glasses to be Bakor (14.3% ZrO_2, 12.9% SiO_2, 72.1% Al_2O_3), followed by fused high-alumina refractories. W. F. Ford applied phase equilibrium principles to the corrosion of acid refractories. Solubility data were used to assess the comparative resistance to glass of fused tank blocks.

Comeforo and Hursh stressed the effect of wetting as a factor in the penetration of molten glass into porous refractories. A break was observed in the relationship between the rate of penetration and the pore size of 99% alumina bodies with two liquids of markedly different properties. This break was ascribed to a change in pore volume with a change in pore radius.

Conventional siliceous glass-furnace lining is made more resistant to alkalies by coating with MgO and Al_2O_3, $3Al_2O_3$ and $2SiO_2$; or $2Al_2O_3$ and SiO_2 in an amount up to 10%, thus increasing the life of a furnace 3 to 4 times by this means (Parodi, 1957). Busby and Eccles (1961) observed that both fusion-cast zirconia-corundum and fusion-cast mullite refractories exude a glassy phase at above 1200°C, which leads to considerable sticking to, and subsequent reaction with, other types of refractories except those containing MgO. Very high-Al_2O_3 fusion-cast refractories were the most stable materials of those tested.

Steinhoff noted that fireclay brick (43% Al_2O_3) had a preferred position in the durability of checker brick for glass-melting furnaces, because it forms a nepheline, high viscosity coating with the soda in the alkali atmosphere. Corundum and zircon brick take soda from the alkali atmosphere and form beta alumina or sodium zirconate, which cause cracking because of the resultant volume expansion. Yamanouchi and Kato (1946) found, however, that beta alumina is superior to alpha alumina, diaspore, or pyrophyllite for glass melting crucibles, and ascribed this to the formation of a thin surface layer of nephelite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$). Bron, Savkevich, and Mil'shenko obtained a slag in the production of metallic chromium containing 80 to 86 wt % Al_2O_3, 9 to 12% Cr_2O_3, and 2 to 4% Na_2O (mainly beta alumina), which they suggested for use in open-hearth checkers, cupolas of hot blast stoves, ladles, and roofs of steel-melting furnaces.

12-4-5 Calcium Aluminate Slags

Some slags produced in metallurgical operations fall in the $CaO-Al_2O_3$ and $CaO-Al_2O_3-SiO_2$ systems, and may have economic value because of their ability to develop hydraulic bonding power or because the alumina may be recovered. Nagai and Katayama found

that the composition $3CaO \cdot 5Al_2O_3$ is a high quality refractory cement in combination with aluminous grogs in resisting corrosion by glass fluxes, slags, and ashes. The slags in the system $CaO-Al_2O_3-SiO_2$ show an exothermic peak at 750 to 1100°C by DTA, at which temperature crystallization occurs and the latent hydraulic property decreases.

Samaddar, Kingery, and Cooper (1964) found that the corrosion rate of single-crystal and polycrystalline corundum was the same in a 40 wt % CaO, 20% Al_2O_3, 40% SiO_2 anorthite slag, indicating that the presence of grain boundaries and crystal orientation does not have a significant effect on the corrosion rate of dense (97.2% theoretical) alumina in this slag. At 1350°C alumina is by far the most corrosion-resistant in comparison with mullite (92.5% theoretical density), anorthite (85% theoretical density), and vitreous silica; at 1500°C alumina is still superior, but the differences are less pronounced. Nagai, Suzuki, and Ota found that the mullite component of brick is eroded by molten lime cement, and gehlenite and glassy substances form. Diaspore is less resistant to molten cement than corundum. DeKeyser and Wollast measured the initiating temperature at 900°C. Carter and MacFarlane determined the sulfur equilibrium between $CaO-Al_2O_3$ slags and $CO-CO_2-SO_2$ gas mixtures at 1500°C from which the activity of lime and alumina in these melts could be deduced. The approximate values for the free energies of formation of $3CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot Al_2O_3$ from their constituent oxides were derived.

Sharma and Richardson measured the sulfide capacities and limiting solubilities of calcium sulfide in lime-alumina melts at 1500°C, using a gas and slag technique. The activities of lime and alumina were obtained over the entire liquid range.

Bertrand applied the ternary eutectic $CaO-Al_2O_3-SiO_2$ in a eutectic range suitable for making a slag for the reduction of lead and antimony in order to obtain these metals directly from the ores in the crude state without roasting or the use of costly flotation equipment. Toropov and Volkonskiǐ synthesized slags from a mixture of $CaCO_3$, Al_2O_3, and SiO_2 by fusion in a Tammann-type furnace. The slags were rapidly cooled by water granulation. The vitreous products were crystallized, at 850°C for small crystals, chiefly spherulites; at 1300°C the crystals were much coarser. The crystalline slags were more active hydraulically than the vitreous. The slags heated at 850 to 1300°C developed higher strength than the original slag, attributed to the development of the crystalline phases $12CaO \cdot 7Al_2O_3$ and $CaO \cdot Al_2O_3$.

Volchek developed hydraulic slags ($12CaO \cdot 7Al_2O_3$, and $CaO \cdot Al_2O_3$), and Mori, carbonating hydrated products from $6CaO \cdot Al_2O_3$ compositions in the system $CaO-Al_2O_3-SiO_2$. Ermolaeva

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investigated the viscosity of melts in the system. Samaddar and Lahiri concluded from tests on synthetic slags containing fixed ratios of $SiO_2:Al_2O_3$, but varying CaO content, that the liberation of lime during hydration is the mechanism of activation of the slags.

12-4-6 Aluminum Slag Reactions

Schurecht (1939) prepared refractory coatings with good adherence on firebrick by spraying a slip composed of clay and aluminum powder on the brick and firing. Similar coatings were produced by spraying molten aluminum on the firebrick. Hard, abrasion-resistant surfaces, obtained by this method, and the tight bond were ascribed to heat generated by aluminothermic reactions starting at 750 to 930°C, but capable of increasing the temperature of the coatings to 1500°C within five minutes. The coatings increased the resistance of the fireclay refractories to attack from basic slags, but reduced the resistance to acid slags.

Suzuki and Fujita stated that corrosion of chrome spinel and magnesia spinel by aluminum was negligible in comparison with that by cryolite. Brondyke (1953) found that all commercial aluminosilica refractories could be wetted and subsequently penetrated on exposure to molten aluminum. The penetration and associated pickup of silicon, produced by an aluminothermic reaction, was independent of the porosity, grade of refractory, and the source of the refractory material. The rate was controlled by the diffusion of aluminum and silicon. The reaction caused mechanical disruption of the refractories because of volume expansion. The rate of build-up and adherence to the aluminosilica refractories depended on the silica content. A. F. Johnson (1950) claimed that a refractory composed of a fused mixture of aluminum nitride and alumina is particularly effective in resisting the attack of fused cryolite in the electrolytic reduction. Aluminum nitride is formed by heating aluminum powder and fine charcoal to about 1000°C. The nitride grain is mixed with 50 to 85% alumina and fused in a graphite crucible at 2000 to 2300°C.

12-4-7 Miscellaneous Reactions

West and Gray (1958) found that the greatest reactivity in mixtures of extremely pure silica and alumina is encountered with stoichiometric ratios to form mullite, but not with the formula $3Al_2O_3 \cdot 2SiO_2$, rather with the formula $2Al_2O_3 \cdot SiO_2$. The reactivity also depends on the crystalline modification of the alumina used. A sharp exothermic differential peak at 980°C was ascribed to three simultaneous reactions dependent on the silica-alumina ratio of the mixture: (1) crystallization of

gamma alumina, (2) crystallization of a hydrogen spinel HAl_5O_8, and (3) reaction of silica with the spinel to form mullite.

Eitel (1955) found none of the common refractory materials, including the aluminosilica and high-alumina compositions, satisfactory against corrosion of a fluoride-silica melt used in the manufacture of synthetic fluorine-mica. Ebner placed the order of decreasing resistance to ablation (surface loss by heating effects) of six refractory materials in fluorine-rich hydrogen-fluorine diffusion flames as follows: graphite, silicon carbide, alumina (Remmey AD 99), zirconia, and magnesia. Graphite and silicon carbide were the recommended types, particularly for flame-resistant deflectors to direct the flame away from the rocket motor base. Alumina and magnesia form liquids which flow from the impingement area.

Norton and Hooper found that commercial grades of fire-brick containing 60% or more Al_2O_3 in contact with powdered magnesia showed no reaction up to 1540°C (2800°F). Brisbane and Segnit examined the slagging effects in rotary portland cement kilns. The interstitial material in both high-alumina and magnesite-chrome refractories was attacked. Alkali penetrated the brick, causing an increase in thermal expansion (beta alumina?), which in some cases induced spalling. Kao found that high-alumina bricks (80 to 85% Al_2O_3) provided good corrosion resistance over alkali electrofurnace roofs.

Slags produced in iron-titanium metallurgical processes average about 20% TiO_2 and 60 to 70% Al_2O_3, with small amounts of SiO_2, Fe_2O_3, CaO, MgO, and Na_2O. They are composed chiefly of corundum with TiO_2 in solid solution as colorless crystals in oxidizing atmospheres above 1450°C (Dolkart and Gul'ko).

Chaklader found that traces of alumina (0.22 and 0.44 wt %) catalyzed the transformation of quartz to cristobalite.

13   COLLOIDAL PROPERTIES OF ALUMINA

13-1   PLASTICITY

Alumina generally has been classed as a nonplastic material, without qualification or degree, in referring to its wet-forming behavior. This is too arbitrary. All the wet-forming operations, that are applicable to the plastic clays, can be successfully applied to alumina suspensions, although perhaps not with the same facility. To the extent that crystal form and particle size contribute to plasticity, the crystals of Bayer alumina are a fair match of the clays. The form factor is lost substantially in alumina ground from fused or sintered alumina, however. The addition of as little as 3 to 5% of various ingredients to Bayer alumina compositions often provides adequate plasticity in many forming operations.

Schwerin (1910) and O. Ruff (1924) found it necessary to grind fused and Bayer aluminas with an acid to stabilize the suspensions for slip-casting – a forming process which depends little on plastic properties. The slow release of alkalinity from the Bayer alumina was a significant factor affecting the stability of the Bayer alumina.

Green (1949), Ventriglia, and others have attempted to improve on the inadequately defined concept of plasticity developed by Bingham. Roller treated the water suspensions as solids rather than liquids. Under a compressive force, the dispersions undergo a permanent deformation which does not commence until a certain stress, the Bingham yield point, has been exceeded, a characteristic of the solid state.

Gruner described the fundamental mechanism of plasticity as it applied to amorphous and polycrystalline solid-liquid systems. Clay-water systems were considered too complex for a simple fundamental examination. In the simpler oxide-water systems, chemical forces of hydration of the crystal surface and of ion adsorption were believed to predominate in determining the plasticity. Three types of plasticity were considered: (1) true plasticity caused by reaction between the liquid and solid phases, in which particle size is of secondary importance, and materials with a larger lattice structure have the highest plasticity; (2) limited plasticity, which is caused by chemical reaction such as the formation of oxychloride on the particle surface (cation adsorption) or the adsorption of hydrophilic colloids (humic acid substances); and (3) false plasticity, or the surrounding of nonplastic particles with a highly viscous or sticky liquid or gel.

Haase (1957) concluded that a body has plastic workability if (1) the stress/strain relation shows a threshold value of stress, and (2) the stress necessary to produce a desired deformation is less than the cohesive strength of the body. On

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this basis the workability was defined as being proportional to strength/viscosity. The workability may be increased either by increasing the strength (organic binders) or by reducing the viscosity.

13-2 SURFACE CHARGE AND ZETA POTENTIAL OF ALUMINA

The surface charge which a powdered oxide forms in liquid suspension is thought to determine the extent of flocculation or dispersion and the viscosity of the suspension. These properties affect the value of suspensions in forming processes such as slip-casting. The mixing of different phases, as for example, alumina and clay in water suspension may be affected by a difference in the charge.

Schmäh observed that the surface of very pure alumina gel is alkaline. By electrophoretic methods Fricke and Keefer (1949) determined the isoelectric point or zero point charge (zpc) of gamma alumina to be at pH 9.0, that of amorphous $Al(OH)_3$ at pH 9.4, that of gibbsite at pH 9.20, and that of boehmite at pH 9.40 to 945. The potential-determining ions were considered to be H^+ and OH^-, which enter into electrochemical reaction at the surface in the case of aluminum oxide. The essential part of the surface reaction schematically is as follows:

$$\begin{matrix} \text{H} \\ \diagdown \text{O}(+) \\ \diagup \\ \text{H} \end{matrix} + H_2O \underset{H_3O^+}{\overset{}{\rightleftharpoons}} \diagdown OH \underset{OH^-}{\overset{}{\rightleftharpoons}} \diagdown O^{(-)} + H_2O$$

Positive   Uncharged   Negative
surface   surface   surface
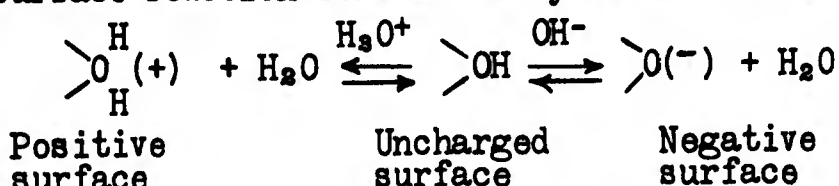
Tewari and Ghosh found the following values for the isoelectric point of hydrated alumina, precipitated and aged under the conditions specified, as follows:

Precipitation	Aging Conditions		
	Fresh Preparation	Rapid aging by heating	Suspensions aged 4 months
Excess alkali	5.08	6.79	5.78
Equivalent alkali	6.63	7.28	7.06
Deficient alkali	7.29	7.43	7.32

The zeta-potential is considered by some to be a significant factor affecting the behavior of colloidal suspensions. It is the electrokinetic potential which represents the difference in potential between the immovable liquid layer attached to the surface of the solid phase and the movable part of the diffuse layer in the body of the liquid. O'Connor et al. (1956) found that the surface of natural corundum has a positive zeta potential by the streaming potential method in water at 17 to 20°C, but it changes to negative on heating to 1000°C. They suggested that the formation of a surface charge was probably caused by

dissociation of a surface hydroxide, but the type of hydroxide formed depended on the reactivity of the surface; severe surface distortion caused by grinding might induce complete hydroxylation to Al(OH)$_3$, but less distorted particles might hydroxylate only to AlO·OH. In any case, the alumina hydroxides are more stable in contact with water at room temperature than alpha alumina. They also suggested that heating the samples restored the corundum surface and annealed out the strains, hence AlO·OH was the main surface phase dissociating to produce a negative surface.

The zpc of corundum and the hydrated aluminas have been investigated also by Johansen and Buchanan; Modi and Fuerstenau; Gayer, Thompson, and Zajicek; Pike and Hubbard; Dobias, Spurney, and Freudlova; Robinson, Pask, and Fuerstenau; and Yopps and Fuerstenau. The reported values for zpc of corundum vary from pH 6.7 to pH 9.4; the values for the hydroxides vary even wider, from pH 5.1 to pH 9.4. This may result from the different methods of determination used: electroosmosis, microelectrophoresis, pH of minimum solubility, etc., or perhaps impurities may be a factor. From the Helmholtz-Smoluchowski equation, in aqueous systems at 25°C,   the zeta potential = 9.69 X 10^4 $\frac{E}{P}\lambda$ (millivolts), in which

E is the streaming potential, P is the pressure drop in the cell, and λ is the specific conductance of the solution.

Anderson and Murray correlated the characteristic minimum that occurs in the apparent viscosity pH curves for oxide slips to the zeta potential of the dispersed oxide. Bakardiev stated that the surface OH groups are distributed inhomogeneously on the surface of gamma alumina. Particles with greater pores (smaller curvature) have a higher OH group concentration than those with smaller pores. Koz'mina and Dobrynina found that the pH of bayerite varied with calcination from 8.9 at 1100°C to 3.2 at 1600°C. The zeta potential of the alpha alumina was markedly dependent on the calcination history.

13-3 FLOCCULATION AND DEFLOCCULATION EFFECTS

Much early investigative work was done to show the relative power of different ions in flocculation and in optimal thixotropic gelation of different types of colloidal suspensions. Comparative flocculation values for a positively charged alumina sol in millimols/liter are as follows: NaCl, 43.5; KCl, 46; KNO$_3$, 60; K$_2$SO$_4$, 0.30; K$_2$Cr$_2$O$_7$, 0.63; K$_3$Fe(CN)$_6$, 0.080 (Ishizaka, 1913). The ion in the electrolyte of opposite charge to that on the alumina sol is the effective ion. The increased potency of the effective ion with increasing valence is similarly reflected in the relative values for thixotropic gelation in millimols per liter for an alumina sol: KCl, 330; Na$_2$SO$_4$, 3.5; K$_3$Fe(CN)$_6$, 1.5; K$_4$Fe(CN)$_6$, 1.0 (Aschenbrenner, 1927).

Tar et al. concluded that aluminum hydroxide obeys the

Freundlich absorption equation for dye absorption: $x/m = ac^{1/n}$, in which x is the weight of substance adsorbed by a weight m of adsorbent from a solution whose volume-concentration at equilibrium is c, and a and n are constants. In the presence of the dye and an adsorption peptizer the solubility of the gels increased in the order: base-gel, gel treated for 6 to 12 hours, gel treated for 1 to 3 hours.

Raychaudhuri and Hussain compared the buffer curves of freshly prepared gels of alumina, silica, and mixed alumino-silicates of varying ratio of SiO_2/Al_2O_3 with similar gels that had been aged for one year, as well as with some native clay minerals, bauxite, halloysite, kaolin, limonite, and mont-morillonite. The freshly prepared materials possessed much less buffer capacity relatively. Their buffer capacity passed through a maximum with increasing SiO_2/Al_2O_3 ratio, but the aged gels' buffering capacity continued to increase, attaining a maximum value with pure silica gel. Krleza found that the mutual floccu-lation of $Al(OH)_3$, $Fe(OH)_3$, and silicic acid sols, when their constituents were present in about the proportions found in baux-ite, differed little between nascent and aged conditions. De-creasing concentration caused a decrease in turbidity, and in-creased the pH required for flocculation. At maximum turbidity, negative and neutral potentials were observed in the different sols; some were acid, others neutral or basic. The flocculated material was acid, but all three ingredients took part in the flocculation.

Howard and Roberts (1953) reported a continued increase in pH with aging of suspensions of commercial Bayer alumina that had been adjusted with hydrochloric acid to the pH range 0.4 to 8.6. The time required for final equilibrium and the final pH depends on the ratio of Al_2O_3/acid. The change on aging was as-cribed to the gradual diffusion of sodium aluminate from the interior of the Bayer grain. This effect has a marked influence on the stability of aqueous alumina suspensions for slip casting or extrusion.

Shulz classed alumina as an acid oxide with SiO_2 and B_2O_3. Voitsekhovskii and Vovnenko found that the potential of Al_2O_3 (E_0) suspended in water or in 4.5n NaCl, 4.5n LiCl, or 1m Na_2SO_4 solutions became positive with respect to the potential of the liquid, as the pH of the suspension was raised. The curves going in both directions of pH formed a hysteresis loop, which met only at the points of origin of both low and high pH.

Shiraki investigated the slip-casting properties of calcined aluminum oxide. An addition of gypsum to the suspension in-creased the viscosity, but additions of $AlCl_3$, $MgCl_2$, $CaCl_2$, HCl, H_2SO_4, and HNO_3 yielded the maximum viscosity. Casting in an acid medium was favorable, but became difficult at pH values below 3.0, and also in the alkaline range. At pH 7 to 8, cracks occur in the body and the body sticks to the mold. At pH above 9.2, the

strength of the cast body suddenly decreases. The addition of 5% alumina, which had been heated in concentrated HCl, to non-treated alumina gave a body of high strength. In casting alumina slips, HCl and HNO_3 were considered more suitable peptizers than H_2SO_4 or an alkali. Alumina calcined at 1300°C and having hygroscopic properties was found to make a good casting slip when treated with hot HCl. Barium compounds were detrimental as binders or mineralizers, but mixtures of talc with 3% ZnO, ZrO_2, $MgCl_2$, $SrCl_2$, $AlCl_3$ were considered necessary to good sintering.

Hauth (1953) stated that acid-leached, ground, fused alumina can be deflocculated in either an acid or a basic medium. The viscosity, dilatancy, yield value, and sedimentation volume of both types of suspension were related to the concepts of diffuse double layers and zeta potentials. Hauser (1952) has drawn attention to the shortcomings of the Helmholtz double-layer theory and of the Gouy-Freundlich diffuse double-layer theory. A new concept of solid double layers caused by dipole formation in the surface layers of colloidal matter was presented.

Howard and Roberts (1951) investigated the effect of various electrolytes on the stability of a commercially pure alumina suspension by observing the change in concentration with time at a fixed distance below the surface. In water alone, the suspensions flocculated with time. Neutral salts flocculated the suspension, but no further deflocculation took place on further additions. Flocculation and deflocculation, following the progressive addition of an acid or acidic salt, was explained by a reversal of the charge on the particles, a theory which was supported by electrophoretic measurements from which the mobilities of the alumina particles could be calculated.

Ludvigsen and Andsager mentioned that ceramic processes require rather high concentrations of body or glaze slips to prevent unmixing of the plastic and nonplastic components. In peptized suspensions for casting porcelain, a concentration of 65 to 70% is necessary, but it is often possible to prevent unmixing by a 15% concentration in flocculated suspensions. Barium chloride was found to have a marked flocculating effect on thin suspensions of kaolin and feldspar, so that these suspensions can settle without losing the original composition in the upper and lower layers. Similar considerations are applicable in the case of alumina slips.

Van Olphen (1964) discussed the nature of the flocculation behavior of hydrous clay suspensions in relation to the anisometric shape of the particles and the double layer structure. The interior net charge on the crystallites is compensated by positive counter ions adsorbed on the flat face surfaces which carry a negative electric double layer of constant charge. At the edges of the crystal plates, a broken bond surface is exposed. Under neutral or acidic conditions, the double layer on the edges is positive. The formation of voluminous flocs or

gels is ascribed to crystal orientations edge-to-face, but this formation can be prevented by the adsorption of suitable anions at the edge surfaces. Presumably, a similar situation holds for alumina crystals in suspension, but with the charges on the particles which apply to this system.

G. W. Phelps (1961) described the effects of soluble sulfates on the casting properties of ball clays.

The sensitivity of colloidal suspensions of alumina to very small amounts of electrolytes indicates the importance of the quality of the water used in preparing wet suspensions for forming operations. Phelps and Maguire (1956) discussed the effect of the usual soluble-salt impurities in water on the plastic clay systems. Durum discussed the quality and availability of suitable water for ceramic purposes. Morrison (1941) and W. E. Coombs stressed the need for softening or deionizing ceramic processing water.

Nirmala and Srivastava observed that stable emulsions of aluminum hydroxide could be prepared in nonaqueous liquids such as kerosene-aniline. This was not possible with other dry solid oxides such as Cr_2O_3. In this case the aniline was the continuous phase. Colloidal suspensions are often stabilized in hydrophobic liquids by the addition of small amounts of polar compounds, such as oleic acid.

Iler (1964) stated that the mutual absorption of colloidal silica on alumina and of colloidal alumina on silica and silicate materials occurs at about pH 4. The film is essentially a mono-particle layer. Alumina particles, which were positively charged, acquire a negative charge from the adsorbed silica. Since the coated particle has the same charge as the surrounding silica colloidal system, no flocculation occurs. This well-known protective principle can be applied to prevent the thickening or flocculation of alumina when mixed with clays or other negatively charged ceramic components. On the other hand, Okura et al.(1963) stated that the presence of silicic acid or of SO_3 tends to shift the isoelectric point of aluminum hydroxide toward its acid side, increasing its negative charge, which aids flocculation.

Kukolev and Karaulov investigated the rheological properties of aqueous suspensions of fine-ground, technical-grade, calcined alumina over a wide range of pH and concentration of water suspensions. The alumina had been precalcined at 1450°C. Two pH ranges were found in which maximum zeta potential values were reached, corresponding to the minimum viscosity and also to the viscosity of the limiting structural breakdown. Applied to casting slips, higher densities were attainable with acid pH, preferably under deairing conditions. Heating the slips to 30 to 40°C reduced the viscosity and increased the casting rate. Dextrine was considered the best bond for increasing the wet strength

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Graham and Thomas found that hydrous alumina reacts in at least two steps with acid, the initial step being attributed to a rapid conversion of surface hydroxo groups into aquo groups. A subsequent slower reaction is deolation of the oxide structure. The reactivity decreases with increasing calcination temperature of the alumina, the effect being ascribed to increasing oxolation of the alumina structure. With increasing temperature, the number of surface hydroxo groups passes through a maximum and becomes zero for fully calcined alumina. The rate of neutralization of various 0.2N acids by hydrous alumina at 25°C was most rapid for HF, and decreased in the order: H_3PO_4, HC_2O_4, H_2SO_4, HNO_3, HCl, CH_3COOH, H_2NSO_3H, and $HClO_4$, which agrees reasonably with the tendency for the negative ion to form stable aluminum complexes. Graham and Horning found that the addition of hydrous alumina at 25°C to 0.1M or 0.05M solutions of the potassium salts at pH 7.0 increased the pH to the following values: fluoride 9.6, oxalate 8.6, sulfate 8.0, nitrate 7.3, chloride 7.3, perchlorate 7.1, and phosphate 7.0. The increase was attributed to the displacement of OH groups from the surface of the alumina by the anions. Marion and Thomas claimed that the pH of maximum yield of aluminum hydroxide resulting from the addition of hydroxyl ion to solutions of aluminum ion is not a constant, but varies with the nature and concentration of the anion present. Fluorides or oxalates raise the pH of maximum precipitation; sulfate, lactate, and chloride gradually lower it; while citrate and tartrate cause a sharp drop. These investigators advanced the theory that the basicity of the anion, the binding affinity of the anion for aluminum, and the resistance of the bound anion to displacement by added hydroxyl ion account for the change in pH.

Fricke and Schmäh said that the solubility of very pure aluminum hydroxide in water is less than 10^{-6} mole/liter. According to Szabo et al. (1955), the solubility products for aluminum hydroxide are as follows:

		20°C	30°C
$(Al^{3+}) \times (OH^-)^3$	$=$	1.25×10^{-33}	1.92×10^{-32}
$(AlO_2^-) \times (H^+)$	$=$	1.80×10^{-13}	1.34×10^{-13}

Ashley and Bruni prepared colloidal alumina sols by reacting weak aliphatic acids with fine aluminum pellets; Ziese et al. prepared them by reacting precipitated aluminum hydroxide containing 0.1 to 5.0% of the anions of strong inorganic acids to steam at 5 to 12 atmospheres for from one to 10 hours. Gregg (1960) discussed the preparation of highly dispersed colloidal solids by various methods including fine grinding, calcination of a decomposable salt, sublimation, precipitation, and removal of one constituent by dissolution or evaporation. Bugosh (1956) prepared a stable colloidal, amorphous, hydrated alumina sol by reacting a water-soluble aluminate with a monobasic acid having a dissociation constant greater than 0.1, an aluminum salt of the acid within the pH range 3.5 to 5.5. Conrad and Lenne prepared peptizable sols by milling bayerite, $Al(OH)_3$, until only a trace

of the bayerite X-ray pattern was detectable. Yuille prepared a stable thixotropic aqueous dispersion by adding a water-soluble aluminum salt to an aqueous solution of an alkali metal base until a pH of 3 to 5 was reached, then by adjusting the pH to 6 to 9 with ammonium hydroxide, followed by dispersing the precipitate by means of a water-soluble phosphate, and by milling the dispersion until the particles averaged one micron or less.

Weiser, Milligan, and Purcell (1941) observed that the alumina floc precipitated in water purification practice at pH 5.5 to 8.5 is boehmite, free of basic aluminum sulfate. Flocs precipitated from aluminum sulfate below pH 5.5, particularly after aging for 24 hours show the X-ray pattern for basic aluminum sulfate, $Al_2O_3 \cdot SO_3 \cdot 1.5 H_2O$. Gels prepared from aluminum nitrate and aluminum chloride solutions at a pH around 4.0 conformed to boehmite. The formation of basic aluminum sulfate has been observed to occur in hot, concentrated, highly acid solutions of aluminum sulfate on dilution, if the water is not mixed in rapidly.

13-4 ADDITIVES

Several classifications of organic binders for ceramic forming have been presented, as for example, that of McNamara and Comeforo (1945). The natural and synthetic resins and other temporary ceramic binders, applied in adjusting the rheological properties of clay ceramics, are also applicable to alumina.

Luks (1956) classified the general types of binders for alumina in three general groups as aids in unfired strength and to facilitate machining operations. These include: (1) the water soluble types (dextrine, gum arabic, polyvinyl alcohol), (2) the water swelling, gelatinous types (gum tragacanth, carboxymethyl cellulose, starches), and (3) emulsion types (wax and resin emulsions). As a class, the water-soluble binders afford the greatest increase in strength, but they tend to migrate, causing difficulty with prefired machining, and in addition promoting the formation of hard-shell, soft-center forms. The water-swelling types create plasticity, bond strength, and generally uniform distribution. Difficulty is sometimes encountered with slow drying rates, resulting in fractured ware. The emulsion types contribute appreciably to internal lubrication, especially advantageous in dry or nearly dry forming operations.

Brown and Coffin claimed a marked freedom from migration for polyvinyl alcohol in partly or completely hydrolyzed condition. Popil'skii and Nemets preferred oleic acid to paraffin as a plasticizer for highly dispersed alumina mixes, but the amount used (18%) was excessive by present standards. Lawson and Keilen mentioned the water-soluble forms of pine-wood lignin as deflocculants in casting operations. Bartos described a method for evaluating the gel-forming strength of bentonite-water suspensions

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in forming operations. Krannick (1961) stressed the use of ethyl silicate and its hydrolysis to polysilicic acids with subsequent gelling and dehydration to solid SiO_2. Hydraulic bonding is provided up to 230°C, and ceramic binding at higher temperatures. The binder is often used for quick set of dipped coatings.

Some organic binders have high ash contents (Ref. Organic Binders, 1962). Alginates contain 25% ash, as well as requiring a bactericide. Methyl cellulose and polyvinyl alcohol have not over 1% ash, but the latter is precipitated by many sodium salts (Na_2CO_3, $Na_2B_4O_7$, etc.), it forms thermoplastic films, has a tendency to foam, and decomposes at 180°C. Methyl cellulose is soluble in cold water, is not ionized, does not react with metal salts, and decomposes at 230°C.

Budnikov, Marakueva, and Tresvyatskii claimed that alumina wax-stearin-oleic acid suspensions exhibited thixotropic and dilatometric properties.

Isostatic pressing requires less than 4% wax emulsion lubricants for satisfactory molding of small forms.

14 GRINDING CERAMIC ALUMINA

High mechanical strength in sintered alumina requires fine grain size of the heat-matured body. Since some grain growth occurs during sintering, the raw alumina must be still finer. Fine grain size, achieved by grinding massive particles to size, requires the expenditure of much energy. Fine grain size can also be obtained by producing the raw alumina in the desired crystal size, by controlled calcination of hydrated alumina or an aluminum salt. In this case the separation is easier. Owing to the platey nature of the crystals, the ground alumina possesses more physical anisotropy than massive-ground particles, and might be expected to behave differently during sintering. The use of different types of grinding equipment alters the properties of the ground alumina. This is usually observed as a change in length of the ground-particle size distribution or as a difference in surface area. Vydrik stated that the sintering density of the body at a given firing temperature is related primarily to the inverse square of the mean surface radius of the particles.

Avgustinik observed that hexagonal alpha aluminum oxide is more brittle than stabilized zirconia. The grinding rate constant shows good correlation with impact strength. Materials with higher coefficients of thermal expansion have lesser bond strengths and higher values of grinding rate constant. The mean square thermal displacement values showed good correlation with microbrittleness, while higher values of the grinding rate constant corresponded to higher values of shear modulus. No correlation was found between microhardness and the grinding rate constant. As the grinding rate constant is proportional to the effective power of the mill, mills operating in the brittle rupture range are the most effective.

Bond (1963) has discussed recent advances in grinding theory and practice. Three principles of particle breakdown were defined and compared with the Rittinger and Kick theories. Equations were given for calculating product sizes from surface area measurements, and for calculating powder requirements and mill capacities. Forchheimer discussed the hardness scales and the factors that affect the toughness of alumina (crystal size, chemical composition, porosity, grit size, and grain shape).

Several different types of grinding equipment have become available during the last two decades for preparing ceramic materials in the finer sizes for forming operations. These include, among others, various types of fluid energy mills, vibrating ball mills (Sweco), and the Attritor. Improvements in conventional ball milling have also been realized with the

development of high-alumina mill liners and grinding balls, rubber liners, air-swept mills, Hydroclone classifiers, and other classifying means for removing the ground product from the sphere of action efficiently. The Stag mill is a ball mill provided with peripheral slots to allow removal of the completely ground material from the mill. It should be advantageous in grinding massive alumina. Novel grinding methods include igniting an explosive mixture and allowing the waves to pass in dis-integrating contact with the solid material, and continuously re-peating the operation (Haltmeier, 1958), or generating com-pressional shock waves of ultrasonic frequency, adapted to pro-duce alternate compressive and expansive forces in a small area of the material (Nilsson, Nilsson, and Hagelin, 1961).

Each of these grinding devices has its advantages and dis-advantages. The air classification systems are limited in their ability to separate finer particle sizes. The fluid energy mills generally produce narrow, less plastic size dis-tributions, devoid of extreme fines, and have poor efficiency in breaking up massive alumina such as the fused and tabular grades. The ground products have markedly different surface properties than the usual ball-milled products, as indicated by standard oil titrations. The Attritor may accomplish in a few minutes the same extent of grinding that requires hours of ball milling, but wear and contamination from the equipment, and power consumption may be high. It is also necessary to operate in a liquid sus-pension.

Ceramic-grade alumina is usually wet-ground in conventional ball mills in present commercial operations. Tabular alumina for spark plug manufacture is ground with steel balls, which requires that the product be leached with mineral acid to re-move the iron pickup. This operation entails careful handling of the iron solution and of washes to prevent hydrolysis and adsorption of the iron salts on the alumina surface, and to avoid loss of the finer fractions of alumina.

Surface active agents such as Darvan may be added during ball milling to reduce changes in the viscosity of the slurry, and to allow use of the minimum amount of water. Pickup of contamination from mill and ball wear in bench-scale tests were found to be about ten times higher in wet ball-milling than in the equivalent dry ball-milling in grinding reactive alumina. Slightly higher reactivity, found for the wet-milled product, is attributed to the pickup of finely divided impurities. When using a 30/1 ratio of grinding balls to alumina, required for supergrinding reactive alumina, pickup from the balls and mill (two-thirds from the balls) amounted to 0.88%/hr in the ground alumina. This indicates the desirability of approximately 99.5% Al_2O_3 balls for grinding high-purity alumina. Kitaigorodskii and Gurevich recommended changing the ratio of water to alumina

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from 1 to 0.75, at the same time adding to the mill an adsorbing agent, such as sugar (0.1% by weight of the water), in order to reduce the grinding time by two-thirds.

Dry ball-milling involves phenomena that are not apparent in wet-milling, such as mill packing and agglomeration of the fines. Some aluminas, particularly those containing small amounts of alkalies, are prone to pack when the average particle size approaches one to two microns. The formation of a coating on the balls and mill lining marks the practical limit of size reduction. Bond and Agthe ascribed this effect to (a) static electricity, (b) adsorption, and (c) mechanical impact. They recommended the addition of 0.75% water and 0.13% of a patented lignin compound to prevent the effect.

Heat was found to be an effective preventative of mill packing, and means for supplying it to mills have been devised (Russell and Hardinge). Grinding in a vacuum has practically no effect on the grinding efficiency of ball mills (Viro). The idea of grinding aids developed from the addition of wetting agents. Byalkovskii and Kudinov observed that the hardness of a specific material (a ceramic color) varied as a function of the medium in which it was ground; when dry-ground in air the hardness index was 1910 (sclerometric), whereas in oleic acid it was 420. Berry and Kamack recommended naphthenic acid as a grinding aid, added in small increments to keep pace with the rate of new surface produced.

A. V. Somers (AC Spark Plug Company) contributed significantly to the technical grinding of reactive alumina by demonstrating the effectiveness of a seemingly high ratio of grinding ball weight to alumina weight, 32:1. A charge of 125 grams of alumina of normal Bayer particle size distribution "supergrinds" within 5 hours at 50 rpm when using 4 kilograms of one-inch balls (85% Al_2O_3) in a 1.3-gallon ceramic mill. Efficient grinding ensues because substantially all the alumina being ground coats the grinding balls early in the course of grinding, and the material remains continuously in the sphere of action. An effective grinding procedure at a ratio of about 20:1 has been developed, and which has been translated to the plant scale under conditions that enable the clean separation of the superground alumina from the balls and the mill.

Rose and Sullivan developed a general equation to explain the factors involved in dry ball-milling, indicating that the number of impacts per piece of grinding medium per mill revolution is a constant. This, plus the assumption that the energy per impact is linearly related to the mill diameter, enabled Hart and Hudson to derive an expression: $K = RNDt$, in which K is a constant that yields equivalent properties (e.g., equal fired density), R represents the ratio of grinding medium to alumina

being ground, by weight, D is the mill diameter in feet, t the hours of grinding, and N the revolutions per hour. K was found to have a value of about 230,000 for low-soda reactive alumina, applicable for mill diameters ranging from about 1.5 to 4 feet or more, and for ball sizes of about 0.75 to one inch (85% Al_2O_3). The constant K for the bench scale (8-inch diameter) conforms even closer than stated by the authors if the expression is corrected for the "effective" mill diameter by deducting the ball diameter in each case. A grinding aid (0.3% naphthenic acid), and a compaction aid are generally used. Hydrophilic and hydrophobic grinding aids have been developed. Green densities exceeding 3 g/ml at only 5000 psi forming pressure were attainable, making it possible to sinter an all-alumina composition to a density of 3.88 to 3.90 g/ml within one hour at 1700°C at less than 9% shrinkage.

Rose and Trbojeric showed that the charge in mills at 1.5 times the critical speeds oscillates in a pendulum-like manner; the leading edge of the charge ascends to an altitude of about 45 degrees above the horizontal, and then, owing to deceleration of the charge, because of slippage along the shell, the leading part collapses and falls as a coherent mass. This produces a heavy blow which can cause more grinding than merely the sliding of the charge on the shell.

McCreight (1954) correlated the ceramic properties (compressive strength) of alumina and an alumina porcelain with ball-milling time, granulation, and dry pressing. Minima in the curves of the single-component oxide were found between 30,000 and 50,000 revolutions of the ball mill. Granulation by slugging, that is, by forcing pressings at 6000 psi through a 10-mesh sieve, provided 30% greater compressive strength, 1.5% less shrinkage, and 1% less absorption in the specimens, as compared with specimens formed from ungranulated material. High-pressure hydrostatic forming was preferred.

Poluboyarinov and Kirshenbaum claimed that dry grinding of Bayer alumina with small steel balls is faster than grinding with porcelain balls. It requires only four to six hours with steel balls, while 10 to 15 hours are required with porcelain. The amount of iron pickup is small and does not affect the quality of the production for many purposes. Actually, the Bayer structure of the calcined aluminas can be completely disintegrated into crystallites within one-half hour in a laboratory-scale one-gallon ball mill, rotating at 70 rpm, and charged with 12 kilograms of 1/4-inch steel balls and one kilogram of alumina. With this ball size, attrition of the crystals is relatively very slow. The product is suitable for appraising crystal size distribution, but is too discolored for fine ceramic ware.

Poluboyarinov and Ershova (1949) found that alumina ground

with porcelain balls does not attain the proper sintered condition until 1750°C has been reached. Alumina ground with steel balls (HCl leached) attains the same sintered condition at 1600°C. Alumina prefired at 1450°C sinters much better than unfired alumina. Rybnikov suggested that Bayer trihydrate (gibbsite) can replace calcined ceramic alumina, and claimed that it is easier to grind in ball mills, needs no precalcination, and sinters more readily with clays. This was refuted by Arandarenko and Poluboyarinov. Bayer trihydrate is usually quite difficult to grind because of its gummy nature. It has been added in small amounts (about 5%) to alumina during grinding to improve the isostatic molding properties. It has an adverse effect on the reactivity and green density of reactive aluminas, however.

Berry and Kamack investigated the surface activity during dry grinding and claimed there was no limit to the fineness of the particles in ball milling, except for the tendency to reagglomerate. The practical limits in their dry-grinding tests on ilmenite, limestone and silica, however, were about 1.0 to 1.3 microns, unless a grinding aid was used to prevent packing. They found an increased grinding rate with decreasing ball size, but the minimum effective ball size depends on the mill diameter. With balls between 1/2 and 1/16 inch diameter, the ball size and the mill size are both significant factors affecting the grinding efficiency.

Reagglomeration during dry grinding is a very advantageous factor affecting the reactivity of alumina in dry forming processes. The reagglomerated particles contribute to better free-flow in transport to molds, and are relatively denser than agglomerates formed by wet methods, thus providing higher compacted density. Crystal orientation is likely to be more randomized. The addition of lubricants and binders can be restricted to the surface requirements of the pelletized particles, thus reducing the amount of burnout necessary in the subsequent firing operation. Papadakis summarized research on the ability of a material to break down and to reagglomerate, and derived equations for the optimum use of ball mills.

The agglomerated nuclei formed during ball-milling act as seed for dry pelletizing operations. Actually, the pelletizing equipment may consist of a small horizontal cylinder, rotating at a speed sufficient to cause cascading of the powder. Lubricants, compaction aids, e.g., stearic acid, wetting agents, and temporary binders can be added during the grinding and pelletizing operations. The pelletizing operation may be performed in heated apparatus to enable the use of high-melting waxes or to remove moisture. Most isostatic compositions require removal of the free water below about 0.2%. Also, because of the high compaction densities attainable with the modern reactive aluminas,

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it may be necessary to preheat pressed forms at temperatures just sufficient to volatilize organic additives prior to firing.

Alternatively, the agglomeration and pelletization effects may be destroyed, often with some difficulty, by aqueous suspension. If hydrophobic additives were used in the grinding or pelletizing operation, their resistance to wetting can be circumvented by the addition of soaps or detergents to the alumina. The main advantage of completely dry forming operations, namely high compaction density, is substantially lost by converting to wet operations.

Okuda et al. described the effect of rubber linings about one-third of an inch thick on the efficiency of wet milling alumina and other hard materials. Rubber linings withstand hard wear relatively better than ceramic linings, but ball wear is greater with the rubber lining.

Sintered alumina grinding balls (99.5% pure), formed by isostatic molding and fired at temperatures above 1550°C, may have densities exceeding 3.88 g/ml. A common appraisal for resistance to wear of alumina grinding balls consists of charging 6 kilograms of the balls (1-inch diameter) with 200 g tabular alumina, minus 325-mesh, and 150 ml water, to a 1.3-gallon mill and rotating at 70 rpm for a 2-hour period. The ball charge is washed, dried at 110°C for 15 hours, and weighed. The test is repeated until the weight loss remains constant, renewing the charge of tabular alumina for each 2-hour period. Wear losses not in excess of 0.1%/hr are considered satisfactory. Ball wear appears to be proportional to the surface crystal size, suggesting that impacts during ball-milling cause the loss of particles in crystal units rather than by wear.

The advantage of alumina in comparison with steel grinding balls lies in its freedom from introducing objectionable discoloration, as in the grinding of pigments, glazes and colors. The advantage of alumina in comparison with porcelain or native ceramic materials is its superior hardness and relatively higher density. Clay discussed the use of high-density grinding media particularly for milling porcelain enamels.

15   FORMING ALUMINA CERAMICS

The early forming methods for alumina ceramics were taken directly from methods in vogue for clay ceramics (B. Moore, 1942; Kiley, 1946). The poor plastic properties of the available alumina types and lack of knowledge of their physical properties restricted the scope of forming methods. Slip casting, dry and semidry cold pressing, extrusion, isostatic forming, and the Verneuil process were among the available methods. Ball-rolling was soon developed (Derfler). More recent developments such as hot pressing, hot rolling, flame spraying, and fusion casting appear to have developed with aluminum oxide as the principal agent.

Various forming operations have been discussed in <u>Critical Compilation of Ceramic Forming Methods</u>, A. G. Pincus, project coordinator, January 1964. It contains an extensive bibliography on "Characterization of Particles and Assemblies of Particles" by Mular and Mee, covering the period 1958 to July 1963, and another on "Forming of Particles" by Pincus, Rose, and Mee for the period 1955 to July 1963. Many of these latter references apply specifically to the formation of alumina, but in many, forming is incidental to other properties, particularly fired properties, which are not indicated by the classification method used. In the cited survey the role of particle preparation as an important factor in forming operations was emphasized, and different methods of producing fine particle size were mentioned including: comminution, precipitation, atomization, thermal decomposition, vapor deposition, and thermal quenching, all of which can be applied to alumina particle production. The physical properties of alumina particles upon which the forming and fired behavior depends, have been discussed in other sections to some extent. Particle distributions can range from completely anhedral crystals to substantially completely well-developed crystalline platelets. The ability to control particle size distributions in the subsieve range, so as to obtain higher packing densities during forming has been mentioned. The adverse effect of porosity in incompletely ground Bayer particles on the fired density is a factor. Methods for improving the flow of dry particles in the subsieve range by pelletization and the incorporation of lubricants and binders in the pellets have also been considered.

In the cited survey the forming processes were arbitrarily divided into the classification: cold forming, hot forming, melt forming, and miscellaneous. Cold forming includes such operations as: rigid die forming; flexible die forming (isostatic, polymeric die liners); extrusion; vibratory compaction; plastic forming (organic aids); slip-casting; jiggering; impacting; ramming; cement gunning and casting; surface coating from suspensions (enameling and dip coating); spraying and slush

coating; electrostatic spraying; and possibly other distinct modifications.

Hot forming includes many of the preceding dry operations performed at high temperatures and pressures and combining forming and sintering operations in many cases. Isostatic hot pressing has been applied to specimens in a volume 1.5 by 3 inches at 2200°C and 40,000 psi. Larger installations capable of forming specimens 13 inches by 4 ft, operating at 1550°C and 15,000 psi helium gas pressure have been constructed. Hot rolling of ceramic plates and sheets has been performed on isostatically formed bodies, preheated to 1520°C with metal rolls having ceramic shells of sintered alumina.

Melt forming processes include operations most generally applicable to glass, but also applicable to alumina or to high-alumina compositions, as in fiber drawing (Fiberfrax, high-alumina glasses); fusion casting (abrasive and refractory fused alumina, and high-alumina cast refractories); flame-sprayed coatings; and crystallization of glasses, self-nucleated; sprayed forms (free standing shapes); single-crystal-growing by flame fusion (Verneuil), temperature gradient in molten alumina or in saturated molten lead salt, or by vertical pull (Czochralski).

The miscellaneous forming methods in the cited reference include: forming from vapors; forming with fibers; electrophoretic-forming; impregnation; reaction sintering (particularly applicable to alumina as one final component of the thermitic reaction); high-energy rate forming; and machining and grinding.

15-1 COLD FORMING OF ALUMINA

Hofmann, Scharrer et al. (1962) discussed the fundamentals of dry pressing. Bodies consisting of clays or oxides, when dry pressed, contain some water. The main cause of the cohesion of these moist particles is the Coulomb force between the ions adsorbed on the surface of the particles. The cohesion is greatest with platelike particles as is the case with Bayer alumina. The cohesion also increases with increasing valency (in the order Na, Ca, Ba, La, etc.), which is the basis of the Hardy-Schulze flocculation rule. An unexpected result is that the greater the cohesive strength of the moist framework, the less the shrinkage during drying and the lower the compaction density. They found that lanthanum ions provided very high strength with decreased plasticity. An increase in dry strength resulted when the calcium ions of natural clays were replaced by sodium ions.

Haase (1960) investigated the mechanism of dry pressing. The facility with which the pressure was distributed through

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the dry powder in a steel die was measured as the ratio of
the pressure transmitted to the bottom punch to that applied by
the top punch (Pb/Pt), the difference representing the friction
between the particles and each other and the wall of the die.
A pressure-calibrated, mercury-filled steel chamber measured
the compression. For dry samples Pb/Pt decreased exponentially
as the height of the pressed cylinder increased and was
approximately 0.5 for height/diameter = 0.5. As the moisture
content in the sample increased (up to 8%), Pb/Pt increased.
Unsaturated long-chain fatty acids (especially oleic acid)
increased Pb/Pt, but lubricants such as machine oil were no
more effective than water. Oleic acid also formed a more or
less permanent film on the die, which greatly increased the
transmission of pressure.

Cooper and Goodnow (1962) found that radiographing of
lead grids introduced into a powder provides a simple means
for inferring the density distribution after compaction. The
technique was used on alumina dry-pressed in one direction,
and showed qualitatively that wall friction is the major
source of density variation. W. C. Allen (1961) reviewed the
development of the fundamental mathematical relations between
compositional, pressing, and firing factors for ceramic materi-
als. It was believed that apparent fired density is mathemat-
ically predictable from the volume shrinkage, pressed density,
and ignition loss. The temperature required to meet a de-
sired density is affected by the amount of additives, particle
size, forming pressure, and the time of holding the maturing
temperature. The ratio of the linear shrinkage values parallel
to and normal to the pressing direction (HS/LS ratio) is a
function of the particle orientation, and it allows the
estimation of liquor shrinkage from the volume shrinkage. The
HS/LS ratio is affected by the type of additive, granule
density, granule size distribution, and forming pressure.
Linear shrinkage can be controlled by the use of controlled
firing techniques which result in constant density and loss on
ignition. Meerson (1962) concluded that the compressive force
consumed by external friction may be several times higher than
the extrusion force for brittle, hard materials. Friction
between powder particles was not considered a cause for non-
uniform density in the compact, and the assumption that the
walls exert a direct compacting effect was rejected. External
friction is the main cause of density gradient in specific
directions in the compact.

Croskey (1949) developed a production method for casting
slip relying on controlled weight and casting rate. Hauth
described the mechanics of slip casting using fine-ground fused
alumina fines. Deflocculation could be attained by the addi-
tion of the proper amount and type of either an acid or base,
following ball milling and acid treatment to form a suspension
in water. Both drain and solid castings were possible from

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acidic or basic slips through a range of pH from 3 to 12.5, and of density from 2.60 to 3.00. Shiraki observed the effect of grinding time on the particle size distribution, the effect of concentration and particle size on the viscosity of the slip, and the effect of temperature on the casting operation. He found that the viscosity of Bayer alumina slip changes during aging, and that the most suitable condition for casting is attained after more than a week's aging. Casting in the acidic range was recommended. Yamauchi and Kondo (1949) found that one-half the alkali in calcined alumina can be removed by washing and heating to 1300°C, and two-thirds is removed by the addition of 20% HCl (1N). The slip viscosity was maximum at pH 5 to 8, but was most suitable for casting at pH 4 to 5, obtained by adding about 1% $AlCl_3$ to the alumina. Drained alumina slip recovered after casting contained dissolved gypsum from the mold, and showed increased viscosity, but this high viscosity could be decreased to the original value by the addition of barium chloride. Boiling the slip generally improves the slip-casting compositions prepared from Bayer aluminas by reducing the drift caused by release of alkalinity and by eliminating air bubbles.

Ramsay (1950) recommended the use of flocculant that is insoluble in cold water but soluble in hot water (about 0.1% of either hydrolyzed polyvinyl alcohol or phenyl-acetic acid) to control deflocculation obtained with sodium phosphate. Blaha (1950) added albumin or gelatine to the slip at a temperature at which the cohering substance is soluble. Intricate slip-castings could then be prepared by adjusting the temperature in the mold to cause the cohering substance to gel. Maxwell, Gurnick, and Francisco developed a freeze-casting method which allowed the slip-cast form to dry by sublimation.

Blackburn and Steele invented the method of inbedding a fluid pressure supply in the plaster mold so that after the water of plasticity had been absorbed from the ware by the mold, a uniform pressure (50 to 80 psi) could be applied to release the ware from the mold (Ram method) Suction could be applied during the initial casting period.

Chatterjee and Chakravarty noted that the alumina slip remained flocculated during aging. It acquired a net positive charge in acid media. Dietzel and Mostetzky investigated the mechanism of dewatering of a ceramic slip by the plaster mold, and found that the diffusion coefficient is satisfied by the expression: $Dp = (x/\sqrt{t})^2$, in which x is the distance to which the water has penetrated in time t, for values of D ranging from 8.5 to 17.0 X 10^{-2} cm^2/sec. On the basis of this theory, the casting growth is parabolical. Nies and Lambe (1956) considered the absorption capacity of the gypsum mold from its

crystal size and pore spaces, and evaluated the drying rates of gypsum mold structures under typical commercial conditions. Data were developed to show the maximum rates of water movement into and out of the molds under practical conditions. Salmang (1956) stressed the importance of surface tension on ware cracking in slip casting. Rempes, Weber, and Schwartz developed a "film technique" for slip casting a variety of metals, cermets, and ceramics, employing a thin layer of sodium alginate on the inside surface of the mold so as to serve as a tenacious porous membrane (0.2% Keltex solution). Schifferli (1959) has given a general review of the method, showing some of its advantages and limitations when used with refractory oxides, cermets, and powdered metals. Recent investigations are concerned with better control of flow properties (Worrall, 1963; Hamilton, 1959; Kukolev, 1963; and Buehler, 1963; Hermann and Cutler, 1962).

Alumina compositions are slip cast in sizes as large as glass tank blocks. Popil'skii and Galkina (1960) describe the vacuum treatment of slips and the repeated vibration of the plaster molds during the casting of high-grog-containing refractories. Eldon Miller (1964) developed a slip cast alumina refractory containing from 1 to 10 wt % of volatilized silica and from 0.1 to 0.3% dispersant such as sodium phosphate, which could be vibrated during setting without surface cracking.

Schwartz, White and Curtis compiled slip casting fabrication data for various types of crucibles.

Hydrostatic or isostatic pressing, in its primitive form, consisted of immersing the powder compact encased in a rubber bag in a pressure vessel containing water or oil that could be subjected to about 4000 to 5000 psi.

Vassiliou prepared crucibles, combustion boats, etc., by a simple hydrostatic pressing operation, using rubber molds to distribute the pressure uniformly. The isostatic process was a pioneer development in spark plug manufacture by Champion Spark Plug Company (B.A.Jeffery, 1932; H. W. Daubenmeyer), using rubber molds. From spark plugs the method has been applied to electron tube elements, and in the fabrication of ceramic radomes, and grinding balls, among many increasing applications (Anderson, 1958; Schaefer and Stoia, 1962). Alumina radomes have been prepared by the optional methods of forming on a rigid, smooth-surfaced, nonabsorptive mandrel (Anderson, Brandt, LeClercq, and Fargo) or within such a mandrel.

As isostatic forming is substantially a dry-forming process (moisture less than 0.2%), it was necessary to create free-flow of the particles for easy transport to the mold, and this was done by spray drying to form spherical particles in the nominal range of about 20 to 70 mesh. The usual pressures applied in isostatic forming have been around 4000 to 5000 psi.

G. D. Kelly (1961) investigated the effect of higher hydro-static pressures (up to 100,000 psi) on the body properties. Powder-packed unfired bulk densities increased from 2.03 to 2.59 g/ml, and fired densities from 3.75 to 3.89, for a change in forming pressure from 3000 to 100,000 psi. Fired strength improved only slightly at low pressures and actually declined at the higher pressures, suggesting that fired strength (and pore structure) was independent of forming pressure, and that optimum strength is attained only under a particular set of firing conditions. (It is possible that as the compacted density approaches the fired density, the removal of small amounts of volatiles causes strains and cracking defects.) It was concluded that the gains attained beyond 6000 psi hard-ly justify the higher forming pressures. No significant dif-ference was claimed between the pure powder-packed bodies and specimens prepared by spray drying a composition containing combustible binders (Cumar P-10 resin and collodion), although it might be expected that the removal of the organic matter would cause loss in density and in strength.

Bell, Dillender, Lominac, and Manning investigated vibra-tory compactions as a forming method. Three "nonplastic" powders, pure alumina, an alumina-chromium cermet, and a titanium carbide-nickel cermet were subjected to mechanical, electromechanical, pneumatic, magnetostrictive, and exponential horn driver units as vibratory sources. In the alumina com-positions the size distribution of particles was varied by mixing AWIF 38900, 38600, and 38500 (Norton Company) with T-60 tabular alumina (Alcoa). For comparison, the same compositions were formed by dry pressing and were re-pressed hydrostatically at 47,500 psi. The vibratory energy was applied at 2 impacts per cycle, one in each axial direction, at about 70 cycles per second. The alumina samples were dampened with 0 to 8% water prior to vibrating. The conclusions derived from the investiga-tion were that specimens formed by low-frequency vibration have properties which are about the same as specimens formed by dry-pressing followed by hydrostatic re-pressing. The vibratory method has these advantages over hydrostatic forming (a) no binder is required, (b) the method is considerably faster (on a laboratory scale), (c) less equipment is required, and (d) intricate shapes can be formed in one operation. Different powder compositions and particle size distributions may require different vibratory compaction procedures, but all compositions investigated were successfully formed by vibration. Particle size distribution has a considerable effect on the compacted density.

Quayle et al. (1945) described a method of making a ceram-ic body, which comprised mixing the ceramic material with a thermoplastic polymerized bonding material, shaping, and heating the form in two steps. One involves the depolymerization of the bond to form a volatile material which leaves the body

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uniformly without decomposition; the other involves the sintering of the ceramic material.

Schwartzwalder (1949) described injection molding of single and multiple oxide spark plug compositions. In this process an intimate mixture of the alumina composition, thermoplastic resin, and a plasticizer is heated to about 150°C and injected into a cold die (water-cooled). The press opens automatically and the set pattern is ejected. Howatt (1948) used as the thermoplastic material, ethyl cellulose, polystyrene, or wax, and a plasticizer such as pine oil or solvent resin. The amount of resin required for this process was large and the shrinkage during firing was unusually high, making the technique less attractive than other forming methods for spark plug manufacture.

Moteki applied injection molding to the production of high-alumina porcelain and found that the physical, mechanical, and electrical properties were practically the same as those obtained by dry pressing or by casting. The method was considered satisfactory for making cutting tools and insulators. Randolph (1961) pointed out that careful matching of the thermoplastic resins and oils with the particle size and density of the ceramic is necessary. The oils must be baked out at a slow rate, leaving the resin to provide sufficient green strength for machining operations prior to final firing. Attainable tolerances are ± 1% of the fired dimension, and the thickness ranges from 0.02 to 0.25 inch.

Ryshkewitch (1960) summarized the prior information on the extrusion of alumina. Cold extrusion processes tax the ability of the "nonplastic" single oxides to acquire plastic properties sufficient to flow and assume a continuous formed shape. The addition of small amounts of various organic plasticizers or of the plastic clay materials to ground Bayer alumina in the proper consistency with water is sufficient, however, to allow auger extrusion.

White and Clavel (1963) reexamined the extrusion properties of non-clay oxides, using alumina powder of less than 5-micron particle size. The extrusions were forced through a 1/8 in. diameter die from a 1-in. diameter extrusion cylinder. From tests in which 23 wt % of hydroxymethyl cellulose solution (20 wt % organic) acted as the plasticizer, a pressure of 4400 psi for a flow rate of 0.1 in./sec, and 4650 psi for a flow rate of 0.5 in./sec were measured. It was concluded that the plastic dispersion was a thixotropic type. The alumina was not thixotropic in rubber-xylene plasticizer, however.

Rogers and Mooney (1955) molded an 88% Al_2O_3 composition containing 10% $3CaO \cdot 5Al_2O_3$ and 0.52 part polystyrene, 0.11

part hydrogenated peanut oil, and 0.27 part of a more volatile oil (50 to 150°C). Cornelius, Milliken, and Mills (1957) extruded attrition-resistant alumina trihydrate particles impregnated with an aqueous solution containing nitric acid sufficient to form a minor amount of aluminum nitrate in a moist compact. Brennan and Field (1960) kneaded finely divided calcined alumina containing 1 to 18% combined water with 0.2 to 1.1 volumes of aqueous ammonium hydroxide per volume of the calcined alumina, extruded the composition, dried, and calcined it.

Richter (1962) plasticized alpha alumina for extrusion with gel-like aluminum hydroxide of nearly nonthixotropic properties (5 to 10% Al_2O_3, ratio oxide:sulfate or chloride 10:1). Zet (1963) discussed various organic plasticizers for extruding alpha alumina shapes; end-closing techniques, and methods for firing of ceramic pipe in a tunnel kiln at 1700°C.

Howatt et al. (1947) prepared thin ceramic sheets of titanates for capacitor dielectrics by extrusion of heavily loaded plastic pastes onto a moving metal belt. Siegrist also extruded thin ceramic plates, having a fired thickness of about 10 mils, through an orifice having the width and thickness of the unfired extrusion.

Thompson (1963) mentioned two methods for forming thin ceramics for mounting devices and vacuum tube spacers in a thickness range from 0.005 to 0.100 inch (1) extrusion (J.L. Park, 1960) and (2) casting or knife coating (J. L. Park, 1961). The extrusion process uses a water-soluble polymeric organic binder (polyvinyl alcohol) and a water-soluble plasticizer (propylene glycol, glycerol), both of which volatilize above 100°C. The moisture content is adjusted to form a heavy paste which is deaired and extruded at moderate pressure through a rectangular die to form a continuous strip or tape. The tape is carried through a dryer in which the moisture is reduced to less than 0.5%.

Young, Wilkins et al. (1960) described nonglaze-containing, screen-printed, conducting patterns comprising silver-platinum alloys as two-dimensional electrodes. Bulk alloy ultimate tensile strengths for the silver-platinum alloy system at firing temperatures of 1000 to 1500°C on two ceramic substrates were given.

Young, Owen et al. (1960) described the production of screen-printed electrode films of alloyed silver and platinum. Powders containing no glaze have good adhesion to refractory substrates and acceptable conductivity. Extensive physical and electrical property data were presented. The use of evaporation-annealing, or vacuum deposition on a hot substrate, as a substitute for cycle-annealing of gold-palladium thin-film resistors was discussed. The effect of electron bombardment and

radiation damage was discussed. Radiation damage varied from none for the resistors to a permanent effect for a film capacitor. The useful operating temperature for screen-printed $MoSi_2$ resistors was about 650°C.

The mass production at RCA of miniaturized alumina and titanate wafers for the "micromodule," a small block-form electronic circuit was described (Ref. Anon. "Ceramic Wafers"). Held (1963) described a capacitor element comprised of a ceramic wafer composed of dense nonporous aluminum oxide, characterized by a relatively high and uniform dielectric strength and a nonvarying dielectric constant up to 540°C, and having conductors of gold, silver, or platinum, or their alloys on each side of the ceramic wafer. A thin layer of glass was fused to and covered the exterior portions of the wafer, bonding the conductors to it, and increasing the resistive path around the wafer.

The knife coating process casts a coating onto a non-porous carrier material. The ceramic powder is mixed in a ball mill with an organic volatile solvent, a wetting agent, and an organic plasticized binder. The viscosity is adjusted to 500 to 1000 cpoise sec. One of the best water-soluble binders is methylcellulose.

15-2 HOT PRESSING

Ridgway and Bailey (Norton Company) in 1937 described a method of making a self-bonded granular material of a metal oxide of the group Al, Mg, Zr, Ti, Th, Ce, and Cr, which comprised the steps of enclosing the granular refractory metal oxide in a mold space, heating the material while subjecting to pressure within the mold to a temperature close to its melting point, at which it is plastic, and compacting it into an integral mass, and as soon as it has been compacted, cooling to a point materially below its melting point. Comstock (Norton Company) in 1952 described the method of preparing molded articles of alumina having high compressive strength, high density, and substantially no porosity by hot-pressing in a graphite mold at a temperature of 1650 to 1800°C and at least 500 psi pressure, a mixture consisting of 98.7 wt % alumina, 0.4 magnesia, and 0.9 cobalt oxide. The alumina used should have a purity better than 99%, and have microcrystallinity (98% of its particles under 2.5 microns, with 50% under 1 micron). The formed product has a density of at least 3.94 g/ml, and compressive strength above 450,000 psi.

Watson (1950) patented a graphite mold for hot-pressing refractory crucibles, and Ballard (1951) patented the process for hot-pressing any oxide having a melting point above 1850°C by heating at 1650°C and pressing at 500 psi. Livey et al.

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(1964) have patented a method which comprises hot-pressing at 600 to 1000°C and not less than 10,000 psi, a stoichiometric refractory metal oxide powder having an average crystallite diameter of less than 0.1 micron, or a nonstoichiometric powder having insufficient excess oxygen in the oxide to alter the crystalline form of the corresponding stoichiometric compound and having an average crystallite diameter of less than 0.1 to 0.25 micron. Murray, Rogers, and Williams (1954) discussed the theoretical aspects of hot-pressing in terms of the Shuttleworth-Mackenzie theory relating the end-point density with the applied pressure, surface tension, yield stress, viscosity, and the number of closed pores per unit volume. The predictions of the equations agreed fairly with the experimental results.

Riskin and Goncharov (1957) claimed that hot-pressing is more suitable for obtaining dense bodies (65% Al_2O_3) than recrystallization by sintering at 600°C and pressing at 7100 psi. Pointud and Caillat (1957) found that a temperature of at least 1550°C was necessary to attain a density of 3.96 g/ml. Mangsen, Lambertson, and Best (1960) developed a rapid method for evaluating aluminous materials for their hot-pressing characteristics. A rate equation proposed by Murray et al. was found to hold for two aluminas, thus making it possible to predict the effects of changes in the hot-pressing conditions.

Francis, Swica et al. (1960) determined the relations between time, temperature, pressure, and grain growth in hot-pressing with alumina grain to determine the technique necessary for the production of dense polycrystalline alumina having a grain size in the 4 to 5 micron range for use in thermal conductivity studies. Alumina having a density of about 95% theoretical and grain size in the desired range could be hot-pressed rapidly at the maximum temperature. Jackson 1961, Accary and Caillat, Scholz (1963) investigated new theories regarding hot-pressing. Densification cannot be expressed by a linear plot of log porosity vs. time, and various modified expressions have been suggested. Vasilos and Spriggs (1963) observed that apparent diffusion constants calculated for the densification process are orders of magnitude greater than for pressureless sintering, which might be explained by enhanced diffusion under stress. Alternatively, however, lower calculated coefficients, which are more in agreement with pressure-less-sintering results are obtained when pressure correction terms, modified by porosity, are applied to the existing relations. It was concluded that in the pressure range covered, densification beyond the initial stages is a diffusion-controlled process.

Hamano and associates found that enhanced grain growth and orientation occurred in alumina, hot-pressed at 1700 to 1900°C. The grain growth was associated with the Na_2O content of the alumina. A temperature increase under high pressure

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caused a layered structure; the c-direction of the alumina crystallites tended to be parallel to the hot-pressing direction. McClelland and Zehms (1963) examined the asymptotic end-point density of hot-pressed aluminum oxide over the range 1100 to 1500°C and 500 to 6000 psi. The pressure dependence was explained on the basis of a plastic-flow model which exhibits a critical shear stress. The temperature dependence suggested that the critical shear stress is a thermally activated process having an activation energy of 39 kcal/mole. Spriggs, Brissette, Rossetti, and Vasilos (1963) hot-pressed in high-density alumina dies. The contamination and reducing atmosphere of conventional graphite die-pressing was eliminated; it was possible to attain higher pressures and lower temperatures; and fabrication of otherwise easily reduced oxides was achieved.

Budworth, Roberts, and Scott (1963) devised a technique for joining alumina components by hot-pressing. Polycrystalline pieces have been joined to each other and to single-crystal alumina.

Reed (1961) used the induction plasma torch to grow crystals of sapphire at higher temperatures than is possible with flames and in inert or reactive atmospheres. Meyer (1964) found that the fusibility of various refractory powders, including alumina, is not related to the melting point or to the energy of melting. The pores which are found in plasma-fused spheres of alumina (and zirconia) are due to the formation within the plasma of nitrides which are later reoxidized in contact with air, with the liberation of nitrogen. A noble gas plasma is recommended for oxides of this type.

15-3 MISCELLANEOUS FORMING METHODS

Hallse (1963) applied to alumina forming a high-energy unit (Dynapak, General Dynamics Corp.), able to compress a ram with energies as high as 2 million in.-lb at velocities approaching 850 in./sec. He concluded that it probably would be necessary to evacuate the whole die assembly, to heat the ceramic powder, and to use a shock absorber to obtain sound compacts.

Some factors which influence forming, or are influenced by it, are shown in the following references.

According to the U. S. Atomic Energy Commission patent Brit. 832,309 (1960), finely divided ceramic alumina powder is granulated homogeneously in order to obtain uniform density in pressed and sintered shapes. The powder is first mixed with two liquids of widely different volatility. The more highly volatile liquid, which predominates initially, facilitates

mixing to a plastic mass, but is volatilized during granulation, leaving the desired amount of moisture in the granules. In the case of alumina and magnesia a sudden increase in strength occurs at temperatures which correspond apparently to the destruction of the absorbed water film on the surface of the particles and to the replacement of hydrogen or hydroxyl bonding between particles by ionic bonds. This occurs at temperatures well below those at which sintering proper commences (Clark et al., 1953). Mong and Donoghue found it advantageous to include a portion of a compound of aluminum that decomposed to alumina upon heating in the preparation of alumina refractories. Brandes (1957) claimed the method of including not less than 20% gamma alumina by weight for compositions containing alpha alumina or other principal components.

Viola and McQuarrie investigated the effect of different treatments of raw alumina (Alcoa A-14) on the relationship between the unfired and fired densities of alumina compacts. They obtained an expression:

$$K = [(1/\sqrt[3]{D_u-D_o})-(1/\sqrt[3]{D_f-D_o})] / [(1/\sqrt[3]{D_u-D_o})-(1/\sqrt[3]{D_t-D_o})] ,$$

in which D_u, D_f, and D_t are respectively the unfired, fired and true (3.99 g/ml) densities.

16 SINTERING

16-1 INTRODUCTION

Sintering may be defined as the consolidation, densification, recrystallization, and bonding obtained by heating agglomerated powders during or following compaction, at temperatures below the melting point.

Alumina has remarkable properties for a variety of applications when it has been prepared in massive form by the process of sintering. It may appear as a single-oxide component or in combination with various ceramic oxides or other refractory materials, including metals. The composition may be substantially crystalline or may contain vitreous phases. The composition may vary throughout a wide range of texture, porosity, transparence, and other properties. The versatility of alumina in these applications is dependent in large part upon its favorable refractoriness, hardness, chemical inertness, high strength, high electrical resistance, good thermal shock resistance, and availability in cheap, high-purity forms.

Only a brief review of the theoretical aspects of sintering is possible within the scope of this review. Our present knowledge of the process has been largely aided by investigations of the sintering of alumina, however. Several theoretical models have been proposed for the sintering process, representing conditions in which no vitreous phase is present as well as conditions involving vitreous phases. These models are probably not faithful representations of the actual mechanisms of sintering (Wilder), because they postulate uniformly sized spherical particles and other idealized conditions. In some cases the observations are valid only for the initial stages of sintering. Surface tension has generally been considered a driving force of sintering, whether the sinter consists of pure crystalline phases or includes a liquid phase. Three stages of sintering are usually considered: an initial period of neck growth between adjacent particles, a stage of material transport or densification, and a final stage of grain growth with elimination of isolated voids. These are overlapping phenomena.

Kuczinski in 1949 developed an equation to distinguish between four transport mechanisms for inducing neck growth during the first stage of sintering, having the form: $\frac{x^n}{a^m} = f(T)t$, in

which f(T) is a function of temperature, t is the sintering

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time, and n and m characterize the mechanism responsible for the formation and growth of the neck of radius a. Transport by viscous flow fits x^2, by sublimation x^3, by volume (lattice) diffusion x^5, and by surface diffusion x^7. Herring derived linear scaling equations analogous to those of Kuczinski for determining the time, t_1, required to attain the same degree of sintering for particles or clusters of different sizes. The equations are: $t_1 = \lambda t_2$ for plastic flow; $t_1 = \lambda^2 t_2$ for sublimation; $t_1 = \lambda^3 t_2$ for volume diffusion; and $t_1 = \lambda^4 t_2$ for surface diffusion, where $\lambda = a_1/a_2$, the ratio of particle diameters. The rate of each transport mechanism increases in proportion to the ratio of particle sizes raised to the power representative of the particular mechanism. Ultrafine particle size is particularly effective for those stages of sintering dependent upon volume and surface diffusion.

Rhines proposed yet another concept of sintering, based on the topology of closed surfaces and which ignores dimensions, area, contained volume, and difference in direction. The parameters are: P, the number of particles in the powder; N, the number of separate surfaces required to define the shape of the material at any stage; C, the number of contacting points between particles; and G, the topological genus. The genus $G = C-P+1$. During the first stage of sintering, the genus increases somewhat, to complicate the exposition. During the second stage, the genus decreases to zero as the pores become isolated. In the third stage, the genus remains at zero and the pores disappear. Mackenzie and Shuttleworth, and Clark and White derived a sintering model based on plastic-flow transport, however, which has served to account for the phenomena of hot-pressing in the hands of Murray, Livey, and Williams. Felten refuted this for low-temperature hot-pressing of alumina, and suggested boundary sliding as the process responsible during the initial increase in compact density. Coble in 1963 observed that neck areas in hot-pressed sintering at 1530°C are greater than in pressureless sintering, and are constant for all periods between 10 and 480 minutes. For alumina, plastic flow contributes only slightly to densification at the pressures normally used (less than 10,000 psi). It was concluded that the final stage of densification occurs by increased diffusion under the influence of stress.

Wilder and Fitzsimmons used the relative rates of sintering fused alumina in a wide range of particle sizes, in an attempt to confirm the plastic flow transport mechanism. They found that even loose aluminum oxide powders exhibit sintering if the

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particle size is small (less than 20 microns). The values of n ranged from less than one to greater than 5. It is difficult to conclude from these experiments that the transport is by plastic flow. Navias in 1956 performed sintering tests on 40-mil sapphire spheres to verify the plastic-flow theory of neck development. Contact lenses were observed by heating the spheres by induction in a vacuum or in hydrogen at about 1900°C. The spheres eventually developed the hexagonal shape of cut gem stones. The tendency for fragmentary crystals to perfect their crystal form suggests this effect as a factor in sintering. Ground Bayer aluminum oxide is likely to be predominantly well-developed single crystals, while ground fused alumina or tabular alumina is substantially anhedral.

Kuczinski, Kingery and Berg; Coble; Johnson and Cutler; and others find that the sintering of alumina is a bulk diffusion process.

Burke investigated the role of grain boundaries in sinter-ing. Grain growth changes the configuration of grain boundaries relative to pores, and thus may affect the shrinkage rate. He concluded that the grain boundaries act either as sinks or as diffusion paths for lattice vacancies. Additives increase the sintering rate if they increase the diffusion rate or impede grain-boundary movement. Secondary recrystallization, that is, discontinuous grain growth of a few large grains that are nucle-ated and grow at the expense of a fine-grained matrix, is the general mechanism of sintering. Grain growth involves grain disappearance. Secondary recrystallization engulfs the pores. Kingery estimates the energy change corresponding to a change in crystal size from about 0.1 micron to 1 cm at 0.1 to 0.5 cal/g. The difference in free energy on the two sides of a grain bound-ary is the driving force that makes the boundary move toward its center of curvature, thus decreasing its curvature. If all grain boundaries are equal in energy, they will meet to form angles of 120°.

Coble in 1958 obtained experimental measurements of the rate of shrinkage of Linde A aluminum oxide compacts, the neck growth between single-crystal sapphire spheres and plates, and the effect of particle size on neck growth. The temperature depend-ence of the rate of shrinkage and neck growth in aluminum oxide is characterized by an activation energy of 165 kcal/mole. The observed data are mutually consistent with a bulk diffusion sintering model.

In 1961 Coble presented photomicrographs of pore and grain boundary structures that provided a qualitative description of the course of densification. During sintering the density increases linearly with the logarithm of time, and the grain size increases with the one-third power of time. Incorporation of the time dependence of grain size growth into late-stage bulk diffusion sintering models leads to corrected models by which a semilogarithmic behavior can be predicted. The sintering process is then controlled by bulk diffusion of aluminum ions; the oxygen transports along grain boundaries.

In summation, it appears likely that each of the cited theoretical models may contribute to the sintering operation under specific conditions.

The distribution of pores and their location with respect to the grain boundaries influence the time required to attain fired density. Normal grain growth in the final stage reveals the pores generally at 4-grain corners. An alternative condition, however, is that in which the pores collect in the centers of crystals often with a clear margin around the boundaries (Burke), resulting from secondary recrystallization. The conditions required to obtain these effects, about 12 hours at 1800°C or 2 hours at 1950°C, are well beyond those normally used in sintering alumina, both in duration and in temperature. Schatt and Schulze observed that the free surface (that of the original particles which have not lost their identity for complete intersintering with adjacent particles) shows a polyhedral terraced structure, considered to be the natural result of grain growth by solid diffusion.

Entress and Skatulla used electron micrographic methods for studying crystallization, pore dislocation, grain boundary intergrowths, etc., in sintering high purity commercial alumina for sapphire production (99.5% Al_2O_3) and industrial alpha aluminum oxide (98% Al_2O_3). They claim that all of the phenomena observed in sintering can be explained by an elementary diffusion theory. The one-component oxide systems are separated into two classes: (1) "active oxides" in which the sintering process is caused by structural defects (below 10^{-5} mm) cooperating with heat radiation effects, namely, collective crystallization and secondary recrystallization, and (2) "passive oxides" which are either fused products or naturally grown minerals that do not undergo any crystalline conversion or thermal disintegration. Secondary recrystallization confirms the diffusion theory and

cannot be reconciled with an explanation based on surface tension effects or plastic flow.

Tresvyatskii found that the rate of the process and densification are greatly retarded if large numbers of closed pores are formed within the crystals.

Pavlushkin (1963) stated that the shrinkage of corundum compacts commences at 1100°C (0.5%), reaching 10.5% at 1450°C. Actual sintering begins at 1400°C, and crystal growth is observed at 1600°C. The sintering temperature decreases with decreasing particle size down to 0.5 micron average diameter, then increases again. Hijikata and Miyake claimed that the temperature of incipient sintering (1000 to 1050°C) does not depend upon the particle size and the sintering atmosphere. The finer the particles, however, the faster and greater is the shrinkage. Bruch found that the densification rate is markedly dependent upon both the initial density and the sintering temperature. The rate of grain growth is independent of the initial density. Bruch recognized that the rate of sintering is very strongly controlled by the size of the pores in the initial compact. His empirical equation relating densification to initial porosity has the form:

$$\log P = 10 \log P_0 - \frac{0.434 \, nQ}{RT} + n \log t -$$

23.43, in which P_0 and P are the initial and final percent porosity, n and Q are constants having the values, -0.4 and 150 kcal/mole, respectively for their particular sample of Linde alumina, t is the sintering time in minutes, R is the gas constant, and T is the sintering temperature (°K). His equation relating grain growth to sintering temperature has the form:

$$\log D = \log K - \frac{0.434 \, mQ}{RT} + m \log t,$$ in which D is the grain

diameter in microns, K is a constant having a value of 5.66, and m has a value of 1/3. The other terms have the same values as in the preceding equation.

Bruch assumed that the large pores forming in "subnormal" sintering result from coalescence of pores rather than from the presence of relatively large void spaces in the original compact. Bolling emphasized that the ratio of the time required for bubble coalescence to the time required for void space to disappear is a measure of the probability that the void space will disappear faster than it can form larger pores. If the ratio is small, large pores should form, and sintering will be slowed; if the ratio is large, the pores which form should be

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small and isolated, and rapid sintering rates will be maintained. He concluded that the exponents n and m in the densification and grain-growth processes (Bruch's equations) are related as follows: n is about equal to -m.

Vergnon, Juillet, Elston, and Teichner found that rapid heating of alumina, whether alpha or delta phase, is more effective for shrinking the form. Both the ultimate percent compression and the rate of compression increase with the temperature. The rate is proportional to the initial specific surface, but is much greater for delta alumina than for alpha alumina. The activation energy for delta alumina is 145 kcal/mole, and for alpha alumina 55 kcal/mole.

Poluboyarinov and Vydrik found that sintering is dependent upon the prior firing and dispersion of the alumina. With increasing firing temperature, the activity falls off, making it necessary to grind finer to obtain a completely sintered body. Volosevich and Poluboyarinov showed that the density of pure corundum ceramics increases with increasing firing temperature (T_f) and is affected by the particle size of the raw material; for instance the density of the body formed from corundum with a particle size of one micron increased from about 3.0 g/ml at 1400°C to a maximum of 3.80 at 1600°C, and was not affected by a further increase in T_f up to 1850°C. The density of a body prepared from corundum with a particle size of 5.6 microns increased from 2.5 to 3.6 g/ml as T_f was increased from 1400 to 1850°C. If the raw material had a particle size less than 2 microns, the temperature of the preliminary heat treatment had little effect on the sintering. The rate of crystal growth became significant when the density of the fired body reached 3.5 to 3.6 g/ml. In the firing of pure corundum (99.8% Al_2O_3) with a particle size of one micron, sintering was completed at 1750°C, and the average crystal size was as coarse as 120 microns. The maximum bending strength, 36,000 psi, was obtained on the product fired at 1650°C. These data should not be considered optimum, because other factors of significance relating to the conditioning of the raw material were not considered. Improved sintering is illustrated by the performance of the reactive aluminas.

Kitaigorodskii and Gurevich in 1959 found that the strength of sintered alumina passed through a maximum with increasing temperature, in their tests at about 1800°C.

Sintering in the presence of a liquid phase has been

considered to be an expedient process for obtaining the desirable properties of high-alumina porcelains at reduced maturing temperatures. Bulavin; Kukolev and Leve; and Kingery investigated the mechanism of this process. The surface tension of the liquid phase is the major driving force. The viscosity of the liquid phase is a significant variable. Three separate densification processes were believed to occur: rearrangement of solid particles to give increased density; solution precipitation in which material is dissolved away from contact points, allowing the centers of the particles to approach each other; and finally, coalescence of the solid particles. Bulavin assumed that there was no liquid formation at the expense of partial solution of the crystalline phase. In this case, the first stage of sintering involves redistribution of the primary fusion and neck formation. A second stage involves the filling of the intercrystalline spaces with the liquid.

It is generally observed that the strength and elasticity of a porcelain is increased by additions such as alumina, having high elasticity. The effect is often ascribed to changes in the matrix, as for example, increased mechanical strength of the vitreous phase by partial solution of the alumina, localized around the alumina grains. Binns investigated the changes in fracture strength and Young's modulus of hot-pressed mixtures of glass and dense alpha alumina grain, within the concentration range, 0 to 40% alumina. The mixtures attained maximum density at 600 to 700°C. It was concluded from this work that elasticity and strength of the composite can be increased markedly beyond that of the glass. The rate of increase in elasticity is independent of the grain size of the alumina, and indicates that the composite solid behaves partly as a constant-strain system. The resulting uneven stress distribution is believed to be responsible for the observed increase in strength. Differences in thermal expansion of the glass and alumina always lower the strength and elasticity (for coarse crystalline grains), the reduction being most pronounced when the thermal expansion of the glass is higher than that of the crystalline inclusion. This is explained by the observed crack system formed during cooling. When the thermal expansion of the crystalline grains is higher, the cracks tend to follow a line parallel to the glass-grain interface, and to enclose individual grains; when the thermal expansion of the grains is lower, cracks tend to run normally to the interface and to pass from grain to grain, thus producing more disruption of the glass. With finer crystalline inclusions (around 10 microns), the strength reduction and tendency to crack formation is less.

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Allison, Brock, and White (1959) applied the rheological principles derived from aqueous suspensions to the behavior of closed-packed ceramic refractories bonded by a Newtonian liquid at high temperatures. Such systems are dilatant, that is, the particles assume a less dense packing when the body is sheared. With liquids that wet the solid particles, the magnitude of the cohesive force between the particles decreases progressively with increased liquid content. The yield point is usually considered the compressive strength. At loads above the yield point, three stages of flow can be detected, (1) decelerating, (2) constant, and (3) accelerating; the curves are similar in form to creep curves of a metal. The accelerating flow is associated with dilatancy. A distinction is made between highly vitreous bodies, whose behavior under stress approximates that of a viscous glass, and bodies which consist primarily of solid crystals with minor amounts of liquid phase. A further distinction is made between bodies in which the liquid phase forms continuous films around the solid particles and those in which the liquid phase forms discrete globules, so that solid-solid bonding occurs. The magnitude of the compressive and tensile strengths observed near the hot-strength peak, however, is apparently too great to be accounted for entirely on the basis of liquid bonding; partial solid bonding is probably present.

16-2 SINTERING ATMOSPHERE

The atmosphere during the sintering of alumina might affect the rate of sintering or the amount and nature of residual porosity. The oxygen deficiency observed by Bevan et al. when alumina is heated in water vapor might explain differences in sintering rate. Walker found that the rate of sintering of aluminum oxide at 1650°C is faster in hydrogen or argon than in air. Water vapor retards the rate in comparison with air. Oishi and Hashimoto found that the rate of grain growth of aluminum oxide at 1600 to 1960°C is in the same order, that is, dry hydrogen was most effective, followed by carbon monoxide, argon, and air. There was little difference between firing in air and in a vacuum. Vines et al. found that the internal porosity of dental porcelains can be reduced by firing in a vacuum, or in a diffusible gas (helium, hydrogen or water vapor), and by finish firing and cooling under pressure. They showed that gas diffusion controls the shrinkage rate during the final stage of firing. Low final densities resulted from firing in nitrogen or in carbon dioxide at one atmosphere. Theoretical densities were achieved in vacuum or in helium. In this case, however, the pores were trapped in a continuous glass structure. The mechanism of pore elimination from porcelains may differ somewhat from that of crystalline structures.

Coble in 1962 found no observable effect on the sintering rate of alpha alumina containing 0.25% MgO in hydrogen or oxygen atmospheres introduced at a dewpoint of -70°F. The hydrogen reacted with the alumina furnace wall to form H_2O and aluminum

suboxide. If the hydrogen was too dry when it met the specimen, the specimen slowly evaporated. Complete elimination of porosity was attained in hydrogen, oxygen, or vacuum, if 0.25% magnesium oxide was used as a grain-growth inhibitor. The pores generally become sealed off at about 95% of the theoretical density (about 3.98 g/cc).

Kuczinski, Abernethy, and Allan reported no action of oxygen pressure on the rate of neck growth between single-crystal sapphire spheres except in dry hydrogen mixtures, in which a faster rate was observed. Paladino and Coble have since found that the oxygen ion diffusion coefficients in single-crystal aluminum oxide are several orders of magnitude less than aluminum ion diffusion coefficients in polycrystalline aluminum oxide. In polycrystalline alumina, oxygen ion diffusion is enhanced by the presence of grain boundaries. As the slower rate controls the process, this would indicate that below a certain grain size, about 20 microns, the aluminum diffusion rate controls, while above this size the oxygen rate controls.

Dawihl and Doerre attempted to clarify the functional dependence between texture and deformation of polycrystalline alumina (<0.2% impurity) below 1000°C, the range of significance for interpreting the lifespan of alumina cutting tools. During the sintering of the specimens, surface area was used to measure the diffusion of the alumina, initially of high surface area, about 11.6 m²/g. Diffusion of the alumina was detected at 850°C, and was marked at 1100°C (2.3 m²/g). The pressed specimens were claimed to have less than 3 microns grain size when sintered between 1800 and 1900°C. Strength and hardness tests at room temperature, 500°C, and 1000°C showed that porosity was the major factor decreasing compressive strength until the grain size exceeded 3 microns. Initial grain growth began at 1500°C, accompanied by screw dislocations and etch pits.

16-3 SINTERING ADDITIVES

Additives other than temporary binders have been used in ceramic alumina compositions for several purposes. Among these purposes might be cited: crystal growth repression, crystal growth acceleration, acceleration of sintering or shrinkage rate, reduction in maturing temperature, alteration in porosity, changes in physical or chemical properties, and removal of impurities. Examples of these are shown in the various applications and preparation methods for ceramic aluminas.

Crystal growth in sintered alumina was early recognized an unfavorable factor affecting strength and thermal shock resistance. Although relatively pure fine-crystal aluminas were available, it was found that mere fineness of the starting alumina is not sufficient to avoid excessive crystal growth. Ryshkewitch ascribed excessive crystal growth on the surface of

sintered alumina to water vapor, since hot-pressed specimens do not show this effect. He observed that giant crystal growth is favored by small amounts (above 0.2%) of TiO_2 or ZrO_2 at sintering temperatures around 1800°C. Crystal growth was repressed by SiO_2, Cr_2O_3, and particularly MgO, if the sintering temperature was held below the point at which eutectics form with the alumina. He explained the action of growth repressors as the result of physical separation of the alumina particles. Magnesia, first suggested by Ryshkewitch, was considered the ideal additive (about 2.5%) for sintering aluminum oxide because its eutectic point is at 1925°C, well above the practical sintering point of pure alumina. Usually, as little as 0.02% magnesium ion is effective, but the temperature of inhibition is somewhat lower than the eutectic point.

Dawihl and Doerre state that as little as 0.25% MgO added to alumina causes spinel formation at 700°C. The spinel is not soluble in alumina, but dissolves up to 50% (mole) Al_2O_3 in solid solution at 1700°C. Roy, Roy, and Osborn observed that Al_2O_3 should precipitate to about 5% (mole) in cooling below 800°C. The spinel is observed at grain boundaries. Microscopic examination shows that amorphous substances exist on the edges of fused corundum crystals that unite the grains; they appear to be silicates of metals (Miyabe and Nishigaya).

Much of the early investigation of the effect of additives during sintering was undertaken to obtain suitable spark-plug porcelains. Reichmann in 1931 found that all-alumina sinters prepared from 2-micron fused alumina contained air pores and were grossly crystallized. Better results were obtained by calcining slip-cast forms of a mixture of gamma alumina and alpha alumina obtained from the Bayer process. When AC Spark Plug Division of General Motors Corporation commercialized the process, it was found more practical to develop other forming methods, as for example, injection molding (Schwartzwalder, 1949).

A search was made for additives that would reduce the firing temperature and obtain more compact and pore-free crystalline porcelains. McDougal; Fessler; and Schwartzwalder and their co-workers obtained patents on the addition of oxides of barium, strontium, cerium, manganese, nickel, cobalt, tantalum, or thorium; clay-lithia-magnesia, zirconia-silica; calcia-magnesia-silica; zirconia-silica-alkaline earth oxide; zircon-kyanite; and silica-strontia-magnesia. Monazite sand was also claimed as a suitable additive. The effective compositions usually ranged between 85 and 99% Al_2O_3.

Jeffery in 1942, and Riddle developed compositions containing up to 90% sintered alumina and the fluxes: calcia-magnesia, alkaline earth oxide-aluminum silicate, or beryllia-magnesia-calcia. Feichter reduced the sintering temperature to about 1650°C at 92.2% Al_2O_3 by adding a mixture of talc,

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fluorspar, clay, and chromic oxide. Bonnet prepared compositions containing about 80% Al_2O_3 and calcium or magnesium phosphate and hydrous silicates of magnesium or aluminum (bentonite or kaolin). Products having zero porosity were claimed upon firing at 1440 to 1540°C. Luks added manganese oxide as the principal flux. Austin and Rogers added CaO in the form of tricalcium penta-aluminate. Early German patents assigned to Robert Bosch specify the addition of natural or synthetic zeolite in which the alkali oxide has been replaced, wholly or in part, by an alkaline earth oxide, and all or part of the silica has been replaced by titania, to enable firing at 1500°C. Plastic talc-kaolin-feldspar binders were used with ground fused alumina. Eitel described the status of the German spark plug compositions prior to 1946.

Nakai and Fukami reported increasing strength and crystal growth in the following order for 2.5% additions of the following to alumina: $Na_2B_4O_7$, CuO, Li_2O, and Fe_2O_3.

Bron found that sintering of alumina is retarded by alkalies and alkaline earth oxides. At 1400 to 1500°C, about 2 to 5% TiO_2, added as titanium dioxide, ilmenite or magnesium titanates forms solid solutions which induce sintering to densities around 3.84 g/ml. The solid solution is of the subtraction type for additions of TiO_2, but of the substitution type for additions of magnesium orthotitanate. The former is more effective because it stabilizes the lattice defects in corundum at different temperatures. Defect structure favors the transport.

Robinson used 0.1 to 10% H_3PO_4 or 0.05 to 2% metal fluoride (preferably magnesium fluoride) to control grain growth.

Smothers and Reynolds, using Alcoa Alumina A-11 (0.20% Na_2O, 2 microns median crystal size), investigated the densification and grain growth of pressed compacts at each of four temperatures, 1300, 1400, 1500, and 1700°C. They found that one percent additions of TiO_2, Ti_2O_3 or Nb_2O_5 caused marked shrinkage accompanied by some grain growth at 1300°C. Other additives, effective at 1500°C, include MnO, Cu_2O, CuO, or GeO_2. Additives which did not affect the sintering or grain growth include Ga_2O_3, Y_2O_3, P_2O_5, Fe_2O_3, ThO_2, CeO_2, ZrO_2, and Co_3O_4. Additives which repressed sintering and grain growth include NaF, MgF_2, Sb_2O_5, CaF_2, KI, KCl, KBr, K_2CO_3, $NaNO_3$, Na_2CO_3, $CaCO_3$, MgO, $BaCO_3 \cdot SrCO_3$, SnO_2, Cr_2O_3, La_2O_3, V_2O_5, and SiO_2. They found that grain growth did not commence until an apparent porosity of 32 to 36%

had been reached, regardless of the additive used. They agreed with Bron that additives which form solid solution with alumina (TiO_2) favored sintering, but recognized that there were others which repressed sintering $(Ga_2O_3$ and $Fe_2O_3)$. Hauttmann found that finely divided iron oxide (0.05 to 0.5 micron) accelerated sintering. Cahoon and Christensen obtained faster sintering by additions of oxides of iron, manganese, copper, or titanium provided the amounts and firing temperature were within certain bounds, but crystal growth was accelerated by the iron and manganese. Pavlushkin in 1956 studied the effect of nearly all the elements in the periodic table as additions to alumina. He classified such additions into three groups: the crystal growth repressors Mg, Ni, Co, Th, W, Cr, U, Ta, Si, Ca, Zr, Mn, Tl, Y, Pr, Te, Li, Be, Na, Bi, Fe, Ti, Nb, Mo, Cs, Sr, and V; the growth accelerators Ag, Pb, Rb, Sb, F, Cu, Hg, K, Zn, Sn, Cl, I, S, Br, and P; and the intermediate agents Au, Pt, Pd, Ge, Ba, Cd, As, Ce, Se, O, and B. This is an oversimplification. The concentration of additive, different combinations of anion and cation, and sintering temperature alter the effectiveness. For example, $Na_2B_4O_7$ does not act the same as H_3BO_3. Fluorides are accelerators, but not magnesium fluoride. Pavlushkin pointed out that CaO and Na_2O should be used in amounts not over 0.02% and 0.05%, respectively, to avoid excessive formation of the corresponding beta aluminas.

Bartuska classified the effectiveness of the elements on sintering into somewhat different groups: (positive effect) Cu, Ti, V, Mn, and Fe; (less positive) Li, Be, Mg, Ca, Zn, Zr, Pb, Br, W, and Co; (no effect) Na, Sr, Sn, Sb, and Ni; and (negative effect) K, Ba, Si, and Cr. Reaction with alumina can proceed by formation of an isomorphous solid solution, by simple substitution of aluminum ions by ions of lower or higher valency, by metathesis, by formation of a eutectic melt or a single component melt, and by formation of an inhibitor to sintering.

Pavlushkin in 1962 investigated additives in amounts from 0.001 to 0.030 mole per mole Al_2O_3. Additions of Hg and Mg salts accelerated sintering; additions of Be, Zn, and Cd compounds accelerated sintering in the range 1580 to 1750°C. The alkaline earths retarded sintering. The strength of sintered corundum fired at 1710°C was higher with additions of MgO and BaO. Kukolev and Mikhailova also investigated the effect of impurities on the sintering of alumina.

Cutler, Bradshaw et al. selected additives from metal oxide combinations having low-temperature eutectics in the

systems $MnO-Al_2O_3-TiO_2$ and $Cu_2O-Al_2O_3-TiO_2$. Bodies having small grain size, and bulk densities above 3.80 g/cc were obtained at maturing temperatures of 1300 to 1400°C. Evidence of a "bleeding" liquid that drained away from the sintered pellets justified the conclusion that eutectic liquids formed. It seems probable that such compositions would not have stable high-temperature properties.

Bagley investigated the reaction rate between alumina and TiO_2. A rapid contraction was observed when TiO_2-doped samples were heated in air after first having been heated in hydrogen. Alumina sinters containing both Ti_3O_5 and TiO_2 were in solid solution. The sintering rate increased up to a certain concentration, beyond which the rate decreased. When TiO_2 was added to alumina of less than one micron size, the sintering mechanism was by bulk diffusion; for a crystal size of one to two microns the sintering was by a combination of bulk diffusion and grain boundary diffusion. Addition of soda in amounts from 10 to 10,000 ppm to alumina (Linde A-5175) eliminated exaggerated crystal growth. Samples pressed at high pressures had more exaggerated growth, probably because of trapped soda. A soda atmosphere also stimulated exaggerated growth.

Volosevich and Poluboyarinov in 1957 found that 0.5 to 1.0% additions of MgO, MgF_2, CaO, ZnO, SrO, ZrO, or Cr_2O_3 influence both crystal size and mechanical strength when using "pure" alumina containing only 0.05% Na_2O and of 2-micron maximum grain size, when sintered at 1550 to 1800°C. The initial powder size controls the pore diameter. Reduced mechanical strength and crystal growth were obtained with TiO_2, ZnO, MnO, Cr_2O_3 and Fe_2O_3. In reducing atmospheres the TiO_2 reduces to lower oxides, soluble in the alumina. Glasses in eutectics in the systems $CaO-Al_2O_3-SiO_2$, $MgO-Al_2O_3-SiO_2$, and $CaO-B_2O_3-SiO_2$ lower the sintering temperatures to 1500 to 1550°C, when added in about 5% (wt) concentrations. Kiyoura and Sata claimed that oxides having a high softening point in their systems with alumina are effective in improving high-temperature strength (1000°C); especially effective are CoO, NiO, MgO, and Cr_2O_3, about 2 to 5%.

Degtyareva and associates found that the shrinkage of alumina containing small amounts of TiO_2, $MgTiO_3$, Al_2TiO_5, and $ZrTiO_2$ is proportional to the TiO_2 content, with an activation energy for sintering of 58-87 kcal/mole at 1200-1500°C. The sintering rates in alumina containing small amounts of MgO and SiO_2 increase with the SiO_2 content, with an activation energy estimated to be 46 to 65 kcal/mole.

Jones, Maitra, and Cutler observed increased rates of material transport in the sintering of alumina containing additions of titanium, chromium, manganese, iron, or zirconium oxides in atmospheres of oxygen, nitrogen, and hydrogen. Pampuch reported that additives having lower electronegativity of the metal-oxygen bond than the basic oxide, in general about 1.6 to 2.0, improve sintering. The electronegativity (Pauling) measures the atom's ability to attract electrons, and is proportional to the sum of electron affinity (energy required to add an electron) and the ionization potential (energy required to remove an electron). The most effective oxide additions found were those that form solid solutions with the basic oxide, and in which the cation of the added oxide does not differ greatly in size from that of the basic oxide. Alumina of 4-micron size, containing 1 to 2% additive could be sintered at 1200°C. Kato, Okuda, Iga, and Okawara, in discussing the effects of 2 to 5% (wt) additions of $Mg(OH)_2$, Co_3O_4, Fe_2O_3, Cr_2O_3, TiO_2, or MnO_2, concluded as follows: sintering is promoted by the addition of MnO_2 but retarded by Cr_2O_3; the other oxides promoted it slightly. X-ray analysis shows spinel structures when $Mg(OH)_2$, Co_3O_4, or MnO_2 is added. Since the lattice constant of the manganese spinel increases with the content of MnO_2, this is regarded as indicative of solid solution. Alumina and Fe_2O_3 or Cr_2O_3 form perfect solid solutions, but Fe_2O_3 may form a spinel, depending on the sintering atmosphere. Both MnO_2 and Fe_2O_3 accelerate grain growth remarkably.

Britsch's criteria for sintering corundum are as follows: the raw alumina should be as pure as possible and contain less than 2% Na_2O; the particle size should be uniform. An extremely fine fraction favors irregular crystal growth. Kaolin is the recommended sintering additive. Popil'skii et al. state that without magnesia, sintering in vacuum, hydrogen, helium, or combustion gases in the temperature range of 1600 to 1900°C produces corundum with a pore volume of not less than 3.5%. With not more than 0.2% MgO, pore volume can be reduced to 0.2% (99% of theoretical density) only in vacuum or in hydrogen. Tuleff also discussed the development of pores as a function of their firing temperature.

Jorgensen and Westbrook concluded that the addition of magnesia or nickel oxide inhibits grain growth during the sintering of alumina by maintaining a high diffusion flux of vacancies from the pores to the grain boundaries, causing a decrease in grain boundary mobility. The segregation was inferred from microhardness tests and autoradiographic tests with [63]Ni.

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The main purpose of a growth repressor is to allow substantially complete sintering, approaching theoretical density before secondary or discontinuous crystallization has reached excessive limits. If secondary recrystallization has occurred and pores become trapped, the theoretical density cannot be obtained within a reasonable sintering time and temperature.

From a practical standpoint, the factors which determine the relationship of pore removal to secondary recrystallization are those factors that determine the reactivity of the raw alumina, the attainable degree of compaction, and the grossness of the pores in the raw compact. Little attention has been given to these factors until recently. A better relationship is likely to be obtained with the "reactive" aluminas which have higher compaction densities than have been attainable with conventional alumina powders in the past. These newer types also have good flow properties for mold filling in the dry condition, and require only low amounts of lubricants and growth repressors.

17 ALUMINA IN REFRACTORIES

17-1 GENERAL

A study of the phase diagrams of which Al_2O_3 is a component indicates the refractoriness that alumina contributes to compositions. General technical information on refractories is provided by such texts as F. H. Norton, Refractories (1950); J. R. Coxey, Refractories (1950); and more recently by Harder and Kienow, Refractories (1960); Singer and Singer, Industrial Ceramics (1963); and Salmang, Physical and Chemical Fundamentals of Ceramics (1961); among others. Refractories Bibliography 1928-1947, and 1947-1956; Modern Refractory Practice (Harbison-Walker Refractories Company), McDowell, Scott, and Clark (1962); Mamykin (1958); Whittemore (1959); Jaffee and Maykuth (1960); Pechman (1953); among many others, serve to establish the position of alumina among the refractory oxides.

Alumina is classed as a neutral or amphoteric refractory. Trombe (1949) listed the "superrefractory oxides" as those with melting points between 2050 and 3000°C (Al_2O_3 to ThO_2). According to Navias (1960) the order of increasing refractoriness is: Al_2O_3, Cr_2O_3, La_2O_3, Y_2O_3, SrO, BeO, CaO, CeO_2, ZrO_2; MgO, HfO_2, UO_2, and ThO_2. While the melting point of alumina is at the low end of the superrefractory scale, it is one of the most stable oxides in both reducing and oxidizing atmospheres, and is one of the cheapest and most readily available in very pure form.

Konopicky (1959) confirmed the correctness of classifying refractory fireclay brick by their alumina content. Birch evaluated the refractories of the future (in 1945) as being those with melting points above 1800°C, of which the mainstays are magnesia (2800°C), alumina (2050°C), and zircon (2430°C). In 1964 the most promising future refractories were magnesia and alumina, with zirconia for limited demand, based on such factors as melting point, susceptibility to hydration, reducibility, toxicity, cost, and availability. These oxides and carbon melt above 2000°C, and are available in high purity. Berezhnoi (1963) pointed out the likelihood of new refractories is from binary mixtures. Brandt (1949) considered the use of oxygen as a means of increasing the flame temperature in the open-hearth steel-melting furnace. An analogy was drawn between this type of furnace and the glass-tank furnace. In glass furnaces the maximum permissible roof temperature is a limiting factor. Thielke (1950), Hiester et al. (1956), and White (1963) discussed the changing pattern in the technology of new refractories. The advantage in increased production rate by substituting oxygen for air in the production of steel

is one factor. Kirby (1951) recognized alumina, magnesia, beryllia, zirconia, ceria, and thoria as the pure refractory oxides capable of being used at abnormally high commercial temperatures (above 1800°C). Smutny and Tomshu (1958), and Bray (1951) believed high-alumina refractories were favored in steel production both from the cost and improved properties considerations.

Another factor influencing the selection of refractories is abrasion resistance, as pointed out by Roe and Schroeder (1952) and Lesar and McGee (1956). Venable measured the erosion resistance of refractory linings in fluid catalytic cracking units in petroleum refining. Phosphate-bonded tabular alumina was about as resistant as silicon carbide shapes. Ramming mixes and refractory concretes had decreasing resistance.

Refractories made from calcined bauxite or diaspore may be classed as high alumina refractories, to distinguish them from extra high alumina refractories made from dense sintered alumina (tabular alumina) or fused alumina grain. Alumina refractories containing 80% Al_2O_3 and approaching 90% Al_2O_3 can be made from bauxite. It would seem to be uneconomic to debase bauxite or Bayer alumina in refractories of significantly lower Al_2O_3 content than mullite, in view of the excellent properties attained with limited fluxes in high-alumina refractories.

17-2 HIGH-ALUMINA REFRACTORIES

White (1938) noted that fused alumina refractories are preferably used where high temperature and high bearing loads are combined (piers and supports). Corundum shapes have high resistance to all common slags (Schaeffer, 1939). Fitzgerald (1943) fired a molded mixture of hydrated alumina with 7 to 30% uncalcined clay containing 60 to 75% SiO_2 at a temperature above cone 10 (1260°C), and stopped the firing while the refractory was still capable of further expansion on reheating (approximately 95% Al_2O_3). Schroeder and Logan (1951) added sufficient clay to contribute from 2 to 8% SiO_2 to the fired body, composed of fused alumina grain. The flexural strength was much higher than that for brick made from pure fused alumina grain.

Poluboyarinov and Balkevich (1949) sintered mixtures of electrofused corundum (98 to 99% Al_2O_3) with mixed clays and/or kaolin not to exceed 15%. The clays contained 38 to 43% Al_2O_3. Specimens containing kaolin deformed at temperatures 40 to 90°C below those containing the clays (Latna type). The sintering process continued to 1700 to 1800°C. Reheat shrinkage amounted to 3 to 4% at 1600 to 1750°C. The maximum temperature of

initial deformation was about 1650°C, and for two-side service, 1750°C (with substantially no load). Various other bonds were used, including (1) pure technical (Bayer) alumina, (2) alumina and alum, (3) alumina and clay, and (4) alumina, clay and lime, in total amount of bond from 15 to 45%. The apparent porosity ranged from about 23 to 26% and decreased with increasing bond content. Shrinkage and strength increased with increasing bond strength. The initial deformation occurred at 1830 to 1840°C. The admixtures did not affect the results; it was concluded to use only the technical alumina as the binder, and to form by semidry pressing (6 to 7% moisture). Firing at 1700°C for 3 to 5 hours should give practically constant volume, and an allowable service temperature to 1850 to 1900°C if the load is very small. The same investigators prepared high-density grog (3.80 g/ml) by heating pressed briquets prepared from ground technical alumina (99% Al_2O_3) at 1600 to 1710°C. The crushed briquets were then bonded with wet-ground technical alumina, with the addition of 1 to 2% sulfite cellulose liquor (tall oil) or aluminum sulfate to increase green strength. Mixes fired at 1710°C showed increased shrinkage and bulk density and decreased porosity with increasing bond content. The characteristics of these refractories were superior to those of the fused alumina with a clay bond. The initial temperature of deformation was 1850°C at 28.4 psi. Volume stability was high up to 1900°C. Visible cracks appeared after 15 to 16 heat-shock cycles. The compressive strength was as high as 420,000 psi.

Whittemore (1949) placed the effective operating temperature of pure alumina at 1900°C, in comparison with magnesia and stabilized zirconia at about 2300°C. Lepp and Slyh (1951, 1952) calcined mixtures of alumina and aluminum in almost any proportion but preferably 35 to 90% Al_2O_3, and 10 to 65% aluminum at 815 to 1700°C enclosed in graphite in an oxidizing atmosphere. The product contained alumina, aluminum nitride, aluminum, and carbon. The products had excellent strength and thermal shock resistance.

Morgan Crucible Company (1953) prepared refractory alumina bodies by forming from fine-ground alumina, either with or without a combustible binder. The calcined alumina was ground until 95% passed a 300-mesh sieve. Iron contamination was removed by magnetic separation and by acid leaching. Zhikharevich et al. (1958) presented data on the use of high-alumina refractories of sillimanite, mullite, and mullite-corundum for blast-furnace linings. These linings had low porosity and gas penetration and were volume-stable at 1550 to 1600°C.

Karklit and Gruzdeva (1950) prepared shapes weighing up to 8.8 pounds (97% Al_2O_3) and good for service at 1700 to 1850°C from Bayer alumina by dry pressing with 5% melted

paraffin at about 14,000 psi, and by firing at 1710°C for 5 to 6 hours. The total shrinkage was 17.9%, apparent porosity 0.00%, and density 3.86 g/1 ml, which did not change on reheat. The average crushing strength was 95,000 psi. Cracks appeared after 2 to 3 cycles of heat shock (heating to 850°C and cooling in water), and complete destruction after 6 to 8 cycles.

Riddle (1945) mixed from 11 to 29 parts silicon carbide with 100 parts alumina to obtain a refractory having high strength at 1455°C. E. D. Miller (1964) prepared a readily castable, high-alumina refractory by the addition of 1 to 10% pure volatilized silica and 1 to 5% clay, the remainder being coarse-ground dense alumina or bauxite. The product was characterized by coarse-textured alumina particles rigidly held in a dense matrix of submicron mullite crystals. Pieper (1956) patented a composition containing 17.5 to 25% by weight of silicon carbide with about 75 to 82.5% aluminum oxide of specific size distributions, formed with water containing lignin, and fired at 1650°C.

Saunders, and Somer and Brady described silicon carbide refractories coated with alumina or iron oxide and alumina protective layers. Kappmeyer and Manning (1963) evaluated about 140 brands of high-alumina brick ranging from 60 to 99% Al_2O_3 including mullite brick. The results showed that many brands of high-alumina brick were not as good as some brands of fireclay brick currently available. The alumina content alone is not sufficient to determine suitability for specific steel-plant use. Kappmeyer, Lamont, Manning (1964) found, similarly, that high-alumina plastics and ramming mixes in the steel industry must be selected for their individual properties rather than their overall composition. Powers and Kappmeyer (1965) concluded that none of the newly developed refractories to date shows appreciably better performance in contact with molten steel than Al_2O_3, MgO, or $ZrSiO_4$.

Khemelvskii and Minakov (1957) found high-alumina refractories satisfactory for the baffles in glass-melting tanks. Koldaev et al. (1957) developed a refined technique for preparing mullite-bonded high-alumina blocks (50 to 96% Al_2O_3) which were claimed to be superior to electrofused blocks. The improved technique involved finer grinding of all constituents, the use of TiO_2 as a mineralizer, plastic and pneumatic tamping to shape the blocks, and a 16-hour soak at 1520°C. C. L. Norton (1964) developed a sintered composition for contact with molten glass having high thermal-shock- and corrosion-resistance, formed from a mixture of 10 to 50% alumina-silica grain (80 to 95% Al_2O_3) in graded sizes

to produce low porosity, 4 to 12% bonding clay, and the remainder corundum grain in graded sizes.

17-3 FUSED CAST ALUMINA REFRACTORIES

The terms: fusion-cast, fused cast, and electrocast are equivalent, meaning melting in an electric furnace and casting the homogeneous liquid into a monolithic refractory shape in molds. Though trials had been made earlier with a fused cast refractory "siemensite" by Haglund (German Patent 539,682, June 1927), the commercial manufacture started in 1925 when Corning Glass Works filed a patent application for a mullite block cast from bauxite (Fulcher, U. S. Patent 1,615,750, July 1925). Knuth (1935) appraised this "Corhart Standard" as approximately mullite with free corundum and a vitreous phase. A French subsidiary began operations in Modane, France, in 1929 (Bortaud and Rocco, 1964). The composition was melted at about 2200°C and poured into sand molds.

Benner and Baumann (the Carborundum Company) in 1935 patented a refractory for glass tank use, made by fusing 94% bauxite with 6% soda ash by weight, and containing about 85 to 90% Al_2O_3, most of which was present as bota alumina. Other variations were tried, as for example, incorporating in a bath of molten alumina a mineralizer composed of a halide of an alkaline earth metal, in amount about 1% (Benner and Baumann, 1939).

The Carborundum Company developed three early types of fused glass-tank blocks, having about the following properties:

	Beta Al_2O_3	Beta-alpha Al_2O_3	Alumina-Chrome
PCE	39-40	39-40	38-39
Wt (9 X 4-1/2 X 2-1.2)	10.2 lb	11.4 lb	11.6 lb
Thermal cond. at 620°C cal/cm°C	30	30	30
Coeff. thermal expansion 25 to 1400°C (°C)	7.4 X 10⁻⁶	7.4	9.3

Benner and Easter (1940) developed a glass tank refractory by fusing over 5% iron oxide in the alumina. Zhilin and Ignat'eva cast blocks from blast furnace slags (maximum CaO 39%). Refractories Committee C-8 of the American Society for Testing and Materials included high-alumina block and brick and molten cast blocks in recommended refractory types in the report on refractory service in glass furnaces in 1939.

The fusion casting process avoids the usual bonding of refractories by developing interlocking crystal growth and high densification which withstand deformation at high

temperature and offer exceptional resistance to corrosion, particularly in glass tanks. The blocks are presently cast in graphite demountable molds, which are removed as soon as possible after pouring. The casting is blanketed with insulation to minimize thermal stresses. After cooling, the casting is cleaned and subjected to finishing operations which may involve cutting or grinding with diamond abrasives. Because of the great change in expansion upon cooling, a central cavity forms, which is difficult to fill completely by repeated pourings. Various treatments were recommended. Corning Glass patents (1940) mention filling the cavity with crushed, pre-fused material of the same composition, having enough glassy phase to induce sintering at the lower cooling temperature at which it is introduced, or the cavity is made to take a central position in the block by rotating the block during casting. Field and Smyth (1945) filled the "pipe" with additional molten refractory of the same type, mixed with a sulfate capable of dissociating into sulfur trioxide at temperatures between 400 and 1100°C. Alternatively (1952), they placed a gasifier in a container within the mold prior to pouring; the bottom of the mold was covered before the container disintegrated, the delay allowing the pipe or void to be redistributed into many small closed pores throughout the casting.

Field, Fulcher and Field, and Fulcher, early in 1942 disclosed a cast refractory consisting essentially of crystalline zirconia and corundum in a siliceous noncrystalline matrix (around 20% SiO_2 by weight). The silica could be substituted by alkali oxide in the ratio with contained alumina of less than 1:19. A third variant consisted essentially of zirconia (above 60°) and alumina (not over 25%) substantially free from iron oxide and titania. These led to a low-silica refractory (U.S. Patent 2,424,082, Field, 1947) containing 45 to 92% Al_2O_3, 1.9 to 40% ZrO_2, and only 1.5 to 5% SiO_2, distributed as crystals in an amorphous matrix. The ZAC cast refractories were developments of Corhart Refractories Company and their French associates Electro-Réfractaire. ZED blocks contain about 50% Al_2O_3, 33% ZrO_2, 11 to 13% SiO_2, and 1 to 2% Na_2O. The soda (added as soda ash) provides electrical conductivity and aids recrystallization (Moore, 1950). Lamy (1952), and Hartwig (1956) discussed their favorable behavior in glass tanks even under unfavorable conditions in borosilicate glass melting.

Seki (1937) examined melts prepared in the Al_2O_3-SiO_2, Al_2O_3-MgO, and Al_2O_3-MgO-Cr_2O_3 systems to determine their resistance to basic open-hearth slags, acid open-hearth slags, borosilicate glass, and soda-lime glass. Refractories of the Al_2O_3-MgO-Cr_2O_3 system were found resistant to the glasses but were believed to be not suitable for this use because of glass discoloration from the chromium. The refractories containing high alumina were suitable for glass tanks and acidic open-

hearth steel furnaces; refractories of the Al_2O_3-MgO and Al_2O_3-MgO-Cr_2O_3 systems were found excellent for basic open-hearth furnaces.

The widespread use of basic refractories in the steel industry of the United States following World War II led to the success of electrocast magnesia-chrome-alumina refractories (Field, U.S. Patent 2,408,305, 1946); and magnesia-alumina-silica-zirconia basic cast refractory (Field, U. S. Patent 2,409,844, 1946). The latter contains not less than 15% ZrO_2 and not less than 11% SiO_2, and the moles of MgO are about equal to the moles of Al_2O_3 plus twice the moles of SiO_2. A heat-cast refractory designed for use in open-hearth roofs, consisted of about 15% of a crystalline solid solution of FeO in MgO, a spinel phase consisting of FeO, MgO, Al_2O_3, and Cr_2O_3, and a siliceous matrix. The composition contained 12 to 50% chromia, and 5 to 25% alumina (Corhart, British Patent 665,209, 1951).

The high-alumina fused cast blocks have received further attention. Galdina and Deri (1962) described a fused refractory 'Korvishit', containing 99.2% Al_2O_3 and only 0.15% Fe_2O_3, SiO_2, and alkali. It has a bulk density of 3 g/ml, is refractory to 1930°C, has no open porosity (apparent porosity 10 to 17%), coefficient of expansion (20 to 1200°C) 8.5×10^{-6}, and thermal conductivity 4.5 kcal/hr^{-1}°C^{-1}m^{-2}m. Corhart (1964) claimed that fused alumina refractories substantially crack-free are obtained if they contain 0.36 to 16.5 mol % of an alkaline earth oxide and 0.06 to 2.63 mol % fluorine, preferably calcium fluoride. Castings 1 x 1 x 3 in. withstood 11 to 13 cycles of heating for 10 minutes at 1650°C and cooling to room temperature before spalling loss occurred. The bending strength was 7000 psi. Another Corhart disclosure (1964) revealed the influence of very small amounts of calcia (0.5 to 4%) on the resistance to thermal shock of substantially all-alumina castings, by altering the crystal structure from long straight crystals to a random distribution of fine interlocking Al_2O_3 and $CaO \cdot 6Al_2O_3$ crystals. The raw material must not introduce more than 1.5 MgO or 1% total of other impurities (SiO_2 and Na_2O). A pouring temperature of 2030 to 2050°C was specified. Specimens withstood the previously cited spalling test for 44 cycles before spalling, whereas the pure alumina castings broke after one cycle, compositions with 0.67 to 4% MgO broke after 2 to 9 cycles, and a composition with 4% BaO broke after 7 cycles. These blocks were recommended for arc furnaces and roofs of steel and glass melting furnaces. Alper and McNally (1964) found that the resistance of substantially all-alumina castings to thermal shock was considerably increased by addition of 0.2 to 1.7% SiO_2. In this case, the content of Fe_2O_3 and TiO_2 must be kept below 0.1%, and of Na_2O below 0.6%. A block specimen failed the thermal shock test after 20 cycles of heating. Pure alumina failed on the first

cycle, and one containing 0.2% SiO_2 and 0.1% Fe_2O_3 failed in 12 cycles.

Sandmeyer and Miller (1965) showed the following data for typical fused cast alumina refractories(Harbison-Carborundum).

Chemical Analysis	Alpha Alumina	Alpha-Beta 40:60	Beta Alumina
Al_2O_3	99.34	94.84	94.46
Fe_2O_3	0.06	0.06	0.07
SiO_2	0.08	1.09	0.12
Alkali oxides	0.39	3.58	5.17
Alkaline earth oxides	0.13	0.43	0.18
Bulk density g/ml	3.45	3.17	2.89
Apparent density	3.76	3.41	3.06
True density	3.93	3.54	3.26
Cold abrasion resistance Abrasion loss (cm^3/cm)	0.20	0.55	-
Thermal expansion (0 to 1200°C)*	0.98	0.95	0.79

*Approximated from curve

The thermal conductivity of the alpha alumina type is about twice that of the beta type, with the alpha-beta type falling intermediate.

Fused cast spinel refractories containing beta alumina were developed for use in contact with molten magnesium metal (Field, 1949). The refractories were prepared from metal-grade alumina, soda ash, and calcined magnesite low in silica. The required alkali was about six times the amount of silica present. Sekigushi (1959) found that the spinel refractories resisted molten Fe_2O_3 strongly in open-hearth furnaces and against cement clinker in rotary kilns. Small amounts of Fe_2O_3 prevented peeling or bursting of the refractory. Ribbe and Alper (1964) found that rapid chilling of mixtures in this system show an enrichment of the low-melting spinel in the outer skin, called inverse segregation.

Fused cast mullite refractories, produced from the iron oxide-containing bauxites have been used in certain zones of furnaces containing glass-corroding baths. A suitable composition contains 70 to 80% mullite, 7 to 12% corundum, and 13 to 18% glass (Rustambekyan, 1964).

Chrome-alumina and chrome-magnesia-alumina fused refractories were prepared by mixing chromite ore (preheated at 800°C to develop crystallinity) with fused alumina, and optionally some magnesia, a preferred composition containing 75 wt % fused alumina to 25% Phillipine chrome ore (Sandmeyer,1959).

Alper and McNally (U.S. 3,140,955, 7/14/64) developed a refractory of this type containing 56 to 85% MgO, 13 to 40% Al_2O_3, 0.4 to 4.5 Cr_2O_3, 0 to 3.5% FeO, and minor amounts of CaO, SiO_2, and B_2O_3.

Much interest has been shown in fused cast refractories in the Al_2O_3-SiO_2-ZrO_2 system. Litvakovskiĭ, Busby and Partridge, Solomin and Galdina, Solomin, Schlotzhauer and Wood, and Ono and Shibata have described the preparation from zircon and technical-grade alumina (sometimes bauxite), to keep the iron content low. A highly refractory and corrosion-resistant glass tank body was prepared substantially to the stoichiometric proportions of the equation: $2ZrSiO_4 + 3Al_2O_3 = 2ZrO_2 + Al_6Si_2O_{13}$.

Steimke (U.S. 2,919,994) developed the composition: 40 to 60 wt % Al_2O_3, 12 to 22% SiO_2, and 25 to 45% ZrO_2, bonded with a borosilicate glass (0.5 to 1% B_2O_3, but not over 1% Na_2O, K_2O, and/or Li_2O, and substantially free from TiO_2 and Fe_2O_3. Nagashima, Miyake et al. (1960) prepared crack-free castings at 1900 to 2100°C with mixtures of zircon, alumina, and ores containing rare-earth elements. The ZrO_2 constituted 20 to 40%, the rare earth oxides 2 to 50% of the ZrO_2, the Al_2O_3 30 to 50%, SiO_2 10 to 20%, Na_2O 0.1 to 5%, and CaO + BaO 2%. Ono, Fendo, and Onaka (1962) modified the formula to obtain practical freedom from alkaline earths, to obtain corrosion-proof glass refractories.

Alper, Begley, Londeree, and McNally (1964) claimed that the castings crack less in the molds if they are composed of 15 to 60% ZrO_2, 20% SiO_2, 0.5 to 2.5% Na_2O, 0.05 to 1.5% halide, and the remainer Al_2O_3. The preferred halides are calcium and aluminum fluorides.

Baque (1950) Carrier (1950), and Fabianic (1950) discussed the use of fused cast and other types of refractories used in glass-furnace construction extant at that time. Roy Brown (1962) concluded that beta alumina, fused cast, refractory is alumina saturated with soda, a single phase completely free of glass. It has excellent thermal shock resistance, refractoriness, and alkali resistance, and low thermal conductivity. It has the disadvantage of low abrasion resistance, poor resistance to molten batch carryover, and is costly for certain shapes. Its use was recommended in port necks, feeder entrance covers, and non-glass-contact positions beyond the first and second port areas. Survey of Refractories Used in Glass Tank Furnaces, J. Soc. Glass Technol. 42 (209) 63-99P (1958) describes the qualities and properties of the various types of refractory ingredients (bricks, cements, jointing materials, etc), and their application in tank furnaces.

Refractories are made from practically the entire range of compositions in the system Al_2O_3-SiO_2 from 100% SiO_2 to 100% Al_2O_3. Harvey and Birch (1944) pointed out that a super-duty silica refractory brick should not contain significant amounts of alumina (not over 0.5% Al_2O_3, TiO_2, and alkali oxides), and this has remained a specification for superduty silica brick (Lynam et al., 1952). Keltz (1951) claimed that 0.1 to 0.3% fused alumina provided strength to lime-bonded silica brick. The impurities CaO, MgO, FeO, and MnO form two immiscible liquids with silica refractories with melting points only slightly below that of pure silica. The group Al_2O_3, TiO_2, and the alkalies, however, cause a rapid decrease in melting point as a eutectic composition is approached (Mackenzie, 1952).

High-alumina refractories have been prepared from diaspore, bauxite, and alumina from Bayer plant, calcined, sintered, and fused. The properties of aluminosilicate compositions increase markedly as the alumina content approaches that of mullite (71.8% Al_2O_3). With depletion of the Missouri diaspore deposits, research on aluminosilicate brick was directed to the elimination of high porosity, to enhanced growth of mullite in the 70% Al_2O_3 class, to production of stabilized corundum in the 80% Al_2O_3 class, and to use bauxite to produce refractories comparable with those made from diaspore clays (Day, 1936).

Mullite grog has for some time been prepared by rotary kiln calcination of Indian kyanite, but African kyanite and other deposits were also exploited. Fine-crystal mullite is prepared by sintering the correct ratio of Al_2O_3 to SiO_2 (or a slight excess of Al_2O_3) from a mixture of Bayer calcined alumina and kaolin of suitable purity with respect to Fe_2O_3 and TiO_2. Coarse-crystalline mullite for special refractory purposes is obtained by electrofusion (Hutchins, 1944). Pevzner (1946) described the preparation of "thermite mullite" having the composition 78.6% $3Al_2O_3 \cdot 2SiO_2$, 3.5% $FeO \cdot Al_2O_3$, and 13.5% corundum, prepared by the aluminum thermite reaction. Low titania and alkali content is characteristic of this preparation method.

Bradley et al. (1940), Schober and Thilo, Burgess, Stuckey and Amero, McVay and Wilson, Barzaghi and Angeleri, and Angeleri (1943) investigated the production of mullite refractories from topaz, $Al_2SiO_4 \cdot (F,OH,O)$. During thermal treatment, silicon tetrafluoride was liberated, which raised the alumina content to about 70%. From 600 to 800°C, corundum and aluminum oxyfluoride ($Al_7O_{10}F$) were formed, while above 800°C only pure alumina was obtained.

In the synthesis of mullite from Bayer alumina and clay,

the usefulness of various prospective mineralizers in promoting the reaction has been investigated. Kitaigorodskiĭ and Keshishyan used 3% MgO to promote the reaction of 72% Al_2O_3 and 25% SiO_2 during a heating at 1500°C for 6 hours and then at 1700° for 0.5 hour. The product was a highly resistant refractory, negligibly attacked by molten glass at 1300°C. Fenstermacher and Hummel (1961) attempted to sinter relatively pure $3Al_2O_3\cdot 2SiO_2$ and $2Al_2O_3\cdot SiO_2$ compositions to low porosities at 1710 and 1650°C, respectively, with the addition of 1% magnesia in each case to facilitate the reaction. The $3Al_2O_3\cdot 2SiO_2$-body sintered to a porosity of 7.1% and was substantially all mullite; the $2Al_2O_3\cdot SiO_2$ body sintered to 10.9% porosity and was composed of mullite and corundum. This would tend to refute the claim of Barta and Barta (1956) and others to the existence of many mullites between sillimanite ($Al_2O_3\cdot SiO_2$) and pragite ($2Al_2O_3\cdot SiO_2$). Especially in a reducing medium, SiO_2 was found to evaporate from $3Al_2O_3\cdot 2SiO_2$ until virtually only corundum was left (Toropov and Galakhov, 1951). They reported in 1958, no evidence of solid solutions of $3Al_2O_3\cdot 2SiO_2$ and $Al_2O_3\cdot 2SiO_2$ at 1400 to 2100°C. Tromel et al. (1957) claimed that the very pure mixtures of Al_2O_3 and SiO_2, when held just above 1810°C for 2 hours, contained only mullite or mullite and glass, but no corundum. In the presence of 0.2% Na_2O (a common impurity in alumina samples), the mullite decomposed with the formation of corundum. The pure oxide mixtures required many hours at 1650°C to attain equilibrium.

Weill (1963) investigated the relative stability of the crystalline phases in the Al_2O_3-SiO_2 system.

Reinhart (1955) claimed that B_2O_3 facilitated the sintering of mullite refractories. Kirillova (1958) found that $2MgO\cdot B_2O_3\cdot H_2O$ or CaF_2 favored the crystallization of mullite (about 4%); Locsei (1946) found AlF_3 promoted the reaction. Completely crystalline mullite has a very low dielectric loss; tan $\delta = 2 \times 10^{-3}$. The morphology of mullite was shown by the electron microscope to be the characteristic needle-like crystals if sufficient glassy phase is present in the melt (Lohre and Urban). Halm (1948) observed that acicular mullite, formed from the near-eutectic fusion is very prone to coalesce into globular mullite by alternate dissolution and recrystallization with fluctuating temperature. Karyakin and Margulis found mullite as isometric grains and short prismatic crystals in kaolin brick after 1.5 years of service in covers of pit furnaces.

Poluboyarinov and Popil'skii (1947-1955) attempted to prepare mullite-containing refractories from technical Bayer alumina and several types of Russian clays (Latnenski, Chasov-Yar, and kaolin). Wet-ground charges containing 51% alumina and fired at 1400°C had high apparent porosities (38 to 44%). Firing at 1500°C reduced the porosity only to about 30%. No

sintering was observed at 1600°C with charges containing 82% alumina. Mullite refractories containing about 60% Al_2O_3 were prepared by wet-grinding technical alumina (7.96% SiO_2, 88.86% Al_2O_3), mixing a clay slip on the base of 58.5% clay with 41.5% alumina, forming briquets and firing at 1570 to 1580°C. The reground composition was formed into bricks with 15% clay (6% as a slip, 9% as a dry powder). The pressed brick, fired at 1450°C for 1.5 hr had 0.7% shrinkage, the reheat shrinkage at 1600°C was 0.4%, and at 1650 to 1680°C, 0.8%; the bulk density was 2.31 g/ml; the apparent porosity was 17.8%; and the initial deformation under load occurred at 1480°C. During the firing of mullite-corundum refractories, dimensional changes were observed. Rybnikov (1950) reduced the porosity to about 1.7% by the addition of 1% sodium silicate in the grog product and by increasing the firing temperature to 1620°C. Compressive strength was about 47,000 psi. Glass tank blocks were fabricated from mixes containing 75% grog, 25% of the original mullite mixture, and 9 to 10% water, and fired at 1650°C for 8 hours. The blocks ranged in porosity from about 16 to 20%.

C. Jones (1954) prepared synthetic mullite by calcining an intimate mixture of Bayer alumina, clay and ethyl silicate binder at a temperature between 1500 and 1800°C, the initial ratio of Al_2O_3:SiO_2 falling between 72 and 78% Al_2O_3 and between 28 and 22% SiO_2 by weight. Vinogradova et al., and Stavorko (1960) reported on trial batches of thermally stable mullite-corundum brick. Brick suitable for blast furnace stoves contained only 45% Al_2O_3. Brick containing 77% Al_2O_3 plus TiO_2 in the walls of a laboratory furnace, working at 1700 to 1750°C with rapid heating and cooling, showed high stability. After 50 firings (21 hours at 1600°C or higher) the linings were in excellent condition. Heeley and Moore prepared refractory mixes from calcined alumina and specially fine china clay in the proportions corresponding to sillimanite and mullite and containing up to 0.5% Na_2O, added as sodium silicate, in the sillimanite, and up to 3% in the mullite mixtures. The soda addition reduced the true porosity of the sillimanite at firing temperatures of 1400 to 1450°C, the effect diminishing with increasing temperature. The corrosion by molten glass increased as the firing temperature approached 1590°C for both compositions, but was more severe in the case of mullite.

Flood and Knapp concluded from the ternary phase diagrams of CaO, FeO, or MgO with Al_2O_3-SiO_2 that the free energies of formation of kyanite, andalusite, and sillimanite, according to the reaction $Al_2O_3 + SiO_2 = Al_2O_3 \cdot SiO_2$, are of the order of magnitude from 0 to -10 kcal rather than the previously accepted value of -40 to -45 kcal.

Richardson et al. (1947, 1948) found that high-alumina brick and aluminous firebrick were attacked more severely

than silica brick by ferrous oxide. Mullite was quickly decomposed by ferrous oxide to form hercynite; fayalite did not form until the mullite and corundum disappeared. Mullite appeared to be attacked more readily than corundum in high-alumina brick by mixtures of calcium and ferrous oxides. CaO was apparently more reactive than FeO. If the SiO_2 and Al_2O_3 were insufficient to satisfy the CaO, it combined with FeO rather than remain in the free state.

Refractory-grade bauxite used in the production of aluminosilica refractories has been subject to National Stockpile Material Purchase Specifications P-50 (December 5, 1951), conforming to the following percentages by weight:
Al_2O_3 minimum 85.00; SiO_2 maximum 7.00; Fe_2O_3 maximum 3.75; TiO_2 maximum 3.75; and L.O.I. maximum 0.50.
A stringent specification requires that the bauxite be well calcined to a bulk density of 3.10 g/ml.

Notwithstanding the hard-burned densification of the bauxite (or of pure alumina types) the reaction in aluminosilica compositions to form mullitized refractories causes the phenomenon called secondary expansion. J. L. Hall (1941) ascribed the secondary expansion of high-alumina grogs in clay binders to the formation of the relatively less dense mullite. McGee and Dodd (1961) claimed that the expansion results from crystallization of secondary mullite by the action of impurities in aiding the diffusion of alumina and silica. Secondary mullitization and growth began at 1400°C and caused as much as 23% expansion at 1600°C. Small additions of sodium fluoride were effective in controlling the expansion. Patzak (1964) observed the presence of tialite (Al_2TiO_5) in high-temperature calcination of bauxite, and emphasized the effect of the additive aluminum fluoride on mullite formation. Sedalia attributed the higher expansion resulting from bauxite to the formation of beta alumina by the reaction of the alkalies from the bonding clay with the alpha alumina in the bauxite. The linear expansions measured by Hall and Sedalia were less than 4% after 5 hours at 1600°C. Heilich (1962) found that the volume stability of compositions in the mullite range, prepared from either Suriname or Demerara bauxite, could be controlled by adjusting the particle size distribution of the components. Both the strength and the expansion in the desired low range were achieved by increased fineness of the bauxite, at least partially, in the 200 to 325 mesh range.

Leduc (1956) investigated the effect of the bonds: (a) 5% aluminous clay, (b) 5% hydrated lime, (c) 5% alumina cement, and (d) 15% alumina cement on the properties of bauxite bricks. Specimens a, b, and c deformed at 1420°C under a load of 28 psi; specimen d deformed at 1200°C.

Mullite Refractories (1940) presented data showing typical

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applications of mullite refractories in electric induction and arc furnaces, industrial boilers, open flame and crucible furnaces, glass tanks, ceramic kilns, iron and steel furnaces, etc., in the 3300°F (1820°C) range of melting. Mullite is claimed to have a high softening point, a low coefficient of expansion, good resistance to thermal shock and slag erosion, negligible tendency to vitrify, high load-bearing capacity, and chemical neutrality. Remmey (1948) described the properties of sintered mullite structures bonded with mullite. Partridge and Busby (1955) described slip cast mullite and zircon tank blocks. Knauft, Smith, Thomas, and Pittman (1957) described bonded sintered mullite and zircon refractories for use in glass contact areas, superstructures, and feeder forehearths of furnaces melting borosilicate and dense opal glass.

Hawkes (1962) described various methods for producing sintered mullite, based either on Bayer alumina or on bauxite. Mineralizers were found to be of little value. Goncharov et al. found the maximum quantity of mullite was formed for a ratio of $Al_2O_3:SiO_2$ of 1.5:1. The composition of the mullite depends on the proportion of $Al_2O_3:SiO_2$ as well as on their calcination temperature. De Keyser (1963) observed four zones of reaction between the interface of quartz and corundum particles: corundum mullite; a complex phase of cristobalite, corundum, mullite, and glass; and cristobalite.

Rutman (1959) recommended the bonding of mullite brick used in rotary kilns with a mortar to convert the refractory into a monolithic liner. The mortar was composed of 90% ground grog (88% alumina, 10% clay), 10% raw clay and 5% sodium silicate (density 1.45 g/ml). Wicken and Birch (1963) reviewed the properties of high-alumina refractories, among others, used in modern rotary kilns. The inversion point of sillimanite and the related minerals kyanite, andalusite, dumortierite, and topaz invert to mullite above 1370°C. Good refractories of the unfortified type range from 82 to 93%, averaging about 85% mullite. Fortified types (addition of pure alumina) contain 70% or more mullite (20% alpha alumina). The fortified mullites have increased load bearing resistance, spalling resistance, and resistance to slagging.

The refractories made from mullite grain are formed by casting, ramming, power pressing, extrusion, and hand molding. The batches are prepared by grain sizing, bonding, forming, drying, and firing to temperatures from 1315 to 1650°C.

Budnikov and Khramova found that mixtures of 75% mullite and 25% silicon carbide or 60% corundum and 40% silicon carbide, bonded with additions of 10, 20, and 30% clay at 1400 and 1500°C, withstood more than 25 heat-shock cycles. Crucibles made of the same mixes and fired at 1500°C, showed no sign of attack by blast-furnace slag when heated to 1450°C, but the specific

electrical resistance decreased sharply between 400 and 600°C.

17-5 SPINEL, CORDIERITE, ALUMINA-CHROMITE

Spinel refractories, having substantially the molecular formula $MgO \cdot Al_2O_3$ are credited with good resistivity against molten iron oxide (Fe_2O_3) in open-hearth furnaces or against cement clinker slag in rotary kilns for portland cement (Sekiguchi, 1962). Niwa found that after 361 heats in open-hearth furnaces, spinel stood up better than magnesia-chrome brick in roofs. The main cause of failure of spinel-bonded brick was spalling, but the spalled pieces are thinner than with magnesite-chrome brick.

Suzuki found that spinel refractories are sufficiently matured at about 1485°C (cone 18) if boric and silicic acids are used as mineralizers. McCreight and Birch (1957) prepared synthetic spinel by mixing magnesium hydroxide and aluminum hydroxide in proportions to form $MgO \cdot Al_2O_3$ with sufficient water for good mixing. The water content was then reduced to obtain good forming consistency, and the formed shapes were fired to develop spinel crystals. Rybnikov (1956) obtained bulk densities of 2.98 g/ml for spinel prepared from magnesite and aluminum hydroxide, and 2.84 g/ml when it was prepared from calcined alumina and magnesite. The initial softening under load of 28.5 psi was about at 1640°C for spinel containing 30% MgO (ideal 28.3%).

Heuer (1960) claimed a basic refractory brick containing only 0.5 to 10% calcined alumina, the remainder magnesia, in specific size distributions. Increased resistance to cracking was claimed.

Palmeri (1957) investigated the properties of cordierite refractories and their application to the electrical industry. The effect of mineralizing agents on the crystal state of the bodies for different firing cycles was shown.

Alumina-chromite linings containing 10 to 12% Cr_2O_3 developed the best refractory properties (Chatterjee and Panti, 1963). Chromite ores containing over 10% SiO_2 were not suitable in this refractory use. Rammed chromite-alumina linings had twice the stability of chromite brick linings, owing to a somewhat better homogeneity of the material and the absence of joints. When the linings were applied on a calcium aluminate base in the sintering zone of rotary kilns for cement manufacture, higher stability was obtained than with clinker concrete and talc linings (Khvostenkov and Tararin (1939).

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Alumina enters into the composition of refractory container and handling equipment such as ladles, stoppers, crucibles, saggers, molds, troughs, thermocouple protection tubes and insulators, etc. It is used in heat-exchange in the form of powder, pebbles, balls, and checkerwork. Examples of some applications in this category are given.

Ryshkewitch (1960), Stott (1938), Gurr (1939), Thompson and Mallet (1939), Pointud and Roger (1957), and Avgustinik and Kozloskii (1959) describe the production of impervious, all-alumina or high-alumina sintered ware, including laboratory crucibles, combustion boats, and pyrometer tube porcelains. In most cases the small-size ware is made by slip-casting or extrusion, and fired at temperatures below 1700°C.

Meister coated porous alumina (Alundum) crucibles with thoria, beryllia, or zirconia to impregnate the pores effectively. Rutman et al. (1957) prepared thermally stable high-alumina ladle brick and stoppers of mullite-corundum composition (Al_2O_3 75.9%, SiO_2 21.1%, Fe_2O_3 1.0, Na_2O 0.6). The refractory failure was at 1850°C, bulk density 2.62 to 2.75 g/ml, porosity 15.7 to 18.6%, cold crushing strength 10,000 to 14,000 psi, and the initial deformation under load of 28.5 psi was at 1540 to 1560°C. Slag resistance was high, and thermal shock resistance good (18 melts life in comparison with 11.8 melts for fireclay brick). From an assessment of 1990 individual ladle linings ranging from 25.8 to 43.0% Al_2O_3, G. Workman found that in the tapping of steel slags of high Fe_2O_3 content, ladle life increased with decreasing porosity and with increasing alumina content in the range 32 to 43% Al_2O_3. Grebenyuk and Zhuravleva added small amounts of TiO_2 and ZrO_2 to alumina crucible slip-casting compositions to reduce the maturing temperature. Similar rammed compositions were used to line vacuum induction furnaces. The crucibles were good for 18 melts or more at a metal temperature of 1600°C. Karklit and Timofeev (1959) recommended high alumina ladle linings (15 to 25% corundum, 55 to 65% mullite, and 17 to 22% glass). Aldred (1962) claimed a nonglassy composition consisting of sintered crystals of alumina, bauxite, uncalcined and calcined kyanite, fused silica, mullite, or stabilized zirconia, finer than 100 mesh (Brit.S.S.) and embedded in a coarser matrix (10 to 50 vol. %) of a different additive from the same group of refractory materials. Bron (1963) selected refractories in the system Al_2O_3-Cr_2O_3-SiO_2 because of the higher viscosity of their liquid phase, which adds resistance to deformation and clinkering.

Lifshits (1950) recommended high-alumina brick (60 to 70% Al_2O_3) and a porosity of 18 to 20% for the upper row

of nozzles of glass melting furnaces. Urban (1955) reported on
trial installations of checker brick at the Sparrows Point
Plant of Bethlehem Steel Company. When installed in the top
eight or ten courses of checkers (which received the most
severe treatment), brick having an alumina content of 55 to
60% gave better service than the regular fireclay quality;
two brands of high-alumina brick with 60 to 70% Al_2O_3 appeared
very satisfactory. Makarychev, Rybnikov et al., and Ivanov
et al. (1958) were in agreement, that high-alumina brick give
the longest service in open-hearth checkers and glass furnace
regenerators. Some explosive spalling resulting from expansion
of iron oxides at 1600°C was observed.

Hicks (1955) recommended basic refractories, specifically
a 90% periclase, for checker brick in the glass tank re-
generators "because they remain dry," and because high-alumina
brick fail by formation of nephelite.

Ceramic balls or pebbles were developed as tower packing
for the high-temperature heat-exchange in various operations,
such as steam generation, shale oil recovery, the cracking of
crude oil, etc. The problem involved not only suitable form-
ing methods for the ball, but also the design of the equipment
for maturing the balls and equipment for effecting the heat
exchange. The ball form was preferred in order to flow the
heat-exchange medium into the reaction chamber and out, in
order to make the process as continuous as possible. The
requisite properties of the exchange medium; good heat capac-
ity, high refractoriness, chemical inertness, and good re-
sistance to heat shock, impact, and attrition, favored sintered
alumina as a suitable medium. Several methods for producing
free-flowing ceramic shapes were developed, including the
tabular alumina ball process of Alcoa and extrusion processes
in which the extrudate was cut into slugs which were then com-
pacted into spheres. S. P. Robinson (Phillips Petroleum
Company) prepared extruded pebbles from alumina and magnesium
aluminate spinel, among others. Bearer combined 1.8% methyl
silicone, with the alumina so that during the maturing of the
bond at 1590 to 1760°C the silicone oxidizes to form free
silica, which reacts with the alumina to form a mullite bond.
Kistler prepared pebbles (1) consisting of an outer shell
separated from an inner solid sphere or (2) an outer shell and
an inner hollow sphere, for which good resistance to thermal
shock was claimed. Renkey and Reardon (1963) discussed the
preparation of high-purity alumina spheres for heavy-duty
ceramics in pebble-heater beds, which are applicable up to
about 1930°C. Isostatic forming was the preferred forming
method. C. L. Norton (1946) designed a pebble heater in which
refractory mullite pebbles were moved continuously from a
firing chamber to a heat interchanger chamber, for the purpose
of preheating air to 1260°C or steam to 980°C.

Yuzhaninov (1964) measured the loss in alumina as dust from fluidized bed furnaces. The losses depend on the size of the charge, the chemical composition, the velocity of the gas stream, and the depth of the separation zone. The proper depth of separation zone was found to be double the depth of the fluidized bed. Equations were derived experimentally.

Unground, free-flowing calcined Bayer alumina has been used in the placement (bedding) of pottery in saggers, as a substitution for flint, a requirement in British practice (Elliott, 1937). This change was made by all the fine china firms and many others by 1938, not only because of improvement in the quality of the ware but in the health of the ceramic workers (Meikeljohn and Pozner, 1957). In this respect, a voluminous literature on silicosis and its treatment has been generated, of which the following is typical. Cunningham (1940) stated that silicosis in industry is not known to occur from silica combined as silicates, except in the case of asbestos and talc. Jephcott, Johnston, and Finlay (1948) observed that the fumes from the electric furnaces for fused alumina production from bauxite consisted chiefly of amorphous particles ranging in diameter from a few hundredths up to nearly 0.5 micron, and that from 85 to 90% of the fume was alumina and silica. Hannon (1958) described the method for producing a finely divided aluminum oxide powder formed from substantially pure metallic aluminum and less than about 1.2 microns to be used in the prevention of silicosis by inhalation.

Alumina is used in the preparation of saggers for supporting or enclosing ceramic ware during firing. Schaefer and Schwartzwalder (1959) supported ceramic bodies containing at least 90% Al_2O_3 and which require a firing temperature of at least 1700°C, on a sintered mass consisting essentially of 80 to 90% alumina and the remainder zirconia. The grain size of the alumina prior to sintering was not over 100 mesh. Caton (Champion Spark Plug Company) disclosed a sagger composition in 1951 composed of at least 7 parts alumina and from 1 to 3 parts silica to which is added about 2% calcium aluminate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$). The alumina content is at least 85%. Ortman (AC Spark Plug) in 1959 described a sagger composition prepared from either of two different size distributions of tabular alumina but in amount 72 parts, 20 parts of synthetic mullite, and 4 parts each of No. 1 ware clay and Florida kaolin. The composition was mixed with sufficient water and 0.2% sodium phosphate deflocculant for casting in plaster molds. The molds were agitated during casting, and fired at cones 14 to 30, for example at 1410°C.

Zeemann (1957) prepared a monolithic mullite refractory plate to be used as kiln furniture by mixing 49.83% bauxite (64% Al_2O_3, 2% Fe_2O_3) and 50.17% pure kaolin. The mixture was

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milled to 200 mesh, formed by slip casting with 30% water, and fired at 1500°C to 23% porosity.

Alumina is used as the mold material in different types of casting of metals. Neiman (1944) described the precision casting process by investment molding. Principal materials used by the dentist, jeweler, and precision caster were given. Feagin (1951), Janssen (1957), and McIntire (1957), present data on the use of alumina for high-temperature precision casting of metals.

Combustion tubes for small metal resistor furnaces are prepared from high-alumina porcelains and sintered pure aluminum oxide. Impervious tubes have been prepared by slip casting, dry pressing and extrusion. Combustion tubes are often used in dry hydrogen ambients in order to protect the metal resistor windings from oxidation. The reduction of the refractory oxides to suboxides and even to the metal have been cited previously in hydrogen and water vapor atmospheres. Reduction of some of the oxides involved may occur according to the following:

$$Al_2O_3 + 2H_2 = Al_2O + 2H_2O$$
$$SiO_2 + H_2 = SiO + H_2O$$
$$Na_2O + H_2 = 2Na + H_2O$$
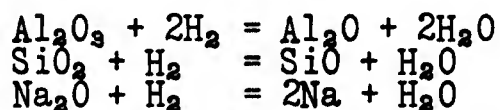
Trostel (1964) measured the temperatures at which the rates of volatilization of reduced oxides became appreciable from an alumina specimen containing 0.5% SiO_2, 0.25% Na_2O, and 0.25% MgO, and found that when flowing dry hydrogen (-57°C dew point), the loss of Na_2O was noted at 1100°C, SiO_2 at 1500°C, MgO at 1700°C, and Al_2O_3 at 1900°C. During a two-hour heating period at 1500°C, about 50% of the Na_2O was lost; in the same period at 1900°C, virtually all the Na_2O, SiO_2, and MgO were lost. A mullite tube rated nominally at 1650° service in air, might deteriorate rapidly in dry hydrogen at the same temperature.

Amerikov and Pirogov (1960) added about 1% TiO_2 to technical grade alumina (98.8% Al_2O_3) for use in preparing small-diameter tubes about 4 to 6.5 ft in length. Aluminum phosphate binders were formed by addition of 20 to 23% H_3PO_4. The green tubes (38% porosity) were fired at 1600°C. Kassel (1964) described the manufacture of large alumina cylinders, 48 in. in length, 20 in. outside diam., and 1 in. thick for use as the "magnetic bottle" included in the Stellerator, a device for creating thermonuclear energy through the process of heating a plasma of ionized gas to 0.5 to 1 million degrees Kelvin. At this point fusion is expected with the release of marked thermonuclear energy. The maximum heat would oe contained well within the walls of the tube. A high alumina composition (Almanox 4462, Frenchtown Porcelain Company) was selected for forming operations. Core casting and joining of segments were the forming methods used. Core casting was successful, and isostatic pressing at 30,000 psi, without the

use of a binder was successful.

Monolithic furnace linings of tabular alumina are often prepared by ramming tabular alumina moistened with aluminum sulfate, phosphoric acid, or mixtures of the two. Pevzner (1954) mentioned some applications for corundum refractories including burner ports in a furnace melting sulfate-fluoride charges. Keith and Whittemore lined a high-temperature laboratory kiln, capable of being fired to 1950°C, with alundum. Kupffer (1962) used 99% Al_2O_3 brick for ceramic skid rails in a pusher furnace. Weltz (1956) described a refractory composition containing 93 to 98 parts of alumina to 7 to 2 parts of boron nitride, for use as journals and bearings.

17-7 REFRACTORIES FOR ALUMINUM AND OTHER NONFERROUS USES

McDowell (1939) recommended high-alumina brick (50% Al_2O_3) for nonferrous metallurgical furnaces. Alumina brick were used in roaster hearths; alumina brick (60% Al_2O_3) were used in the side walls of nickel anode furnaces, and 70% alumina brick were used in different types of lead furnaces.

Burrows (1940) discussed the effect of molten aluminum on various types of refractory brick. Brondyke (1953) found that all commercial alumina-silica refractories were wetted and subsequently penetrated on exposure to molten aluminum. Penetration and silicon pickup were independent of the porosity, grade of refractory, and source. Stock and Dolph have recently reviewed the mode of attack of refractories in aluminum melting furnaces.

The melting point of aluminum is about 660°C, but destruction of the refractory ensues by wetting and penetration by molten aluminum, together with oxidation and thermitic reaction with easily reduced oxides such as silica. Knauft (1943) recommended zircon refractories for aluminum melting furnaces. Zircon and special, bonded silicon have excellent resistance to attack by molten aluminum (Caprio, 1965). Nitride-bonded silicon carbide (Carborundum's Refrax and Refrax-50) or oxynitride-bonded silicon carbide (Norton's Crystolon-63) are types that appear promising in remelt furnaces, metal transport, trough tile, pyrometer tubes, and tube assemblies for induction furnaces (Ref. Norton introduces ....1960). Peskin (1961) found no penetration of the nitride-bonded silicon carbide by molten aluminum in 200 hours.

Brown and Landback discussed the specific properties of ceramic and nitride-bonded silicon carbide, fused cast alumina, and high temperature, ceramic-fiber products in applications in the aluminum industry. Ceramic fiber (about 50% alumina -

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50% silica) has good resistance to metal attack and is used in many molten-metal applications.

The refractory linings used in the critical areas (hearth, charging ramp, lower walls) by the primary aluminum producers are mainly high-alumina brick in the 75 to 95% Al_2O_3 class. The alumina grogs selected for these bricks are usually tabular alumina, fused alumina, or calcined bauxite. The most satisfactory bonds for resisting metal attack are aluminum phosphate, frit, calcium aluminate, and combinations of the latter two (Caprio, 1965). A satisfactory frit material consists of 5 to 15% of a preformed vitreous product consisting of 15 to 80% B_2O_3, 5 to 50% CaO, and 2 to 60% Al_2O_3. The remainder contains not over 15% of one or more oxides, MgO, BaO, BeO, ZrO_2, ZnO, V_2O_3, Cr_2O_3, or Mo_2O_3 (McDonald and Dore, 1961). Dolph (1963) described a somewhat similar refractory using alumina or bauxite as the main ingredient. It was claimed that the brick is free of glassy phase. Roudabush (1958) clad high-alumina brick with aluminum, but with bare ends. Oxidation of the cladding at the joints was expected to prevent corrosive penetration. Dewey (1963) used a rammed mixture of from 20 to 75% alumina in cryolite as the lining for the reduction cell to replace the conventional carbon lining.

Monolithic linings, in general tabular alumina bonded with calcium aluminate cement, are gaining favor for furnace walls and ladles. These structures are inferior in abrasion resistance to the conventional brick, however. Singer (1946) attempted to protect conventional refractories against attack by molten aluminum by applying surface coatings of (a) calcined aluminosilicates (kyanite, sillimanite, or andalusite), (b) carbonates or sulfates of metals of the second periodic group of the elements, and (c) sodium silicate, all applied as an aqueous slurry.

17-8 LIGHTWEIGHT ALUMINA REFRACTORIES

A. J. Metzger compiled a bibliography of articles on lightweight ceramics (1956) and a bibliography on the relevant patents (1956). In the case of those lightweight ceramics containing alumina, the application is generally as a refractory.

Callis (1946) prepared a heat-insulating structure composed of finely divided monohydrated alumina, which is reactive with hydrated lime at room temperature, a fibrous material such as asbestos fiber, and water to form a paste. The material was partially dehydrated. Langrod (1949) mixed wet ball-milled Bayer alumina with 40 to 80% dry unground alumina (Alcoa A-1) to form a thick slurry. The dried cake acquires from 20 to 50% external porosity after calcining at 1300 to 1850°C. Morgan Crucible Company (1951) patented the method of ball milling a metal with iron balls to disperse it in alumina. An acid was

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added to generate hydrogen and to obtain frothed slip, which is poured into a plaster mold to set.

Lesar and Glen (1958) prepared a lightweight insulating firebrick from a composition containing 18.5% expanded perlite (10 mesh), 55.5% calcined bauxite (48 mesh), 5% raw kyanite (35 mesh), 5% raw kyanite (100 mesh), and 3% each of mono-aluminum orthophosphate and dialuminum orthophosphate. After firing the wet-pressed brick at 1260 to 1400°C, the finished brick had a density of 64 to 70 lb/ft³, a modulus of rupture of about 300 psi, no shrinkage on a 1650°C panel preheat test for 24 hours, and no loss on a 1400°C panel spalling test.

Misra and Puri (1961) used powdered aluminum in bauxite, with either sodium chloride or hydrochloric acid to generate hydrogen. Booth and Hess (1960) combined fluxed and expanded volcanic glass with from 1 to 10 wt % alumina, and refired at 760 to 1090°C. Zimmerman and Haeckl (1960) obtained fired bulk densities of 62 to 115 lb/ft³ for a cellular alumina ceramic prepared by mixing Bayer alumina and phosphoric acid with about 0.1% fine metal powder and 1 to 2% water-absorbing foam stabilizer. The foamed product is heated slowly and ultimately to about 315°C to develop 750 psi compressive strength. Wheeler and Olivitor (1961) used orthophosphoric acid and a powdered gaser, calcium silicate as a foam stabilizer, and silica sol as the bond.

Guzman and Poluboyarinov (1959) used a combustible (petroleum coke) as the gas generator, and 1 to 2% TiO_2 to lower the firing temperature from 1700°C to 1550°C. The best results were obtained with alumina that had been precalcined at 1450 to 1600°C. By this method, Trigler et al. (1962) obtained insulating liners for furnaces operating at 1550°C. Products containing about 82% Al_2O_3 and fired at 1200°C, had a softening point of 1855°C, an initial load deformation temperature of 1370°C (14.2 psi), no contraction at 1500°C, an apparent porosity of 59%, a compressive strength of above 470 psi, and a thermal conductivity of 0.5 to 0.6 kcal/hr °C.

Powers (1962) tested alumina foams to determine their suitability at high temperatures (1930°C). The foams had a nominal density of 37 lb/ft³. Kainarskii and Gaodu, and Gaodu and Kainarskii (1963) prepared lightweight insulators, good to 1900°C, with mixtures of alumina, gypsum, magnesium hydroxide, and powdered aluminum. Petroleum coke and phosphoric acid were also used as the foam generator.

Patented variations of lightweight alumina compositions have been described by Kawashima et al. (1962) Griffith, Olsen, and Rechter (1962), Holland (polystyrene and polyethylene foamers, 1963), Konrad and Stafford (hydraulic setting calcium aluminate, nodulated mineral wool), Powder, 1964

(addition of an inorganic gas generator to the stream of
molten aluminosilicate), Pechniney-St.Gobain (1962),
Dreyling and Dreyling (1964), and Perotte. Eubanks and
Hunkeler prepared a low-temperature foamed castable with the
following ingredients: 31 g H_3PO_4, 30 g $Al(OH)_3$, 6.5 g
$Al(PO_4)$, 1.2 g SiO_2 (10 to 20 millimicrons size), 1 g
bentonite, 0.15 g aluminum. The phosphoric acid reacts with
the aluminum to generate hydrogen, and with the aluminum
hydroxide to produce an aluminum phosphate gel. The remain-
ing ingredients strengthen the foam. After cold-setting for
about 0.5 hour, the lightweight ceramic is heated at 85°C for
about 2 hours to cure. The compressive strength ranges from
about 120 psi for a density of 20 lb/ft^3 to 460 psi for a
density of 37.5 lb/ft^3.

Nowak and Conti (1962) developed lightweight ceramic
honeycomb structures. Alumina-silica paper, impregnated with
an alumina-silica slurry was used as a refractory model sys-
tem for developing fabrication techniques. The paper orig-
inally acts as a carrier, but finally serves as an integral
part of the fired refractory. A simple mechanical method was
developed for continuous fabrication of ceramic corrugated
ribbon or sheet. A literature survey of unclassified data
on ceramic foam and ceramic honeycomb for the years 1956 to
1962 was published (Ref. Ceramic Foam...).

17-9 BINDERS FOR ALUMINA REFRACTORIES

Pole and Beinlich (1943) found that alumina was less
satisfactory than low-alumina compositions in the $CaO-Cr_2O_3$
and $CaO-Cr_2O_3-ZrO_2$ systems as a refractory in contact with
molten rock phosphates. Alumina is very reactive with the
phosphate ion. Greger (1950) found that aluminum hydrogen
phosphates are excellent bonding materials for ceramics. The
amorphous, glassy, water-dispersible phosphates containing
1.5 to 1.8 moles of Al_2O_3 to 3 moles of P_2O_5 were considered
the most useful binders. When dehydrated above 260°C the
aluminum phosphates become insoluble in water. Kingery (1950,
1952) reviewed the previous literature on phosphate bonding,
and found three major methods: (1) phosphoric acid with
siliceous materials, (2) phosphoric acid with oxides, and (3)
the direct addition or formation of acid phosphates. Except
for dental cements, no data on bond mechanisms were found.

Gitzen, Hart, and MacZura (1956) prepared refractory
castables composed of tabular alumina grog bonded with
phosphoric acid. Both heat-setting and cold-setting com-
positions were developed, which were characterized by high
bond strength, developed at 340°C, and remarkable resistance
to erosion over a wide temperature range. Excellent service-
ability of these castables in the range to 1870°C was

indicated. Formation of the bond in place by use of concentrated H_3PO_4 gave much stronger bonds than were achieved by aluminum phosphate additions. Hansen and King (1958) reacted phosphoric acid with mixtures of "inert" refractory aggregate, with one member selected from the group consisting of hydrated alumina, raw bauxite, raw diaspore and raw clays.

Bechtel and Ploss (1960, 1963) claimed excellent strengths at low and medium temperature (600 to 1000°C), provided by $Al(H_2PO_4)_3$ without any adverse effect on the high-temperature properties of the refractories (fireclay, bauxite, chrome, and silica). The bond $Al_2O_3 \cdot 3P_2O_5$ began to sinter at 1150°C, and to soften at 1340°C, but a retaining skin of $AlPO_4$ formed which was crystalline and solid at 1600°C. The bond $Al_2O_3 \cdot P_2O_5$ began to soften at 1260°C. Preusser (1961) obtained compressive strengths in excess of 150 kp/cm² (2130 psi?) for corundum or chamotte bodies with diluted phosphoric acid (2 to 15% H_3PO_4) at reaction temperatures of 100 to 400°C. A reaction period of 4 hours at 300°C was equivalent to 6 hours at 200°C. The compressive strengths were much lower than those attainable with 85% H_3PO_4. Margulis and Kamenetskii (1964) found that a bond with the molecular ratio of $Al_2O_3:P_2O_5$ of 1:3.5, at a density of 1.57 g/ml was most suitable as a bonding agent in the manufacture of articles and coatings. $AlPO_4$ raised the thermal stability of corundum materials and at the same time increased their strength.

W. O. Lake (1936) reported that alumina refractories containing from 70 to 80% Al_2O_3 were employed in oil-fired basic furnaces, bonded with high-alumina cement (Lumnite-type cement). One of the earliest applications was as a cast liner for furnace doors. Anderson (1938) divulged the method of preparing articles, as for example, brick, by mixing 4 parts of ground sintered aluminum oxide (natural corundum, emery, etc.), one part of high-alumina cement, and water to provide a satisfactory casting consistency.

H. N. Clark (1946) specified a furnace lining made from a refractory concrete consisting of an intimate mixture of an inert filler with an aluminous cement binder comprising about 60 to 75% alumina, about 20 to 40% calcia, and less than 2% iron oxides. The recognition of the necessity for increased purity of both the cement and specific single-oxide aggregates in hydraulically bonded refractories marked an advance in the development of refractory linings. S. F. Walton (1941 developed a 50:50 batch mixture by weight for hydraulically forming a refractory body containing fused alumina and a high-alumina cement. The cement formed a refractory bond with the alumina having a higher melting point than that of the original cement. Herold and Hoffman (1941) also showed the value of various refractory grogs bonded with Lumnite cement. Gitzen, Hart, and MacZura (1957) appraised a pure calcium aluminate cement

(empirical molar formula $CaO \cdot 2.5Al_2O_3$) in a grog which was substantially tabular alumina and determined an optimum balance between refractoriness and bond strength in high-temperature castables.

L. Jacobs (1960) developed a laminated plastic refractory which consisted essentially of a primary layer stable up to 1870°C, and consisting of at least 60% tabular alumina and a supporting layer of plastic refractory which converted to a glass above 1200°C, and which consisted of a homogeneous mixture of about 60% calcined flint clay (3 to 10 mesh), 10% kyanite (20 to 50 mesh), 10% plastic kaolinite fireclay, and 10% plastic ball clay, the remainder being water.

Scott and Emblem (1951) described the application of ethyl silicate in refractories. This binder has been used in specific applications of alumina in which its remarkable ability to undergo hydrolysis and condensation to yield an alkali-free silica gel is useful. Quick-setting dip coatings for refractory forms is one example.

18 ALUMINA AS AN ABRASIVE MATERIAL

18-1 INTRODUCTION

Bauxite and Bayer alumina are both used to prepare electrofused alumina for abrasives and other products associated with the fusion process and fusion casting. Parché has given a description of the industry. The historical development is mentioned in "History of Abrasive Grain", Grinding and Finishing 9 (2) 22-7 (1963). Schneider (1959) provides chemical and mechanical data on electrocorundum and silicon carbide, and a survey of the technology of their production.

Initially, domestic bauxite sources (Arkansas) were sufficiently pure for fused abrasive purposes, but with depletion of the pure grades, it has become necessary to draw on foreign sources. Calcined South American bauxites (Suriname, Demerara) are sufficiently pure to meet the requirements of about 80% Al_2O_3, and not more than about 8% each of SiO_2 and Fe_2O_3, and 3.5% TiO_2. The fusion process relies on the formation of magnetic ferrosilicon (<15% Si) by addition of iron, if necessary, to provide purification of the product. The heavier ferrosilicon can be run off while fluid, or removed by chipping after the melt has solidified.

Many references relate to methods that have been considered for purification of the melt, or for obtaining the ingot in a more advantageous condition for crushing and sizing. Glezin (1937) mentions the addition of 5% TiO_2 to increase abrasive properties, and 5% Cr_2O_3 to increase the tenacity. Baumann and Benner (1944) crystallized the alumina with at least one metal of the group Fe_2O_3 and Mn_2O_3 in solid solution, and also in a fused matrix of a manganese, cobalt, or nickel spinel (1947). Baumann and Wooddell (1945) prepared an abrasive material comprising at least 90% crystalline aluminum oxide and a matrix of beryl or zircon. Benner and Baumann (1943) claimed an abrasive containing alumina and a minor amount of monazite. Schrewelius (1947) separated the silicon and silica slag as upper layer of the melt from mixtures of chamotte and a reducing agent. By addition of a member of the sulfur group (selenium), aluminum selenide was formed, which could be broken up by hydrolytic action with water to liberate the corundum grain (1948). Ridgway (1939, 1943) purified the fused bauxite product by immersion in fused alkali metal cyanide to dissolve a considerable portion of the slagging constituents still clinging to the grain. Klein (1942) coated the grain with an alkaline earth metal sulfate or with cryolite. Yamaguchi and Tanabe (1954) synthesized artificial emery by firing powdered bauxite at 1350 to 1550°C, and found a slightly poorer abrasive efficiency than that of the native product.

Klein and Ridout (1949) described the properties and applications of 32 Alundum, a grade of fused alumina (99.6% Al_2O_3), crystallized by cooling a molten bath of bauxite containing a metal sulfide. The sulfide in the solidified mass is water-soluble, releasing the alumina grains of controlled size and rough surface.

Frost (1958) prepared a fused abrasive consisting essentially of about 10 to 50% by weight of fine crystals of titanium carbide dispersed in crystalline alpha alumina. Ueltz (1963) sintered (to zero porosity) preformed grains of natural bauxite, characterized by having a skin produced by the sintering process and a large proportion of the crystals randomly oriented in the size range 5 to 30 microns and composed of alpha alumina and mullite, with glass present as an interstitial component.

Pevzner (1949) considered the production of corundum abrasives without the use of furnaces but by heat generated by the thermitic power of aluminum in the reduction of some less stable oxide than Al_2O_3. A product containing 95.5% Al_2O_3, 1.24 MnO, 0.95 CaO, 0.56 TiO_2, 1.08 Fe_2O_3, and 0.64 SiO_2 was claimed to be equivalent to normal electrocorundum from bauxite. It could hardly be justified from an economic standpoint for large-scale operation. Nesin (1964) described the process of making crystalline alumina lapping powder from coarsely crystalline Bayer sources by ball milling and elutriation. Polishing grades of Bayer alumina have been described previously (Section 5-10). Funabashi (1952) stated that aluminum oxide prepared by calcining ammonium alum was the most suitable polishing grade; when calcined at 1250°C the particle size was 0.1 to 0.2 micron, at 1400°C, 0.4 to 0.6 micron. Ordinary alum, calcined at 1400°C and separated by sedimentation provides a particle size of 0.7 to 0.8 micron. Wagner (1956) prepared an abrasive with porous grain by decomposing hydrogen peroxide at 60 to 70°C in a moist cake of ground alumina containing a surface active agent and a manganese compound. A higher degree of uniformity of pore distribution, shape, and size was claimed by this method than is attained by use of NH_4HCO_3 or other CO_2-forming agents. The porous cake was only partially sintered. When the crushed grain was used in making grinding wheels, the porosity was first blocked with gelatine or glue before addition of the cementing compounds.

The Bayer alumina used in producing fused alumina abrasive is a special type selected for its current-carrying ability, moderate to low soda content, and suitability for producing a white product. No additives are required during the fusion process. The fused product is more porous (induced by the volatilization of soda) and is more friable than the bauxite grain, a desirable property for cool cutting.

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The fused grain is crushed and sized to standard sizings adopted in 1930 but revised at later dates (Simplified Practice Recommendations R118-36, National Bureau of Standards, Sept. 1, 1936). Various treatments have been applied to the grain to improve its stability or the final shape by impact crushing, air blasting, or pan mulling, and roasting, washing, or chemical treatment with acid, alkali, or salt baths. The coarser sizes, 6 to 240 grit, are obtained by sieve sizing. If insufficient fines are produced in coarse crushing operations, they may be generated by ball or rod milling. Classification of the finer sizes is by water sedimentation methods, hydraulic flotation, or air classification (Eigeles, 1936; Benedicks and Wretblad; Puppe, 1938). Dumas (1960) described a battery of centrifugal classifiers that accurately produces six standard fine sizes ranging from 22 to 5 microns average grain size. The improved classification system assures consistency of surface removal rate (scratch free) of optical glass and electronic components. Kaempfe recommended that fused grain should be tested for gain on oxidation, titanium content (not over 2%), and the thermal expansion of the unfired material. Terminasov and Kharson used X-rays to detect internal defects in corundum abrasives.

The abrasive applications of alumina are legion, but they generally fall into categories using loose grain, coated grain (cloth, paper, fiber), and wheels and tumbling shapes. The major applications of the finer loose-grain sizes are in optical polishing, lapping, and fine grinding and polishing of plate glass. Coarser grit sizes are used in quarry sawing of granite and marble, lithoplate graining, pressure blasting, tumbling operations, grinding and buffing compounds, in non-skid floor and road compositions, and in set-up wheels.

Coated abrasives are prepared in the form of rolls, sheets, belts, and disks, coated in different grit sizes, and with several different alumina types. A preferential orientation of the grit is also possible, obtained by electrostatic methods.

Abrasive wheels are produced from a wide variety of fused and Bayer alumina materials. There are five types of wheel bonds in general use (Parché): vitrified or ceramic, rubber, resinoid, shellac, and sodium silicate. The wheels are made in an extensive series and degrees of abrasiveness and porosities. Vitrified wheels, hones, and rubs are used in tool grinding, cylindrical grinding (center-type and centerless), form grinding, ball grinding, and heavy-duty snagging.

Rubber-bonded wheels are used in cut-off and snagging wheels where impacts are high. Rubber-bonded wheels provide finer finishes relatively, hence are suited for finishing ball bearing races, drill flutes, cutlery, and in centerless grinding. Resinoid wheels are used in cut-off and snagging wheels, in thread grinding, intaglio stones (engraving finishes) and many

others. Shellac-bonded wheels are used for softer abrasive action, as in hemming wheels for cutlery, grinding, and in roll grinding. The sodium silicate-bonded wheels also provide a soft abrasive action suitable for hemming wheels for grinding and polishing cutlery. Knife hones may be silicate-bonded.

Silicon carbide and corundum are often confused because of their similar properties and uses, not to mention the close similarity in some of the trade names for the artificial products. Some references to the abrasive properties of corundum have been made in Section 5-10.

18-2 LOOSE GRAIN ABRASIVE

Jacquet (1939) described the techniques of surface treatment of metals using files, emery papers, polishing cloths and powders. Four historical periods include (1) before 1900, empirical, (2) 1900 to 1926, scientific methods and the metallurgical microscope, (3) 1927 to 1933, electron diffraction, and (4) 1934 to 1939, electrolytic polishing.

Rollason et al. (1949) claimed that platey crystals are most suitable for polishing mild steel. Gamma alumina at 0.5 m²/g and alpha alumina at 1.5 m²/g were considered to be suitable. The lapping method introduced by Chrysler was described by Mauzin (1949). Silicon carbide was used for cast iron, aluminum, brass, bronze, and brake bands; aluminum oxide for alloy steels, rapid tool steels, malleable iron, and hard bronze. Grain sizes were 180 to 320 for roughing, 320 to 500 for finishing, and 600 for the finest surfaces. Schulz (1952) claimed that fire polishing and acid polishing (etching) processes are suitable only for well-ground glass shapes which do not have rigorous requirements of sharp detail. For optical glass, only mechanical polishing is permissible. Burkart (1952) discussed the fields of application of alumina among the various commercial abrasives in different categories: (A) Coarse abrasives competitive with alumina in some applications include quartz sand, Italian pumice, silicon carbide, and the relatively more expensive boron carbide; (B) Finer surface treatment abrasives include tripoli, diatomaceous earth; (C) Polishing materials include vienna chalk (a mixture of CaO and MgO finer than 1 micron which hydrolizes and carbonates undesirably), chalk (CaCO₃), rouge, and chromium oxide. Stead, Korelova, and Ingalls discussed abrasives used in grinding and polishing glass, especially optical glass. Cerium oxide and a mixture of cerium oxide with other rare-earth oxides (barnesite) is faster than rouge or alumina in optical polishing.

Funabashi compared aluminum oxide with magnesia and silica sand in the polishing of synthetic resins and celluloid.

Forrester (1956) described the production of abrasive aluminum oxide for vitrified grinding wheels; Buchner (1956) described the manufacture of the wheels. Aluminum oxide as the basic grain in bonded abrasives has been described (anonymously) in Grinding Finishing 9 (5) 36-9 (1963). Kingery, Sidhwa, and Waugh (1963) devised a simple model for the microstructure of a vitrified bonded abrasive wheel based on a coordination number of 6 for neck growth of the vitrified bond on assumed spherical particles having a packed solid (abrasive grain) content of about 50%. McKee (1961) presented a table of comparative designations of abrasive grain types used in grinding wheel manufacture. American standard markings for identifying grinding wheels and other bonded abrasives include a letter symbol for the type of abrasive (A, aluminum oxide; C, silicon carbide), a number indicating grain size, a letter indicating grade (A, soft to Z, hard), a number indicating structure (0, dense to 15, open), and a letter indicating the bond or manufacturing process. Both grade and structure are complex characteristics difficult to define precisely. Grade defines the tenacity of the bond for the grain. The grade of wheel has no generally accepted quantitative definition, but is based on the proportion of bond to grain in the original mix. Schlechtweg derived a simple formula for fracture of rotating brittle disks, showing the fracture velocity as a function of the ratio of the outer diameter to the inner diameter of the abrasive wheel. McKee (1963) presented the results of a panel discussion on the merits of using aluminum oxide and silicon carbide bonded together or cemented on a backing. Kistler and Barnes (1940) claimed a method of making an abrasive body consisting of pouring a polymerizable compound which is fluid at room temperature onto the abrasive grain in the mold, heating and without pressure thereby polymerizing the compound around the abrasive grains to a hard condition, and finally stripping the abrasive body from the mold.

Barnes et al. (1942) patented a method for bonding, comprising mixing fused alumina with a rubber latex to form a molded wheel. Abbey (1951) and Taylor (1953) described rubber-bonded grinding wheels strengthened by the inclusion of fibrous material, and combining soft-cutting and polishing abilities.

Hessel and Rust (1951) described bonds of resinous condensation products, Ahrens and Lappe (1951) sintered metal oxide bonds, especially Al_2O_3 at firing temperatures above 1700°C. Maziliouskas (1958) described formulas for frits, and Houchins (1956), vitrified borosilicate bonds. Foot (1960) prepared a new abrasive wheel using alumina bubbles (steam-blown aluminum oxide from the poured melt) with a resinoid

bond, which operates at 9500 sfpm for grinding rubber, leather, and cork without loading.

Zimmermann and Burton-Banning showed that illitic and montmorillonitic clays give higher strength than clays composed mainly of kaolinite, fireclay, or halloysite in abrasive wheel bonds. Bibbins (1962) patented an abrasive wheel with a metal bond consisting of 86% iron and ferrite-strengthening metals, 0.4 to 5 phosphorus, a trace to 0.8 carbon, and 0 to 7% sulfur. The bond melts above 750°C, and after sintering at 750 to 1100°C, grain weakening is induced by the phosphorus.

Horibe and Kuwabara (1961) showed by X-ray examination of the unit cell spacing, that a considerable part of the Ti^{3+} dissolved in alpha alumina abrasive grain becomes oxidized to Ti^{4+} during the firing of the vitreous bond.

Marshall (1964) designed a surface-grinding wheel having the correct degree of strength and impact resistance for surface grinding, without too rapid or insufficient wear of the abrasive face, by crushing fused masses of conventional alumina abrasive material with 0.25 to 1.0% Li_2CO_3. This produced an abrasive grain containing about 0.1 to 0.4% Li_2O in the form of 1.6 to 7.2% zeta alumina phase ($Li_2O \cdot 5Al_2O_3$). Grain containing no zeta alumina was found to be too tough, and that containing about 14% was too brittle or soft.

Wills (1943, 1944) discussed the factors governing fine surface quality obtained by grinding, and pointed out the necessity for a more scientific classification of surface finishes.

Funabashi and Terada (1962) appraised the polishing ability of corundum and mullite barrel-finishing media. There are three classes of media for barrel finishing: metallic, natural mineral, and synthetic aluminum oxide. With the addition of silica, fused alumina, emery, and synthetic alumina, the amount of metal removed increased. Silicon carbide or alumina removed the most metal; iron oxide or chrome oxide gave the best finished surface. The rate of metal removal increased with increasing crystal size, and the surface of the pieces became rougher.

Rea and Ripple (1957) and Finnigan (1953) described the methods used for precision grinding of sintered alumina products to tolerances of 0.000/in. or better. Grinding provides improved surface finishes, the quality of which depends on the abrasive used, the body being ground, and the grinding practices. The use of diamond wheels, slitting tools, band saws, and powders makes the machining of ceramics easy. Royal Worcester Industrial Ceramics, Ltd (1962) surface grind alumina ceramic parts (Regalox) for industrial use to

tolerances of 0.0002 in. Even with shrinkages of 14 to 15% when fired at 1500°C, ware dimensions have been held to 2%. Three types of diamond tools have been developed (1) impregnated diamond wheels (sintered metallic or resinoid bond), (2) electroplated wheels having a single layer of natural diamond grit on the grinding face, held in electrolytically deposited nickel, and (3) micron paste, used for lapping surfaces for ceramic seals and other parts that must have an extremely fine finish.

Baab and Kraner devised a sand-blasting test for determining the relative abrasion resistance of refractory forms. Blasting with uniformly sized abrasive at supersonic speeds is used for precise cutting and machining of hard brittle materials. The "Airbrasive" tool, a product of the S. S. White Company, has eliminated shattering and flaking (Ref. Cutting Hard Brittle Ceramics....). Aluminum oxide is the most widely used abrasive; the best cutting is obtained with 30 to 60 mesh size. Air pressure, grit size, and blast angle all affect the surface finish. Boron carbide is suggested for the blasting nozzles (Ref. Use of Abrasive Grain...(1963).

Rushmer and Elsey (1964) described the production of intaglio stones for finishing rotogravure cylinders to 1 to 2 microinches. The stones are made by molding graded alumina particles with synthetic resin. Sintered alumina balls have been used for conditioning aluminum engraving plates to make them receptive to inks. Many types of abrasive are used in the blast cleaning of surfaces for painting and for maintenance repainting.

The applications of coated abrasives and the equipment in which they are used are well covered in the book Coated Abrasives-Modern Tool of Industry. McGraw-Hill Book Company, New York, 1958, 426 pp. Spencer (1959) described the main types of abrasives (flint or quartz, Turkish or American emery, garnet, aluminum oxide, and silicon carbide) and the main factors influencing their operating efficiency. The methods of manufacture of coatings have been described in "Use of Abrasive Grain in the Manufacture of Coated Abrasives" (Anon., Grinding Finishing 9 (7) 33-6 (1963).

Coated abrasive articles, not necessarily restricted to alumina abrasives, are represented by the following disclosures. Hanford (1959) described a coated abrasive article comprising a backing having a layer of abrasive grain attached to a surface by animal glue and phenolformaldehyde, urea-formaldehyde, or melamineformaldehyde, and a substantial amount of wollastonite (80% minus 325 mesh). Quinan and Sprague (1962) patented the disclosure of a flexible coated abrasive sheet, comprising a woven cloth backing precoated with an elastomer which is a terpolymer of butadiene, styrene,

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and acrylonitrile containing at least 5 wt % of combined styrene, a film-forming, strength-imparting, thermosetting resin compatible with the elastomer, consisting of phenol-aldehyde and urea-aldehyde resins, a resinous bonding coat, and abrasive grains bonded by the bonding coat.

18-4 CERAMIC TOOLS

One of the earliest patent applications for a sintered alumina body was British Patent No. 4887, February 27, 1913, granted to Thomson-Houston Company, Ltd., for a wear-resistant body suitable for use as tools, dies, rolls, bearings, drills and the like. Very finely divided aluminum oxide was mixed with about 10% of a suitable binder (gum tragacanth) and the mixture was compressed in the form of a flat cylinder, e.g. 0.25 in. by 0.75 in. in diam., and was baked at 1300 to 1400°C in an inert environment (tungsten or molybdenum wound resistance furnace). After baking to the consistency of chalk, the piece could be machined or bored easily with diamond dust. After machining, the specimens were refired at 1800 to 2000°C in an inert environment to a "dense condition free from crystalline structure." This may be compared, for example, with a more recent disclosure, German Patent 1,098,427, January 26, 1961, to Trent and Comins, "Process for Preparing Hard Aluminum Oxide Sinter Bodies," which claims (1) A process for preparing hard aluminum oxide base sinter material, characterized by the fact that a homogeneous powdered mixture which consists of 87-96% Al_2O_3 and the remainder, in addition to impurities, of at least 2% each of titanium nitride and titanium oxide, is compressed in the usual manner into a briquet, this briquet being sintered at a temperature of between 1600 and 1750°C.

Ryshkewitch obtained U. S. Patent 2,270,607, January 20, 1942, for a ceramic cutting tool consisting of a molded self-bonded sintered aluminum oxide and containing chromium oxide, the body of the cutting tool having a fine crystalline structure throughout. Westmoreland-White (1946) disclosed the British advances in ceramic lathe tools as being represented by a composition containing a well ground mixture of 94% alumina, 2.5% calcium fluoride, and 3.5% bentonite. The dried particles (minus 200-mesh) were dry-pressed at 20,000 psi and sintered at about 1500°C. Singer (1949), and Graham and Kennicott (1950) felt that ceramic oxide tools did not meet the requirements for cutting tools, and the toughness of titanium carbide and tungsten carbide relative to the pure oxides was cited as a prime advantage. Isaev et al. (1952) stated that red-hot hardness is a main quality in cutting tools. The alumina ceramic tools retained hardness even at the melting point of steel, but certain defects necessitated special attention to tool shape, machining conditions (speeds, etc), the attachment

of the tip, and grinding of the tip. Russian ceramic tools were claimed to exceed the hard-metal tools in the quality of the surface finish, and the cost of the ceramic was only about one-tenth. Speeds 60 to 80% higher than with the hard-metal tools were possible. Both detachable and nondetachable tips were used. Kitaigorodskii and Pavlushkin (1953, 1955) described the properties of "Mikrolit," a superstrong corundum structure containing 99.0 to 99.2% Al_2O_3, a crystal size of 1 to 3 microns, a bulk fired density of 3.96 g/ml, Rockwell hardness of 92 to 93 (scale A), flexural strength up to 64,000 psi and crushing strength up to 710,000 psi. The tools were probably made by hot pressing. Because of their brittleness they were used only in finishing and semifinishing operations that did not involve impact loads. Crucibles made from the composition had extremely high chemical resistance. Trippe (1957) described a technique developed by the Russians featuring the metalizing of the ceramic tips in a vacuum in preparation for brazing to the tool shank.

Rea (1956); Richter and Kammerich; Blanplain; and Taegerman examined the likely applications of alumina tools and some of the precautions necessary to their use particularly for cutting steel. This culminated in the Rodman Laboratory report PB 111757, which was concerned with the possible substitution of ceramic materials for strategic alloys, a possible cost reduction by using the ceramic tools, and the use of the tools to perform machining not possible with conventional hard metal types.

E. and N. Labusca (1957) described the properties of tools prepared from Romanian sources, mixtures of tungsten carbide and cobalt with more than 90% alpha alumina, designated ENC. These were claimed to excel tungsten carbide in the machining of hard materials. Cutting ability was retained to 1200°C at speeds to 720 ft/min; tungsten carbide was found satisfactory only to 850°C. Gion and Perrin gave full details on "Ceroc" ceramic tips, a French development comprising 95 to 100% alpha aluminum oxide of crystal size within 1 to 10 microns. Strength in flexure was 60,000 to 70,000 psi, and in compression 280,000 to 350,000 psi.

During a ceramic tool symposium, held in Houston, Texas, March 1957, Zlatin discussed the progress of ceramic machining operations at Wright Aeronautical Division, Curtis Wright Corporation; D. R. Kibbey and W. T. Morris analyzed the variables in ceramic tool cutting; Haeme and Hook mentioned potential industrial applications; W. B. Kennedy described his experimental machining tests with ceramic tools and the types of applicable ceramic compositions; and J. F. Allen appraised the performance of ceramic cutting tools in production jobs.

McAuliffe,and Siekmann and Sowinski discussed the optimum tool geometry for cutting high-speed steels, super-alloys, and titanium. Rake, edge-cutting angles, and nose radii dimensions were investigated. Ryshkewitch (1957) cautioned the importance of preventing chatter in both the work and the tool tip. F. Singer and S. Singer stated that the desired properties of cutting tools include: high compressive strength, toughness, resistance to abrasion and heat, and unwettability by metals. Matthijsen thought cermets could provide sufficient elasticity and hardness to lathe tools.

Many investigators have lately investigated the performance of ceramic tools. Dawihl and Klingler thought that impact resistance could be improved by heating the bit (by medium frequency current during the cutting operation) Mii et al., and Yamada et al., tested the tools on high speed lathes (to 5000 ft/min) at cutting depths of 0.04 inch. At feed rates of 0.004 in./revolution, the ceramic tools withstood the conditions well, but carbide tools wore exceptionally fast. Wear of the ceramic tools was rapid, however, for tools having chamfers 0.002 inch in width and 45 and 30 degree angles. Marked cratering appeared on the tip surface. Of the three components of cutting resistance, the horizontal component increased the most. Roughness of the machined surface increased, tending to generate burrs, and the surface layer of the work became deformed. Although the results were ascribed to excess chamfering, the blunted cutting edge was probably unsuitable for high-speed cutting. Nakayama et al. (1961) concluded that the use of ceramic tools without chamfer and at very high speeds is desirable. Ceramic tools having tool geometry of -5, -7, 5, 7, 15, and 1.5, and negative land,30 degrees x 0.04 inch,were used successfully for high-speed turning of hardened alloy steels at about 650 ft/min, and at a depth of cut ranging from 0.008 to 0.016 in. and a feed of 0.0016 in./rev. The hardness of the ceramic tools was found to decrease markedly between room temperature and 400°C, but this tendency decreased above 400°C, and above 700°C, the hardness exceeded that of carbide tools.

Haidt (1960) noted the lack of toughness of alumina tools in comparison with the carbide tools. Kolbl (1958) cited the advantages of high cutting speeds at high temperatures, Puehler and Wagner the economy and better surface finishes obtained in comparison with diamond. Shaw and Smith (1958) found that the compatibility of the ceramic tools for various metals ranged from excellent to poor in the following order: nickel, cobalt, gray cast iron, steels, and inoculated cast iron, lead, silver, aluminum, beryllium, and titanium.

Fleck and Gappish examined the grinding surface of ceramic tools with the electron microscope and also by means of the Triafol-SiO-pressure method and found that the edge-life

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depends largely on the grain size of the sharpening abrasive. Only diamond-impregnated grinding wheels can be used to grind and polish ceramic tools, and owing to the brittleness, great care must be exercised. Brewer (1959) discussed such factors as porosity and grain size, tool life, power requirements, and surface roughness. Gill, and Gill and Spence (1958) reviewed the advantages of aluminum oxide tools, and the physical properties of the different commercial compositions.

Staudinger (1960), Gion (1960), Widmann (1964), and Droscha (1964) have reviewed the literature on recent ceramic alumina tool developments. Oishi, Hamano, Kinoshita, and Takizawa (1963) attempted to manufacture alumina cutting tools by hot-pressing, using oxides of Mg, Zr, Cr, or Co. Oxide cutting tools of long life were manufactured on a commercial scale by hot-pressing Bayer alumina with the addition of magnesia at 1800°C at a constant pressing temperature.

Some tool compositions are as follows: Goliber (1959) claimed one composition containing oxygen-deficient titanium oxide in solid solution in alpha alumina in an atomic ratio of Al:Ti from 0.8 to 20. The claimed hardness was 94 Rockwell A, the bending strength 90,000 to 95,000 psi; the product was electrically conductive; another composition contained oxygen-deficient titania in solid solution in alumina, and up to 60% by weight of reduced chromium (preferably 25 to 50%). The Rockwell A hardness was 87.5, and the flexural strength at room temperature was 110,000 psi. Both compositions were cold pressed at 20,000 psi and sintered at 1600°C.

Gill (1959) pressed a mixture of 40 to 93 wt % alpha aluminum oxide (particle size <10 microns), 20 to 59% Cr_2O_3 (<10 microns), and 1 to 54% Cr, W, Mo, Fe, Mn, Co, Ni either alone or mixed together (<15 microns). The mixture was hot-pressed in impervious graphite molds at 1000 to 5000 psi and at 1400 to 700°C. An addition of 1 to 15% pure metallic chromium was found especially suitable. The hardness of the finished pieces was 93 to 94 Rockwell A. Gill (1960) hot-pressed at at least 1400°C and at least 1000 psi an extremely fine powdered gamma alumina having a surface area of at least 200 m^2/g, for such uses as cutting tools, thread guides, nozzles, and wire-drawing dies. White (1960) coated fine 5 to 10-micron sintered alumina particles with ammonium molybdate solution (about 10 wt % Mo) and ignited the mix at 850°C for 15 minutes prior to calcining at 1100°C for one hour. The sieved powder was cold-pressed at 20,000 psi with wax lubricant to give small bars. The bars were sintered in hydrogen at 1800°C for 2 hours. The product had an even texture, a cold bending strength of 25,000 psi, a density of 4.11 g/ml, and an open porosity of only 0.7%.

Csordas et al. (1960) claimed a process comprising

the sintering at 1450 to 1500°C of pure aluminum oxide (99.99% Al_2O_3), the particles being all less than 3 microns, and 90% less than one micron. The sintering time was held for such a short time that 90% of the crystal size was below 10 microns. Ryshkewitch and Taylor (1961) developed a dense, nonporous, and wear-resistant tool material consisting of an intimate mixture of fine-grained silicon carbide particles (8 to 50% by volume) in fine alumina. Schmacher (1963) claimed sintered mixtures of titanium oxide and alumina, obtained by mixing from 1 to 50% titanium hydride with the alumina and sintering the molded form in a mixture of nitrogen and hydrogen at 1800 to 2000°C. Whittemore et al. (1963) prepared molded alumina cutting tools and wire-drawing dies by hot-pressing powder mixtures finer than 325 mesh and containing at least 95% Al_2O_3, at 1400 to 1800°C. Densities of over 3.95 g/ml with crystals averaging not coarser than 7 microns were achieved. As much as 2% Cr_2O_3 or Ti_2O_3 was found to be permissible, and 0.015 to 1% MgO was beneficial in preventing grain-growth. The abrasion resistance increased with decreasing crystal size below 4 microns, and maximum toughness was found with 6 to 7-micron average crystal size. Both crystal size and density increased with increasing time and temperature in pressing; with no MgO, one minute at 1700°C gave high density but the crystal size was too coarse; about 20 minutes at 1450°C gave an equal density with only 2-micron crystals. The crystal size was only 5 microns after 9 minutes of heating at 1750°C when magnesia retarder was used.

Bugosh (1964) hot-pressed fibrous boehmite having 200 to 400 m^2/g surface area, and 25 to 1500 millimicrons average length, and containing from 0.5 to 5% of a grain-growth inhibitor such as magnesium fluoride or an oxide of nickel, cobalt, chromium, or magnesium. Pressing at 1600 to 1800°C and 1000 to 6000 psi resulted in bulk densities as high as 3.97 g/ml, 64,000 psi cooled modulus of rupture, and 92.5 Rockwell A hardness.

Bradt (1964) summarized the comparison of performance of present ceramic tools with those of 1956 as shown in the following tabulation.

Tool Properties	1956	1964*
Rockwell A	86-90	93-94
Transverse Rupture	40 to 60 (K psi)	90-110 (K psi)
Impact fracture	6-8 in. lb	11-13 in. lb
Porosity	0.5 - 2.0%	0.1%
Compression	300-350 (K psi)	425-475 (K psi)
Elast. modulus	42-46 (KK psi)	56-60 (KK psi)

* Conservative, especially strengths, which may exceed by 25%.

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Material Machinable with VR-97	Tool Performance	Best Finish RMS	Usual Speeds SFPM
Steel-Soft to			
RC30	Good	35	600-1500
RC30-RC45	Excellent	25	400-1200
Hard RC45-RC65	Excellent	20	100-800
Cast Iron	Excellent	35	400-2500
300 S Stainless	Poor	35	400-1000
400 S Stainless	Good	35	600-1500
Carbon-Graphite	Excellent		200-1000
Tungsten	Excellent		150-800
Stellite	Excellent		60-600
Tantung	Excellent	-	60-140
Molybdenum	Fair	-	500-800
Titanium	Poor	-	Not recommended
Alum. Bronze	Good	-	1500-2500
Hard Rubber	Excellent	-	To 1000
High temp. alloys:			
Iron base	Poor	-	Not recommended
Nickel base	Poor	-	Not recommended
Cobalt base	Good	-	60-600

Hardness of Steel	Cut Depth	Maximum Feeds	Recommended Speeds
RC-40 to 48	To 1/32"	.030	300-1200 SF
	1/32 to 1/8	.025	300-1000
	1/8 up	.021	300-800
RC-48 to 55	To 1/8"	.015	200-800
	1/8 up	.010	200-600
RC-55 to 65	To 1/32"	.010	120-450
	1/32 up	.008	75-350

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19 ELECTRICAL APPLICATIONS

19-1 SPARK PLUG AND HIGH-FREQUENCY INSULATION

Some early types of alumina spark plug compositions were described in Section 8-1. While there appears to be no major change in commercial spark plug porcelains away from alumina compositions, the search for modified compositions and methods for igniting the fuel in gas engines continues.

Spark plug insulators in the United States vary in alumina content from about 85 to 92%. Wet-ground, acid-leached tabular alumina is used by Champion Spark Plug, low or moderately low-soda calcined aluminas are used by the remaining major producers. The components are either dry-ground or wet-ground. The blanks are formed, in the majority of cases, by isostatic molding from a spray-dried suspension of the components, wax lubricants, binders, and other agents, but compositions are also extruded, cut, and profiled to shape in the leather-hard condition. Oversize ware may be diamond-tooled. The saggered ware is fired in tunnel kilns near 1700°C. Completely dry processes have been proposed. The use of more reactive alumina types would extend the process substantially to 100% Al_2O_3 bodies at about the same firing conditions.

Skunda (1955) described the process of making a spark plug insulator comprising the steps of forming a mixture of ceramic material with a heat-softening resin binder, forming an elongated blank from the mixture, rotating the blank on its longitudinal axis, heating the surface of the rotated blank to above the softening temperature of the resin binder, forming the heated surface to an insulator contour, and firing to remove the binder and to sinter the insulator.

Kato and Okuda (1960) said that insulators prepared from Bayer alumina, the fusion process, and ammonium alum decomposition, with MnO_2 and TiO_2 mineralizers, were excellent high-frequency insulators. Lungu and Nagy, Poluboyarinov (1958), Budnikov, and Smoke et al. (1959) examined various compositions for ultra-low loss characteristics. Rigterink (1958) predicted that it was unlikely that an inorganic insulating material appreciably better than sapphire would be found, unless it had covalent bonding rather than ionic. Improved structures would have no glass phase but very fine crystallites; and 98 to 100% of the theoretical density and lower firing temperatures might be realized by a more sophisticated use of organic additives, more homogeneously distributed. Some advances have been made in this direction.

Schurecht (1957) found that zinc oxide reduces the

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specific electrical resistance below 1 megohm at about 730°C when mixed in amounts above 25 mol. % with alumina. Promising compositions were found in the system BeO-MgO-ZnO-Al_2O_3, but the toxicity of beryllia might restrain its use in spark plug manufacture. Schurecht (1959) found compositions in the Al_2O_3-SnO_2 system in a wide range of concentration of SnO_2 (19 to 81%) satisfactory for the firing end of a spark plug insulator.

Meredith and Schwartzwalder devised a process for forming a low-tension spark plug which included preforming a semiconductor composition around the center electrode, assembling an outer electrode about the preform, positioning the electrodes for a predetermined gap between their ends. The assembly is heated and pressure applied to compress the semiconducting preform so as to cause good adherence to the electrodes and to form a good heat-conducting path between them. Schurecht (1962) produced a semiconducting body by firing a mixture of 5 to 80% copper metal powder and 95 to 20% alumina in an oxidizing atmosphere at 1290 to 1485°C for a time equivalent to cone 10 to cone 18. Yenni and Runck (1961) sprayed consecutive layers of a refractory electrode metal, a refractory insulating material, and a refractory electrode metal onto the end region of a base member. An end portion of the coatings was ground away to provide electrode surfaces.

Norin and Magneli (1960) showed the presence of new phases in addition to $AlNbO_4$ in the system Nb-O, having the approximate formula $NbO_{2.40}$ to $NbO_{2.48}$, and in the monoclinic system. Somers (1963) claimed an insulator body prepared from alumina containing from 0.9 to 1.5% Nb_2O_5 with up to 1% by weight of other fluxing oxides (MgO, kaolin, and talc), having such a smooth surface that glazing the insulator could be circumvented. A 2% wax emulsion in water provided a temporary binder for bisque firing at about 1100°C, with final firing at about 1430 to 1590°C for 2 hours.

Sifre (1963) prepared an insulator body by adding from 0.1 to 1.0% lanthana to alumina (99% pure) by pressure sintering at 1600 to 1700°C to a density of about 3.85 g/ml. The mechanical and electrical properties are the same as for a lanthana-free alumina body, but a sintering temperature above 1700°C would otherwise be required.

Zaionts (1958) described the preparation of spark plug insulators for automobile engines in Czechoslovakia from the ingredients: fused corundum, Bayer alumina, kaolin, flint, limestone, magnesia, sillimanite, and prepared glazes. The body contains 92% nonplastics and 8% kaolin as the bond. The materials are wet ball-milled, filter-pressed, dried, sieved, remoistened (12 to 13% H_2O), and aged for 14 days before forming. The

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formed insulators are fired at about 1715°C on a 14-hr schedule. The glazing is done at 1300°C, and the insulators are tested at 12 to 15 kv. The tensile strength averages 10,700 psi, and effective breakdown voltage about 18.7 kv/mm. The specific resistance at 600°C was claimed to be (1.37 to 1.75) X 10^7 ohm-cm.

Solomin (1959) described two types of spark plug compositions used in the Soviet Union, ground mixtures of magnesium and iron silicates or of alumina and alkaline earth oxides. From 5 to 10%, free or chemically combined iron oxides, is added to the starting mixture.

Jeffery (1940) developed a glaze spray suitable for applying to isostatically formed alumina insulator bodies. Fisher and Twells (1957) described the use of feldspathic glazes with the alkaline earth group composed of alkalies from high potash feldspars, augmented, if needed, by small amounts of potash frits. The area of best glazes was centered around 1.0 RO, 1.5 Al_2O_3, and 15.0 SiO_2 and 1.0 RO, 1.75 Al_2O_3, and 15.0 SiO_2 for one-fire and two-fire glazing, respectively. RO represents alkali oxide.

19-2 ELECTRON TUBE ELEMENTS

Henry (1958) pointed out the differences between electronic ceramics and ordinary ceramics with reference to vitrification, texture, polarization, purity, etc. Spencer and Turner (1958) drew attention to the electrical properties and applications of high-alumina ceramics in industry. Dressler (1964) described the development from electrical whiteware containing alkalies, through steatite and forsterite to alumina and beryllia. The better mechanical and thermal characteristics are particularly important for microwave engineering and for sealing to metal parts with suitable coefficients of expansion.

An early electronic use of alumina was as the cathode insulation in ac electron tubes. This component serves to insulate the tungsten or tungsten alloy resistance heater from the tube circuits, stabilizes the electron emission, and eliminates the ac hum. Leached ground Bayer alumina, or preferably fused alumina, was found satisfactory (Radio Corporation of America, 1941). The wire, coated with a suspension of alumina (maximum impurities 0.5%) in an organic binder (nitrocellulose) was heated at about 1800°C in an atmosphere of hydrogen containing water vapor (saturated at 50 to 55°C). LaRocque described a similar treatment in 1959. Coppola et al. (North American Phillips) prepared a thermionic dispenser cathode which comprised mixing about 90% of a powdered fused mixture of at least 60% alkaline earth oxide, and the remainder aluminum oxide. The mixture was fired at 1650 to 1750°C. Rettner et al.

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presented data on the emission and evaporation characteristics of a porous tungsten cathode impregnated with 5BaO·2Al₂O₃. Active barium was generated by the reaction:

$$2/3\ Ba_3Al_2O_6 + 1/3\ W = 1/3\ BaWO_4 + 2/3\ BaAl_2O_3 + Ba$$
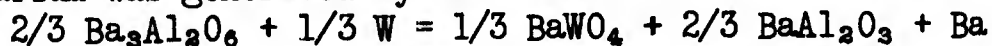
The barium is transported through partly clogged pores. Yamamoto et al. (1953) described methods for refining fused alumina of the soda content present as beta alumina. Four methods of removal were tried: (1) dissolution of the alkali by acid, (2) decomposition by heating at high temperature, (3) separation by heavy liquid, and (4) separation by crushing to fine grains. The last method was the most effective. To increase the heat radiation from the cathode coating, Masuch added 1 to 2% Cr_2O_3, TiO_2, or V_2O_5, or 0.01 to 0.1% Fe_2O_3 or Co_2O_3 to the alumina powder. The insulating layer can be applied by dipping or spraying, or by electrophoresis from suspensions (1 to 35 microns particle size). The dielectric strength of fused alumina cathodes was independent of temperature below 1050°C, but markedly influenced at higher temperatures. Michaelson (1953) showed the suitability of alumina for high-temperature vacuum service in terms of the dissociation pressures. Shalabutov measured the volt-ampere characteristics of the leakage currents of an ac voltage, applied across the heater and its cathode, to determine that the coatings were ionic in nature. The temperature of the heater controlled the polarization of the coating and modified the dynamic effects of the leakage current.

German (Telefunken) ceramic tubes had been in service during World War II, and had been critically analyzed in this country in a number of study contracts issued by the Armed Services (Kohl and Rice, 1958). The main advantages that the ceramic envelope provided was increased ruggedness, resistance to vibration, the ability to outgas at 600 to 700°C rather than at 350 to 450°C for glass envelopes, and a longer vacuum life.

Coykendall (1954) discussed the development of an all-ceramic annular radio tube by the Machlett Laboratories. The tube was capable of operating through a frequency range previously covered by several narrower range magnetrons. The tube was designed as a UHF power triode with a tunable frequency range of 30 to 2000 Mc and a useful power output of 200 watts at the top frequency and up to 700 watts at the lower. Brand et al. (1954) investigated zirconium silicate and magnesium silicate as ceramic sealing materials, but Mn-Mo, MoO_3, and TiH_2 were the favored methods (Navias, 1954).

Sorg (Eitel-McCullough, Incorporated) in 1956 obtained patents on an electron tube constructed of a cylindrical sintered alumina envelope joined to the end members by metallic bonds which also provided the lead-in conductors for

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the anode, grids and cathode, which were arrayed on disk-shaped members appropriately interposed in the correct arrangement. McCullough and Williams (1959) obtained a patent on a stacked ceramic type. Mayer (1962) described cold cathodes for vacuum tubes consisting of the separate oxides of Al, Be, B, and mixtures of them. Bickford and Smith (1959) proposed a semicrystalline composition for electron tube envelopes operating above 700°C composed of 90% Al_2O_3 (-500 mesh, maximum Na_2O 0.05%) and 10% glass frit (60% SiO_2, 14% Al_2O_3, 16% CaO, and 10% BaO), fired at 1625°C. Claimed properties were: coef. of expansion 6.44 X 10^{-6}, flexural strength 42,000 psi, dielectric constant at 25°C 7.5 and at 500°C 8.2, loss tangent at 25°C 0.0003 and at 500°C 0.006, and loss factor at 25°C 0.002 and at 500°C 0.046.

Gallet (1956, 1957) tabulated the characteristics of 50%, 66%, and 95% Al_2O_3 compositions suitable for electron tube construction. Porous ceramic parts were found to be suitable for hot electrode supports because of their low thermal conductivity and ease of release of gases during manufacture. R. Williams (1954) of American Lava Corporation described the production of ceramic components for electron tubes. The majority of insulators used as vacuum tube envelopes are cylindrical, many designs can be machined from extruded stock. Diameters up to 8.5 inches maximum were readily available, with wall thicknesses about 0.1 the outside diameter for the most economical production. Washers, disks, and intricate designs (not exceeding 1.5 inches in thickness are produced normally by wet or dry pressing. Isostatic forming, except for spark plugs, had not received much attention by ceramic manufacturers previously.

By 1958 electron tubes had developed to a state of operation at temperatures as high as 500°C, and at high levels of shock and vibration in nuclear radiation. Some suppliers of electronic ceramics include: American Lava Corporation, Centralab Division of Globe Union, Coors Porcelain Company, Diamonite Products, Frenchtown, Raytheon, Minneapolis-Honeywell, Corning Glass Works, American Feldmuehle Corporation, U. S. Stoneware, Western Gold and Platinum Company (Wesgo), Royal Worcester, Alite Division (U.S.Stoneware), and the Carborundum Co.

Of the various electronic effects in tubes, the photo-electric generation of secondary electrons and the voltage breakdown are influenced by the type of ceramic. The ratio of secondary electrons generated to primary exciting electrons (d) is a maximum of 1.5 to 4.8 at a primary electron energy of 350 to 1300 ev. The voltage breakdown falls into three classes: (1) across the vacuum gap, (2) within the dielectric material, and (3) along the surface. Kohl stated that the breakdown across the gap was independent of temperature to about 1200°C. The volume resistivity at 500°C of sintered alumina (99%) was

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about 10^{10} to 10^{11}, and of sintered alumina (75%) about 10^9. Additional references of significance include: Whitehead (1951), Pomerantz (1946), Navias (1954), Jacobs (1946), F. J. Norton (1957), and P. D. Johnson (1950).

J. D. Cronin (1960) investigated the adaptation of ceramic tube types at high temperatures using an alumina ceramic. Reed (1962) made heat treatment studies on high-alumina ceramics. Wisely (1962), and Moulson and Popper (1963) sought to extend the range of materials available for electron tube envelopes and windows of tubes. Beryllia was considered best for windows, but manufacturing costs were high. Alumina is widely used, and the higher the Al_2O_3 content, the more generally suitable are the properties. In 1961, Varian Associates used mainly high-alumina ceramic parts in microwave tubes; 70% of the high-temperature tubes used ceramic windows and 95% of the cathode types were ceramic (Ref. Anon. Trip to Varian).

Hursh (1949) described the preparation of a ceramic vacuum tube for use in a betatron. The tube was toroidal in form with two tubular arms to which glass connections were fused for the sealed-in electrical leads under high vacuum.

19-3 ALUMINA PORCELAIN INSULATION

From a practical standpoint, ceramic electrical insulation has several advantages in comparison with competitive organic (plastic) dielectrics. Among these are superior electrical properties, higher mechanical strength and absence of deformation or creep at ordinary temperatures, a greater resistance to changes in the surrounding environment, and impervious seals with metals. The flashing of plastic insulators is also likely to leave highly conductive carbonaceous leakage paths. On the other hand, the ceramic insulators cannot be formed as simply or as precisely as the plastics.

A review of ceramic materials for high-frequency insulation in 1937 showed no data up to that time on high-alumina compositions (Thurnauer). With recognition of the superior high-frequency properties of polycrystalline alumina, the availability of suitable grades of Bayer alumina, and the development of practical, economic base compositions and suitable glazes, a rapid increase in the use of alumina in this application has taken place in recent years.

Low-alumina electrical porcelains have been mentioned in Section 8-1. This is a field in which calcined Bayer alumina of low and moderate soda content has been substituted for flint in compositions containing clays and feldspar or preferably, nepheline syenite. The alumina addition, in concentration of 40 to 60% of the composition, is contemplated for high-tension

insulation in the long-distance transmission of electric power. The range of alumina additions extends beyond 85% Al_2O_3, however.

Many applications exist, as for example, bushings for transformers, and cable spacers (PLM Unimold, Diamonite). These latter serve to hold the geometry of high-tension wires rigidly, and to support the cable from the messenger, for line loads to 34.5 kv.

All such applications of alumina conform with the older conventional insulators in carrying a very good glaze, adapted to the alumina composition.

19-4 RESISTORS AND SEMICONDUCTORS

Alumina is used as the nonconducting base or support for semiconducting coatings, or as a homogeneously mixed composition with conducting materials to allow various degrees of resistivity to the flow of electricity. The theoretical exposition of the subject has been treated by Hannay (1959). Resistors of the first type consisting of cylinders of sintered alumina with a layer of semiconducting carbon or metal deposited in several ways, and having low resistance terminals on each end, have served as noninductive resistors in electronic and other applications. In the second type, the alumina may or may not contribute to the electrical conductivity (at ordinary temperatures) depending on whether it has reacted to form new compounds. Otherwise the conductivity is by bridging of the conductive component.

Ridgway (1941) described an electrical resistor formed as a shaped, self-bonded, coherent, dense, continuous, monolithic, prefused, crystalline structure, having alumina as the major phase intergrown with a phase of crystals of essentially titanium dioxide and a lower oxide, which formed an electrically conductive refractory body. Palumbo (1949) impregnated a porous refractory alumina composition with carbon, deposited from a hydrocarbon gas at temperatures between 800 and 1400°C. Verwey and van Bruggen prepared a resistor having a negative coefficient of electrical resistance, by sintering a mass of mixed crystals of FeO, Fe_2O_3, MgO, and Al_2O_3 in the ratio to form spinel, with less than 50 mol. % of iron oxide in spinel form (Fe_3O_4), the sintered mass having a uniform spinel phase which is less than supersaturated with a second phase at 500°C. Heath (1962) produced a resistor by mixing 50 to 80% silicon carbide, 5 to 35% aluminum phosphate, aluminum oxide and reactive P_2O_5, and 0.5 to 10% flux (stannic oxide), pressing to a form, and firing it at 1200 to 1300°C. Navias (1958) dispersed tungsten, molybdenum, or mixtures of the two as a powder in the alumina, and fired in a hydrogen atmosphere, to obtain a resistor with a positive coefficient of resistivity. Huffadine and

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Sanders mixed molybdenum disilicide with the alumina, but relied on 0.5 to 3.0% elemental carbon to provide the electrical conductivity by bridging the molybdenum disilicide particles.

Challande, Hantel, and Montgomery (1962) observed the phenomenon of the acquisition of electrical charge on crystals of alumina by friction with a metal. Wisely (1957), Anon (ref. Oxide Thermoelectric Materials), and W. A. Miller (1956) investigated thermally sensitive conductors, such as $(Al_2O_3)_x$ $(ZnO)_{100-x}$, alkali-aluminum silicates, and porous sintered alumina containing aluminum metal diffused through the pores at a sintering temperature above 1450°C in a nonoxidizing atmosphere.

Methods of developing an electric spark by impact on certain crystalline compositions of piezoelectric characteristics, or by discharge of a capacitor through a low resistance, attracted attention for several applications, including the use as a substitute for present sparking equipment in combustion engines. Sheheen and Mooney (1958) invented such a device, using aluminum oxide impregnated with a semiconducting oxide. A first coating on the body is made up of 86% CuO and 14% CaO, fired at about 1430°C, oxidizing. A second coat containing 86% CuO and 14% $CaCrO_4$ is fired at 1120 to 1290°C. Counts et al. (General Motors) patented semiconductor compositions containing TiO_2, SnO_2, Ta_2O_5 and MoO_3 in which alumina is a component. Harris (Bendix Aviation Corporation) prepared a spark-gap semiconductor containing alumina, tricalcium pentaluminate and the oxides of cobalt and manganese.

Terry (1957) discussed the use of ceramic materials in electric motors and transformers. These applications include coatings, castable refractories, cements, ceramic encapsulants, and sheet insulation. Aluminum oxide anodic coating on aluminum wire, aluminum oxide filler in transformers, and filler in encapsulating plastic are examples of these applications (Walton and Harris, 1958; Fischer, Stone, and McGowan, 1963).

Folweiler (1962) showed that individual ceramic parts for electrical insulation purposes can be joined by filling the surfaces to be joined together with a powder of the same composition and baking under pressure for about 10 minutes at above 1600°C, or for about 100 minutes at 1700°C for a vacuum-tight joint, preferably heated in an inert gas atmosphere.

Stringfellow (1958) composed a ceramic interrupter arc chute having several ceramic arcing plates of low coefficient of thermal expansion and high thermal shock resistance after repeated circuit interruptions. The plates are supported in an interleaved, spaced-apart relation, so that an arc must pass through a stack of the plates. The composition is essentially

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5 to 13 wt % MgO, 37 to 57% Al_2O_3 (Alcoa Alumina A-10), and
38 to 50% SiO_2 and containing more than 50% cordierite crystals. The firing temperature is in the range 1260 to 1480°C.

Brunetti and Khouri (1946) described the printed electronic circuits for generator-powered, radio proximity fuses for the U. S. Army's mortar shells. The wiring and resistor components were printed on a steatite surface. Printed circuits on alumina wafers have been developed. Hannahs and Stein (1952) described the types of printed circuits that use ceramic and plastic bases.

20-1 CALCIUM ALUMINATE CEMENT

Alumina is present in portland cements in relatively low amount. In the calcium aluminate cements it is a major constituent, however, and both its preparation and applications are of ceramic interest. Its presence in slags, its hydration reactions, and its preparation in the Pedersen furnace process for alumina have been mentioned in Sections 3-2, and 12-5. It is designated as aluminous cement, high-alumina cement, and calcium aluminate cement, the last probably being the most acceptable. The major production of calcium aluminate cement is an impure product, generally prepared from bauxite, mainly European grades, and limestone, selected to hold the silica contents in the fired clinker within about 6%. High iron oxide content, about 20 to 30% of European bauxites, contributes little to the hydraulic strength, but acts as a flux during fusion and modifies the setting properties. It provides metallic iron as a by-product, with consequent lowering of the content in the cement, in reduction processes. Titanium compounds, usually not over 3.5% contribute no cementing power, and magnesia, the remaining impurity contributed by the limestone in appreciable amounts, causes a marked decline in strength of the cement, when present in amounts beyond 1%.

A relatively small, but increasing amount of very high purity cement is made from Bayer alumina and high-grade limestone, and containing from 70 to 80% Al_2O_3, less than 0.5% Fe_2O_3, and lesser amounts of SiO_2 and TiO_2. It is intended mainly for refractory applications to as high as 1800°C under some conditions, but is also receiving attention in other applications where refractoriness is incidental.

Typical commercial cements are identified as follows: Lumnite (Universal Atlas Division, U. S. Steel Corporation). The raw materials are high-iron, high-silica bauxite and limestone, melted in a rotary kiln and quenched in water to cool and granulate. This is ground with small amounts of gypsum, and a retarder/plasticizer is added.

LaFarge Ciment Fondu (England). French or Greek bauxite and limestone are melted in an L-shaped reverberatory furnace, cooled on a pan conveyor, and ground without further addition.

Trade names, not well known in the United States, include Fundido Electroland (Spain), Alcement Lafarge (Scandinavia), Fondu Lafarge (France), and Lightning (England).

In an intermediate range of purity are classed the following:

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Refcon (Universal Atlas), total Fe_2O_3 about 1.5%, SiO_2 5.5%.

Rolandshutte (Metallhüttenwerke Lübeck AG, Germany). Bauxite, limestone, coke and iron scrap are melted under reducing conditions in metallurgical blast furnaces, the molten slag is poured from ladles into a shallow pit to cool in sheets, and is then ground. Iron is also a tapped product from the operation. The iron content of the cement is low (about 1.5%), but it is mainly present as ferrous oxide or as relatively, coarse iron particles, a significant factor with respect to carbon monoxide disintegration.

High-purity white cements, available commercially, are represented by Secar 250 (Soc. Anon. SECAR, Paris) and Alcoa CA-25 (Aluminum Company of America Product Data, Calcium Aluminate Cement CA-25, January 1963). Babcock and Wilcox produces complete castables, called Kaocast (Norton and Duplin, 1950). Several refractories manufacturers prepare calcium aluminate cements sporadically.

Some data obtained on typical commercial samples of calcium aluminate cements are shown in Table 15.

Modifications of the raw materials entering into high alumina cement production have been made, primarily to increase the strength in the range of weakness of castables around 800°C, in which the hydraulic bond is largely destroyed and a ceramic bond has not developed strongly. An example is the addition of topaz to the raw mix (Kocher, Atlas Lumnite).

Schneider and Mong (1958) determined the strengths of castables of six groups of laboratory-prepared castables using domestic calcium aluminate cements. In general, the modulus of elasticity dropped remarkably for the initial heating at 200°C, indicating a substantial loss in hydraulic bonding strength. Castables initially heated at 1050°C, retained about the same strength throughout the range of temperature as the minimum measured at 1050°C. Specimens heated at 1300°C, however, recovered a substantial amount of the strength lost at 20(c) to 300°C, indicating the development of a ceramic bond. The strength was substantially retained when measured at 1000°C.

Sainte-Claire Deville probably was the first to be aware of the hydraulic properties of calcium aluminate and its use as a binder for refractories, through his use of equal amounts of powdered alumina and limestone which he wet-mixed to form crucibles for high-temperature investigations. A subsequent search for a hydraulic cement which would not disintegrate in sea water and in contact with sulfates led to the development of the Lafarge "Ciment Fondu."

Table 15
Properties of Calcium Aluminate Cements

Analysis	High-Purity Cements		Intermediate Purity Cements		Low Purity Cement
Total Al$_2$O$_3$	80.0	74.0	53.2	66.6	41.0
Total CaO	17.8	24.0	35.0	23.0	35.2
Total Fe$_2$O$_3$	0.4	0.3	1.5	0.7	10.0
Total SiO$_2$	0.1	0.2	5.7	4.1	7.9
Total MgO	0.2	0.2	0.5	0.5	1.6
Sp.G. g/ml	3.35	3.00	3.00	3.04	3.11
PCE	34-35	26	-	15-16	14

Properties in Alumina-Silica Castable (19.4% cement)

Casting water (%)	9.5	12.0	12.0	12.0	12.0
Flexural strength (psi)					
Cured	970	800	770	600	300
Dried	1190	1100	1020	750	350
Fired	1200	350	550	300	200

Properties in Sintered Alumina Castable (15% cement)

Casting water (%)	10.0	12.8	12.7	15.5	12.7
Flexural strength (psi)					
Cured	830	445	315	220	495
Dried	940	545	595	255	570
Fired	1700	395	395	230	375

Solacolu placed the most favorable compositions on the line from CaO·Al$_2$O$_3$ to the invariant point 2CaO·Al$_2$O$_3$·SiO$_2$-CaO·Al$_2$O$_3$-2CaO·SiO$_2$ on the triaxial diagram. From the standpoint of refractoriness, silica-free compositions would be preferred. The commercial cements are mainly composed of monocalcium aluminate (CaO·Al$_2$O$_3$), but 12CaO·7Al$_2$O$_3$ and CaO·2Al$_2$O$_3$ are usually present. The cement composition acquires faster setting properties with increasing CaO content beyond CaO·Al$_2$O$_3$, and slower setting properties with increasing Al$_2$O$_3$ content of the cement. This is not indicated by the cement formulas, however, because the Al$_2$O$_3$ is not always combined as calcium aluminate. The refractoriness of the cement increases with increasing alumina content. Pole and Moore (1946) fused compositions conforming with 3CaO·5Al$_2$O$_3$ and obtained good hydraulic bonding and a refractoriness of 1495°C for the neat cement. A mortar prepared with one part cement to 3 parts crushed firebrick bent at cone 30 (1650°C). Gitzen, Hart, and MacZura (1957) prepared cements from high-purity Bayer sources and obtained refractoriness to cone 34 (1760°C) for a balanced composition conforming to the empirical formula CaO·2.5Al$_2$O$_3$, in which the predominating bonding phases were CaO·Al$_2$O$_3$ and 12CaO·7Al$_2$O$_3$. The resistance to attack by sulfur acids, a normal, controllable setting time, the rapid hardening of the hydraulic bond (substantially complete within a

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few days), and the retention of high strength after heating at elevated temperatures are the main properties of the cement.

Lehmann and Mitusch (1959, 54 references) and Robson (1962, 589 references) have provided excellent coverage of the manufacture, properties, applications, and analysis of the refractory cements and the mortars and concretes prepared from them.

The scope of application of calcium aluminate cements is so large that only general uses and a few examples can be cited in the following list. Some applications have been mentioned in other sections.

1. Neat cement and mortars

The neat cements are used to seal the suspension hardware of power line insulators and in sealing the center wire of sparkplugs. The porcelain components of the insulators are assembled with mortars of the cement and ground porcelain. It is used to seal the sidewalls of diamond drill borings and oil holes. Casting of the neat cement and mortars, with various ingredients to impart texture or color, against a polished surface imparts gloss to the surface. This has been used to simulate various effects in architectural panels.

2. Nonrefractory applications of mortars and concretes

These applications are dependent upon the ability of the installation to be ready for service within 24 hours of placing, which is the main consideration for their use instead of portland cement. They cover such applications as bridge repairs, paving or repair of busy industrial, business, or military locations, the pouring of piers for machinery, the construction or repair of sea equipment between tides, the sealing of caissons, concreting in mines (Robson). Where forms are used to prepare precast sections, the possibility of faster output per mold enables the more economical use of mold equipment or time.

Precast or driven piles, in diameters seldom greater than 2 ft, were recommended for supporting loads in sulfated ground. They were driven after aging for periods from one day to several years, the essential requirement being to strip the molds within a few hours after casting and to keep the piles wet to prevent overheating. Prestressed beams, lintels, and purlins can be fabricated easier than when using rapid-hardening portland cements.

Calcium aluminate cement is used to make concrete pipes for sewers in acid environments or for carrying acid effluents, in brick jointing in railway tunnels, low-temperature brick flues

and stacks. It has been suggested for radiation shielding at high temperatures. The use of the hydrated additive colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), in the castable for fast-neutron shielding was discussed by Henrie.

Calcium aluminate cement can be pelletized, nodulized, or cast into different granular sizes. Its surface readily fixes metal salts, as for example, silver, of use in catalyzing organic oxidations.

3. Refractory calcium aluminate concretes

Concretes in a wide range of refractoriness are prepared both from the standard calcium aluminate cements and the high-purity white calcium aluminate cements, Secar and Alcoa CA-25. Various types of aggregate are available. Refractory concrete is being increasingly used for kilns, furnaces, coke quenching floors, retort settings, charge-hole blocks, flues, furnace doors, dampers, and general repairs (A. E. Williams, 1951). The concretes prepared from the Lumnite-type cement with chrome ore, magnesia, or dense alumina are stable to at least 1600°C, and those with more common aggregates to about 1300°C. The advantages are good refractoriness, a low thermal conductivity, readiness for use within 24 hours, the facility of casting in any size and shape, trivial shrinkage upon drying, and no necessity for prefiring before placing in service, generally. The same advantages apply to the white pure cement, and in the higher range of refractoriness. Shapland and Livovich (1964) showed a PCE cone of about 13 (1350°C) for the lowest purity commercial cement, about PCE 15 to 16 (1410 to 1450°C) for the intermediate purity type, and cone 34 (1760°C) for the pure calcium aluminate. Robson (page 196) listed the maximum hot-face temperatures allowable for concretes containing different cements and aggregates. They varied from only 250 to 300°C for silica gravel and ordinary calcium aluminate cement to about 1650°C for high-purity cement with firebrick grog (60% Al_2O_3), and to about 1800°C with high-purity cement and fused alumina or tabular alumina. Other aggregates used with the cement include: traprock, pyrophyllite, pumice, magnesite, chromite-magnesite, zirconia, silicon carbide, and the foamed or exfoliated grogs such as vermiculite, perlite, celite, etc. In general, the ordinary cement concretes have poorer refractoriness than the high-purity cement concretes by about 100 to 300°C with increasing temperature. The refractoriness of the combination of cement and aggregate may exceed that of the cement. For example, the overall purity of a castable containing 15% cement and 85% tabular alumina may be over 96% Al_2O_3, thus raising the refractory level by 50 to 70°C into a region above 1800°C.

The concretes may be poured, rammed, or as is increasingly the vogue, gunned (Velikin, 1959; Cook, Cook, and King, 1963,

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1964). Gunned specimens set hotter up to 90°C and faster than their cast counterparts. Gunned linings showed no decreased strength in the temperature region 800 to 1100°C (as had been previously reported). Changes in the gunning procedure markedly affected the properties of the linings. This technique, applied to calcium aluminate concretes, finds increased application in steel-industry and other metallurgical furnace operations. The method is adapted to repair of deteriorated linings.

Livovich (1961) compared portland cement with calcium aluminate cements in cyclic heating tests on castables. Only the specimens prepared with calcium aluminate cements (Lumnite and Refcon) were stable. Cracking and expansion of the portland cement types was attributed to hydration of lime formed in their thermal decomposition. Rengade claimed that mixtures of portland cement and calcium aluminate cement provide quick set, are nearly as strong as portland cement, and are not disintegrated by sea water (contrary to Dorsch).

Lafuma (1954) added expansive cement (calcium sulfoaluminate) to portland cement to counteract its drying shrinkage. Okorokov et al. prepared this form by reaction between gypsum and calcium aluminate at 1100 to 1300°C. Tanaka and Watanabe determined the chemical composition and physical properties of a commercial expansive slag. The cement consisted of 65 parts portland cement and 25 parts sulfoaluminate clinker. Armstrong and Whitehurst mixed calcium aluminate slags containing up to 0.4% fluorine with calcined calcium sulfate (anhydrite) to obtain sulfoaluminate cement.

McGrue (1937) recommended high-alumina cements as binders for concretes used in coke ovens and blast furnaces for steel. Recommended aggregates for insulating concretes included slag, Haydite, Sil-O-Cel and vermiculite. Shapland and Livovich (1964) found that castables suitable for service at 1320 to 1540°C in steel production had poor resistance to attack by alkalies, and that castables prepared from only two of five cements tested were resistant to carbon monoxide disintegration. Calcium aluminate castables follow about the same pattern of behavior as firebrick with respect to carbon monoxide attack, except that castables are more likely to have free iron particles present, either as a result of the cement production method (reduction process) or from pickup during grinding of the clinker. The pickup from fused clinker is likely to be much higher than from the sintered high-purity clinkers. Castables prepared from high-purity cements and aggregate have resistance comparable with superduty fireclay brick (Gitzen, Heilich, and Rohr, 1964).

Wygant and Bulkley (1954) found that suitable concretes for lining fluid catalytic cracking vessels contained about 60 wt % of coarse aggregate (8 to 14 mesh) and 15% fine

aggregate (about 50 to 100 mesh). Crowley (1964) claimed that the addition of $CaHPO_4 \cdot nH_2O$ improved high-alumina, high-purity calcium aluminate concretes. Compressive strengths ranging from 14,000 to 20,000 psi were attained on specimens containing 18 wt % cement and 82% tabular alumina, damp-cured for 24 hours and heated at about 540°C.

Feagin (1959) used 3 to 35 wt % calcium aluminate binder in refractory aggregates of periclase, zircon, silica, and kyanite in proportions to provide controlled expansion in the precision casting of metals (about 5.53% linear expansion from room temperature to 1150°C). Kuntzsch and Rabe described the use of "fire concrete" as a substitute for fireclay brick. Cobaugh (1958) described the use of castable refractories in the production of ceramics and glass, Robson (1952) the shaping of supports for electric resistance wires. Refractory concrete was claimed to have higher electrical resistance than the materials of which it was made, its conductivity being about 75% of fireclay brick. Braun (1953) recommended monolithic liners for furnace doors according to a design that eliminates the necessity of providing studs for anchoring or cooling. Tatousek and Peters evaluated the cast refractory for hot-top linings, and claimed that the cast liners were more difficult and costly to install, but their life was longer. Erosion of the cast tops caused excessive metal losses, when lined with "high alumina-silica" aggregate (48% Al_2O_3, 39% SiO_2, 10% CaO). Schwarz and Hempel (1960) successfully replaced chamotte brick walls of tunnel kiln cars with refractory concrete containing about 14 to 17% cement and chamotte granules. Williams (1958) described general metallurgical furnacing equipment in which concretes can be used. The details of methods for support and reinforcing are too voluminous to report in this survey.

Ricker claimed that up to 2.25 wt % of one alkaline earth carbonate added to the cement used in preparing castables increased the concrete strength.

The methods used for curing calcium aluminate concretes have an important effect on the strength. Neville (1958) found that loss of strength always occurs in high-alumina cement concretes that have been moist-cured continuously or intermittently at 25 to 40°C. The loss was associated with the inversion of metastable hexagonal $CaO \cdot Al_2O_3 \cdot 10H_2O$ to cubic $3CaO \cdot Al_2O_3 \cdot 6H_2O$. Budnikov and Kravchenko claimed that these hydration products still may have higher strength than structures composed mainly of the hexagonal calcium aluminates. Schneider (1959) found by X-ray diffraction and DTA that $CaO \cdot Al_2O_3 \cdot 10H_2O$ was the principal phase of hydration at room temperature; $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $Al_2O_3 \cdot 3H_2O$ (gibbsite) were formed as by-products at 50°C, the principal phase being $CaO \cdot Al_2O_3 \cdot xH_2O$, in which x was less than $10H_2O$. At 500 to 600°C, the principal phase dehydrated to $CaO \cdot Al_2O_3$; the by-product $3CaO \cdot Al_2O_3 \cdot 6H_2O$

transformed to CaO and $12CaO \cdot 7Al_2O_3$. Longuet and Tournadre claimed that both $CaO \cdot Al_2O_3$ and $CaO \cdot 3Al_2O_3$ form $3CaO \cdot Al_2O_3 \cdot 6H_2O$ at about 30°C.

Gitzen and Hart (1961) observed that the tendency to explosive spalling by calcium aluminate castables on initial heating could be circumvented by decreasing the cement concentration and increasing the particle coarseness in order to increase the permeability. Control of the ambient curing temperature was a more desirable method, however, that did not sacrifice castable properties. King and Renkey claimed that the addition of up to 1.5% boric acid to the refractory castable produced an explosion-resistant castable.

Tseung and Carruthers (1963), on the basis of an arbitrary selection of size distribution of aggregate in a castable formulation for which a low water/cement ratio (0.5) was found to be optimum, concluded that curing at 75°C for 6 hours immediately after casting gave appreciably stronger castings at all temperatures than 24-hr curing at room temperature. This appeared to refute the conclusion of Gitzen and Hart (1961) that a curing temperature of 90°F (32°C) was optimum for resistance to explosive disruption of a castable containing the same ratio of aggregate (of idealized size distribution) to cement, but of a higher water/cement ratio (0.615). This water/cement ratio was the lowest attainable that would satisfy a practical casting consistency. It appears that the water/cement ratio is a critical factor affecting the optimum curing temperature, particularly when the ratio does not provide sufficient water for complete hydration.

Some confusion between the results of different investigators for the mechanical properties of the castables stems from differences in the early stages of firing the castable. The prolonged duration of steam in the castable in the temperature range between 100 and about 250°C appears to be a deteriorating factor. From this, it would seem to be more effective to dry the castable completely below 70°C (if practical) before firing.

Wygant and Crowley (1964) found that in actual large-scale installations it is necessary to prevent moisture from escaping from the lining during curing. Internal temperature rise did not impair the strength. The application of impermeable membranes (organic resin or asphalt coatings) had been used successfully for 8 years in installing liners.

Tulovskaya and Segalova concluded that at 5°C $CaO \cdot Al_2O_3$ hydrates to aqueous $CaO \cdot Al_2O_3$ and aqueous $2CaO \cdot Al_2O_3$. The aqueous $CaO \cdot Al_2O_3$ then changes to aqueous $2CaO \cdot Al_2O_3$. At higher temperatures both hydrates transformed to $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

Onofrio (1963) subjected castables to a high-frequency electric field (radio frequency) during curing. Crepaz and Raccanelli (1963), on the basis of DTA tests, determined that the products of hydration of calcium aluminate cement are $Al_2O_3 \cdot 3H_2O$, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, $4CaO \cdot Al_2O_3 \cdot 19H_2O$, $CaO \cdot Al_2O_3 \cdot 10H_2O$, and $2CaO \cdot Al_2O_3 \cdot 8H_2O$.

Treffner and Williams (1963) observed that fine-crystal, low-burned calcium aluminate cements develop fast heat of hydration. Increasing the Al_2O_3 content of the cement to the limit, $CaO \cdot 2Al_2O_3$, decreased the hydration rate for the same equivalent crystal size. The rate of hydration decreased with increasing impurity of the cement. The optimum castable strength was obtained with crystal sizes not less than 20 microns.

Kimpel (1962) claimed a cement composition containing a mixture of 30 to 40 wt % plaster of paris, 15 to 30% aluminum oxide, and 5 to 10% diatomaceous earth, 1 to 4% ball clay and 20 to 36% water. Weltz (1960) claimed a low-density insulating castable containing 50 wt % fused alumina bubbles, 25% dense alumina (14F and 48F sizes), and 25% calcium aluminate. Mikhailov and Litvinov (1963) found that most glass fibers corrode in lime and cement. A glass of good durability consists of 61.9% SiO_2, 6.1% Al_2O_3, 13.5% CaO, 7.9% Na_2O, 1.0% K_2O, and 8.7% other oxides.

Talaber (1961) claimed that the high alumina cements reach maximum strength after two years, then slowly decline. Resistance in compression is lost faster than in tension. Iron does not affect strength or durability. The underwater durability is superior to that in air. The final products are hydrated alumina and calcium carbonate. Mehta stated that unless this retrogression in the hydraulic strength can be circumvented, the future of calcium aluminate cements in structures intended for long duration is uncertain.

20-2 BARIUM AND STRONTIUM ALUMINATES

Barium aluminate prepared by sintering mixtures of pure alumina and barium carbonate is soluble in water, but more so in dilute alkaline solution (Akiyama et al., 1938). The presence of silica, however, influences the solubility.

Braniski, during the period 1957 to 1961, investigated the possibility of partial or complete replacement of the lime in calcium cements (both silicate and aluminate types). The tests showed the existence of $3SrO \cdot SiO_2$ and $3BaO \cdot SiO_2$. Barium blast-furnace cements, barium slag cements, and barium cements were found to have exceptional resistance to attack by sea water. Barium aluminous cement melted at 1730°C. Owing to the high

density of the barium aluminate cements, good protection against
X-rays and gamma rays was provided, though not to the same
extent as with the barium silicate cements. When BaO is substi-
tuted for CaO in aluminous cements, the products are not hydraulic
but merely water-soluble, air-hardening cements. Braniski and
Ionescu (1960) found that replacing part of the lime by about
3% BaO in raw mixes for barium aluminate cement promoted the
sintering of the clinker and the strength increased by about
10%. Refractory concretes containing various grogs were excep-
tionally resistant to spalling. The refractoriness with corundum
was 1865 to 1900°C, with bauxite 1750 to 1790°C, with clay 1670
to 1690, with chrome-magnesite 1880 to 1960°C, and with magnesia
1920 to 1980°C. The refractoriness of $BaO \cdot Al_2O_3$ is much higher
than that of $CaO \cdot 2Al_2O_3$, and the early strength is extra-
ordinarily high.

Braniski (1961) claimed that the hardening of barium alumi-
nate cement involves the dehydration of the alumina gel re-
leased by hydrolysis, and also the dehydration of the barium
aluminate and silicate present. Crystallization of $3BaO \cdot Al_2O_3 \cdot 6H_2O$ also caused hardening. After heating at 800°C for six
hours, the cold strength of $BaO \cdot Al_2O_3$ cement was reduced by 40%.
It was concluded that barium aluminate cement is the most
suitable binder for basic refractory concretes.

21 ALUMINA IN GLASS, ENAMELS, AND GLAZES

21-1 INTRODUCTION

Alumina enters glass compositions in a variety of ways. R. W. Hopkins mentioned the following sources, mostly native: perlite, sand, aluminum hydrate, bauxite, clay, kyanite group minerals, topaz, cryolite, anorthosite (a feldspathic rock), and blast-furnace slag. Aluminum hydrate probably represents the largest volume of Bayer source material used in the glass industry, but actually several grades of calcined Bayer alumina and ground tabular alumina also enter into glass manufacture, not to mention the alumina used in making the refractories essential to the production of glass. Since the purified Bayer aluminas are valued somewhat higher than the native alumina sources, it is evident that the principal reason for their use is their freedom from certain impurities, as for example, iron oxide. The substitution of Bayer hydrate for feldspar in plate glass batches reduced the iron content from 0.15 to 0.09%, caused the greenish tint to almost disappear, and increased the light by 1.5% to a total transmission of 87.8%/cm thickness (Zaporozhtseva and Gorbai).

The major groups in the glass industry are container glass, flat glass, pressed and blown glass, and glass fibers, and in that order of decreasing value of production. Of these groups, the role of alumina in fibers has been discussed in Section 26. Alumina is a component of nearly all of the remaining types of glass, regardless of the source. About 90% of all glass produced contains at least 2% Al_2O_3. Silica-soda-lime glass, borosilicate glass, and lead glass contain up to 3% Al_2O_3; E-glass for continuous fiber production, about 15%; and hard aluminosilicate glasses for cooking ware and combustion tubes, about 20% (Simpson, 1959; anon Glass, 1964). Within this rather small range of concentration alumina has a marked influence on the properties of the glass.

In accordance with Zachariesen's rules, alumina falls in the class of oxides having an anion to cation ratio of 1.5, hence is considered a glass former having substantially directional, covalent, anion-cation bonding. Each oxygen ion is linked to no more than two atoms of aluminum; the number of oxygens surrounding aluminum must not exceed 4; the oxygen polyhedra share only corners with each other; and at least three corners in each polyhedron must be shared. The arrangement of polyhedra is irregular and hence isotropic. The description of glass networks and some other theories of the glass structure have been presented by Rooksby et al. (crystallite theory); Porai-Koshitz, 1960; Weyl, 1960 (acid-base hypothesis); Stevels; and Appen, 1954 (skeletal-coordination theory). Salmang (1957) gave little attention to the crystallite theory. According to Weyl, the

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glasses are classified by their acidity or alkalinity, based
on the degree of screening of the positive core of the molecules.
Molecules with a well screened positive core have zero acidity;
as the screening becomes less complete, the condition becomes
acidic. Rindone, Day, and Caporali (1960) and Graham and Rindone
(1964) have measured the acidities of glasses containing variable
amounts of alumina, and find an increase in acidity for in-
creasing substitution of Al_2O_3 for SiO_2 in the glass. The
first additions increase acidity, supposedly, by forming AlO_4
tetrahedra which use a part of the nonbridging oxygen ions to
fulfill the coordination requirements. Dietzel and Scholze
(1955) concluded from refractive index measurements that the
aluminum ion in the mullite region of glass in the system
$BeO-Al_2O_3-SiO_2$ is present in both 4-fold and 6-fold coordination,
with the 4-fold coordination increasing with increasing silica
content. Dubrova and Kefeli found that the coordination of
aluminum in glasslike silicates is 4 and 6, based on absorption
spectra.

Appen (1953) and Haray-Szabo correlated the properties of
glasses with changes in the oxygen coordination number. In
silicate glasses, alumina undergoes a change from 6 (corundum)
to 4 (glass). Partial properties of alumina are calculated for
crystalline silicates showing a coordination number of 4 in
albite, nepheline anorthite, and celsian, and a coordination
number of 6 in sillimanite and kyanite. Al^{3+} with a coordina-
tion number of 6 is unlikely in alkaline glass, but the re-
fractive index contribution of Al_2O_3 to glass drops, fused from
the compositions $MgO \cdot Al_2O_3 \cdot 2SiO_2$ and $BeO \cdot Al_2O_3 \cdot 2SiO_2$, is that of
corundum. In sillimanite, one-half of all aluminum atoms have
4-coordination, the other half 6-coordination.

Warburton and Williams (1963) found that the addition of
alumina (whether coarse or fine-ground) to mixtures of lime
and silica lowers the temperature required to yield a glass-
forming liquid. Alumina improves glass with respect to re-
sistance to water and acid. The simplest method of intro-
ducing it is to add it as feldspar; for hard glasses, high
additions are usually introduced as mixtures of hydrated alumi-
na and feldspar in the ratio of 10:1 in German practice (Arnot,
1937).

W. B. Silverman (1939) stated that alumina lowers the
melting temperature of soda-lime-silica glasses when either
wollastonite or tridymite is the primary phase. Silverman
(1940) observed that a wide area of the sodium oxide-dolomite-
lime-silica glass system cannot be devitrified if it contains
up to 6.4% Al_2O_3. Parmelee and Harman (1937) found that
alumina raised the surface tension of molten glasses from about
3.0 dynes/cm at 1200°C for 0% Al_2O_3 to 3.35 dynes/cm for 6%
Al_2O_3. This was confirmed by Okhotin and Bazhbeuk-Melikova (1952).

Barrett and Thomas (1959) correlated the surface tension and density with composition of glasses in the $CaO-Al_2O_3-SiO_2$ system.

Dietzel (1943) noted the phenomenally low expansion coefficients in silica glasses containing aluminum ions. Schweig observed the favorable effect on viscosity and liquidus temperature, and Hlavac (1950) noted that as little as 3% Al_2O_3 improved the viscosity, and liquidus temperature for glass produced by the Fourcault process. The chemical resistance was improved, but even the presence of aluminum ions in 0.5N NaOH solutions inhibited the corrosion rate of 42 types of quartz glass, barium silicate glass, and antimony silicate glass (Molchanov and Prikhed'ko). The electrical conduction of sodium aluminosilicate glasses becomes a minimum for the atomic ratio Al/Na = 1, from which it was concluded that the size of the oxygen shells increases as AlO_4 tetrahedra are introduced into the network. Beyond this limit, aluminum is assumed to go into 6-fold coordination as a network modifier, allowing the coordination shell of the sodium ion to again decrease (Isard). Alumina increased the tensile strength of soda-lime-silicate glasses, even at low concentrations of about 1% (Watkins, 1950). The function of alumina in lead silicate glasses is to facilitate the reduction of the lead (Kitaigorodskii, Mendeleev et al., 1963).

Lacy concluded that aluminum is unlikely to occur as a truly interstitial cation in glasses and melts having a high proportion of basic oxides. Compositions with a molar excess of Al_2O_3 over the basic oxides do not contain AlO_6 groups; rather triclusters are formed in which an oxygen ion is shared between three tetrahedral groups. The properties of glasses support the Zachariasen-Warren theory (Lacy, 1963).

Lyle, Horak, and Sharp (1936) found that 1.5 to 2.5% Al_2O_3 markedly improved the durability of glasses in the $Na_2O-CaO-SiO_2$ system in terms of an expression: Log durability D = a + b log N, in which a and b are constants, and N = % Na_2O + Al_2O_3.

21-2 BOTTLE GLASS

Kotshmid (1959) stated that glass bottles produced on automatic machines initially contained 4% Al_2O_3, which was gradually increased at the expense of SiO_2. The high-alumina glasses have an extended working range and do not require higher melting or fining temperatures (bubble removal). Springer showed that alumina makes both melting and fining easier. W. Koenig (1943) found that green bottle glass melts easier with Al_2O_3 contents as high as 17 to 20%, but a practical limit of 15% is dictated by the sensitivity to acids. Brown bottle

glasses containing 3 to 4% pyrolusite ($MnO_2 \cdot nH_2O$) are readily melted with 15 to 16% Al_2O_3. The tough and lustrous surface of alumina bottle glass is affected less by mold imperfections.

References to glass containers and alumina in glass containers include Kuehl, Shaw, and Anon, Container Glass, 1940-1943.

21-3 DEVITRIFIED GLASSES CONTAINING ALUMINA

The devitrified glasses have been called glass-ceramics (USA), vitroceramics (Europe), and sitals (USSR). Emrich (1964) referred to them as devitrified ceramics. In general, they consist of more or less complete crystallization of pre-formed glass articles by induced and controlled nucleation and crystallization. Devitrification has usually been undesirable in glass because of the adverse effect on transparency and other properties, but nucleation has been used for many years to produce ruby glass, opal glass, and lately photosensitive glasses. The present interest in devitrified glasses stems from the ability to produce polycrystalline ceramics of almost ideal fineness of particles, randomly oriented, and homogeneously distributed, and without the defects of porosity and gross crystal growth, inherent in the conventional sintered polycrystalline ceramics.

Albrecht (1954) described alumina-rich silicate glasses that spontaneously crystallized at proper temperatures to form hard substances. Schneider (1926) discussed the use of aluminum hydroxide for the manufacture of opaque glass. Blair, Silverman, and Hicks detected the crystallites in opal glass as low-temperature quartz with traces of low-temperature cristobalite. W. B. Silverman (1939) discussed the devitrification of soda-lime-silica glasses, and Swift (1946) the effect of alumina on the rate of crystal growth. Zschacke claimed that Al_2O_3 and B_2O_3 actually reduce opacification. Alumina does not produce opacity unless fluorine is present. Okhotin and Ushanova (1959) found that additions of fluorine to a high-alumina, alkali-free, 3-component glass (23.3% CaO, 14.7% Al_2O_3, 62% SiO_2) and a 4-component glass (15.4% CaO, 4.2% MgO, 18.5% Al_2O_3, 61.9% SiO_2) reduced the viscosity. Callow (1952) found that the substitution of zinc oxide (up to 6%) was also effective with fluorine. Lungu and Popescu-Has (1958) developed homogeneous crystallization of special glass batches by addition of fluorides to the melt, and by careful reheating. Mechanical strengths higher than those of the original glasses were obtained, but the recrystallization temperature range was above

the softening point of the glasses.

Nagaoka and Hara (1962) investigated the submicroscopic crystallization from $Li_2O-Al_2O_3-SiO_2$ glasses by additions of P_2O_5. With increasing Al_2O_3 (1 to 5%) the number of phosphate crystallites increased and the crystallized $Li_2O \cdot 2SiO_2$ apparently decreased. Cristobalite, quartz, spodumene-quartz solid solution, and β-spodumene were also crystallized products.

Stookey (1960, 1961) prepared crystalline or semi-crystalline ceramics of high mechanical strength and good dielectric properties by heat-treating glasses containing from 2 to 20% TiO_2 as a nucleator, and at least 50% crystallizable glass-making ingredients consisting of SiO_2, Al_2O_3, and one or more of the oxides of Li, Be, Mg, Ca, Zn, Sr, Cd, Ba, Pb, Mn, Fe, Co, Ge, B, P, and Ni. An original glass composition of 45.5% SiO_2, 30.5% Al_2O_3, 11.5% TiO_2 and 12.5% MgO had a coefficient of expansion of 37.5 X $10^{-7}/°C$ and a density of 2.75 g/ml. After reheating under controlled conditions at 870°C and finally at 1345°C (deformation temperature 1370°C), crystallization of phases other than TiO_2 occurred. The product had a coefficient of expansion of 14.1 X 10^{-7}, a density of 2.62 g/ml, and a flexural strength of 37,500 psi. The claimed strength was not exceptional in comparison with polycrystalline alumina, but there was an advantage in lower density for air-borne ceramics. This is the basis of the trademarked Pyroceram 9606, announced by Corning Glass Works early in 1957. It can be formed by conventional methods in the glass industry: blowing, pressing, and drawing. It has been tested in radomes for guided missiles, and in electrical insulation. Kitaigorodskii and Bondarev (1962) developed similar materials from slags, various sital compositions, for which a softening temperature as high as 1500°C has been claimed. These products have apparently been used mainly in construction.

The devitrified products from compositions containing MgO had large amounts of α-cordierite; those with CaO had anorthite; those with BeO yielded beryl; compositions with ZnO contained either zinc spinel or willemite (Hinz and coworkers).

King and Stookey (1960) developed a relatively weaker devitrified glass but of very low coefficient of expansion (10 X $10^{-7}/°C$ between 0 and 300°C) from a composition containing 71 wt % SiO_2, 2.5% Li_2O, 18% Al_2O_3, 4.5% TiO_2, 3% MgO, and 1% ZnO. A semicrystalline body having an average flexural strength of 21,000 psi was claimed. The devitrification temperature was 1150 to 1200°C. Compositions of this type are the basis of Pyroceram 9608. Okhotin and Ushanova investigated

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fluoride-crystallization from high-alumina glasses; Brown and Kistler examined the devitrification of high-SiO_2 glasses in the system Al_2O_3-SiO_2; and Mariya the devitrification of phosphate glasses. Devitrification to cristobalite was found to proceed more rapidly in the Al_2O_3-SiO_2 system than in the ultra-pure silica glasses, but their fluidities (reciprocal viscosities) were lower for the same temperature. The devitrification growth rate, g, was of the zero order, and followed the temperature-dependent expression: $\ln (g/T) = (B/T) + \ln A$, in which A and B are constants and T is the absolute temperature in the range 1561 to 1730°K. Hayami, Ogura, and Tanaka (1960) crystallized hard bodies containing dark green chromia crystallites.

Stookey (1961) developed a new photothermally opacified glass containing 2 to 25 wt % Al_2O_3, and in which the ratio, Al_2O_3/Li_2O, is significant at 1.7:1. Olcott and Stookey (1961) developed a glass body having on its surface a thin semi-crystalline layer (in compression) of the same oxide composition as the glass. The composition contains 65 to 72 parts SiO_2, 4 parts Li_2O, 22.5 to 30 parts Al_2O_3, and at least one crystallization catalyst (TiO_2, B_2O_3, Na_2O, or PbO). The formed body is heated from one to 40 hours at a temperature at which its viscosity is 10^7 to 10^{10} poises, until crystallites of beta-eucryptite form within the surface. The factor of crystal growth being initiated and controlled by surface crystallization and orientation (epitaxy) was investigated by Vogel (1961) and others. Flexural strengths obtained by the Chemcor process of Corning Glass Works, of the order of 100,000 psi, in comparison with 15,000 to 35,000 psi obtained by the older techniques of chill tempering, have opened new opportunities for this type of ceramics. The first product, Centura Ware has remarkable strength in comparison with conventional china. Presumably, the surface condition must be protected by a coating to take scratches and abrasion, otherwise the ware might be expected to suffer the same deterioration as is experienced with other types of tempered glass.

Corning Glass Works (June 1964) has developed a metal-ceramic body obtained by enveloping a silicate glass form in a molten bath of 20 to 35% silicon, the remainder being aluminum, at 900 to 950°C. By diffusion and thermitic reaction, the final form contains 72 to 82% Al_2O_3, 11 to 21% Al, 1 to 3% Si, and Al-Si alloy in the ratio around 27.3 Al-Si:72 Al_2O_3.

The main applications of the Pyrocerams appear to be in cooking utensils.

21-4 BORON GLASSES

Alumina appears in high concentration in at least one type of low-soda, borosilicate glass, Pyrex 1720 (Corning Glass

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Works). A composition containing 58 wt % SiO_2, 19% Al_2O_3, 12% MgO, and 5% B_2O_3 had the following properties: specific gravity 2.53 g/ml, linear coefficient of expansion (0 to 300°C) 0.0000042/°C, softening point 915°C, dielectric constant at 1 mc and 20°C 7.2, and $\log_{10}$ resistance at 250°C 11.4. Similar glasses were developed in Europe, as for example Kavalier glass (Czechoslovakia), described by M. B. Volt (1947). Their applications in chemical equipment, piping for corrosive liquids, and many other applications are well known. Difficulties in the melting of these glasses have been overcome by the use of fused block refractories, as for example, Corhart ZAC (Ishino). Ginsberg discussed Pyrex and Superpyrex types.

Chandappa and Simpson delineated the area of glass formation in the system Na_2O-Al_2O_3-B_2O_3 as the triangular field bounded by the compositions: (1) B_2O_3, (2) 60 mol. % B_2O_3-40 mol. % Na_2O, and (3) 60 mol. % B_2O_3-20 mol. % Na_2O-20 mol. % Al_2O_3. As Al_2O_3 replaced Na_2O, softening temperatures increased, but strain points, annealing points, thermal expansion, density, and refractive index all decreased.

Galant and Appen stated that the addition of alumina to boron-free glasses causes an increase in the index of refraction. It also causes an increase in the presence of up to 5% B_2O_3 in the glass. Beyond 6% Al_2O_3, however, the index decreases. The addition of alumina to glasses containing 11 to 17% B_2O_3 causes a sharp reduction in the index, the variation in index being in the range between 1.4817 and 1.5079. Tamura et al. found that alumina represses the volatility of B_2O_3 from alkaline earth-borate glasses. Danilov and Joffe prepared Uviol type borate glasses (high ultraviolet transmission of Hg wavelength 254 millimicrons) containing either 17.5 or 15% Al_2O_3.

Kitaigorodskii, Keshishyan et al. (1958) recommended glasses in the system BaO-Al_2O_3-B_2O_3-SiO_2 containing up to 30 mol. % Al_2O_3 for electrovacuum processes on the basis of their favorable coefficient of expansion, electrical resistance, and dielectric losses. Bills and Evett (1959) to the contrary, found borosilicate (and other glasses) to be undesirable construction materials in clean-surface experiments and measurements because the glass appears to decompose at temperatures above 350°C, liberating water vapor and decomposition products not readily pumped out of a vacuum system. These so-called Cabal glasses, show a definite 10% increase in the expansion coefficients. The temperature at which this occurs, the softening points, the dc conductivities, and the dielectric constant vary with the composition, suggesting that Abe's screening hypothesis is applicable and that the Cabal glasses segregate into borate and aluminate phases.

Cap (1950) found an anomalous coefficient of expansion

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for glasses in the system Li_2O-Al_2O_3-B_2O_3. Hirayama measured the electrical resistivities of glasses in the aluminoborate system, containing Group II metal oxides, as high as 10^{11} ohm-cm at 450°C, and activation energies ranging from 26 to 42 kcal/mole. The covalent nature of the group IIB aluminoborates was indicated.

21-5 LITHIUM GLASSES, PHOSPHATE GLASSES

Alumina sharply decreases the solubility of the lithium silicates in water (Williams and Simpson). Glasses in the system Li_2O-Al_2O_3-B_2O_3, containing 20 to 70 mol. % Al_2O_3 have expansion coefficients ranging from (63 to 101) X 10^{-7}. By addition of silica to the system, heat-resistant glasses stable against crystallization were obtained having a coefficient of 36.5 X 10^{-7} or less (Bezborodov and Ulazoskii). Tanigawa (1963) applied the low-expansion, thermal shock-resistant, and high-strength lithia-containing glasses as a vitreous bond for natural petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$). The flexural strength was about 8000 to 10,000 psi, and coefficient of linear expansion (5 to 10) X 10^{-7}/°C (40 to 900°C). The bodies withstood repeated cycles of water quenching from 1000°C.

Gelstharp; Takahashi et al.; and Drexler and Schütz prepared glasses in which silica was partially or wholly replaced by aluminum phosphates. The aluminum orthophosphate glasses are extremely corrosive toward tank block materials, and their stability in acid and alkali was found to be poor. Kumar obtained glasses in the system PbO-B_2O_3-$AlPO_4$ and in the system Al_2O_3-B_2O_3-P_2O_5 for good electrical properties were obtained. Syritskaya and Yakubik prepared stable phosphate glasses in the system ZnO-Al_2O_3-P_2O_5.

Borosilicate glass containing from 5 to 15% Al_2O_3 and 7 to 24% P_2O_5 has been converted into porous glass by heat-treating the glass for sufficient time to separate into a silica-rich and a silica-poor phase, and then leaching the glass with water.

21-6 OPTICAL GLASSES

Some examples of the application of alumina to widely different types of optical glass are shown in the following references. Sun and Callear (Eastman Kodak Co.) patented a glass consisting of the compatible fluorides beryllium fluoride 10 to 25 mol. % and aluminum fluoride, the total of the two representing between 40 and 50 mol. %. Sun also claimed a nonborate, nonphosphate, nonsilicate optical glass of which at least 1.5 wt % is BeO, at least 15% is Al_2O_3, and the total of the two oxides is at least 30% of the glass.

Loeffler prepared rare-earth glasses containing 50 wt % La_2O_3, 10% ThO_2, 3.1% BeO, 11.8% Al_2O_3, and 24.9% SiO_2 with a refractive index around 1.75 and a dispersion number (Abbe) about 50. Kreidl (1953) found that small amounts of Al_2O_3 are necessary to prevent devitrification of borosilicate optical glasses which are susceptible to discoloration on irradiation by X-rays, γ-rays, or electrons. Weissenberg and Ungemach added Al_2O_3 to flint glasses to hinder crystallization. Weissenberg and Meinert prepared a glass of about 93.5% TeO_2 and 6.5% Al_2O_3 (10 mol. % Al_2O_3). These glasses with small amounts of added fluorides (LiF, CaF_2, SrF_2, or BaF_2) had exceptionally high indices, 1.833 to 1.944. Elomanov et al. prepared clear glasses of TeO_2 containing up to 10% Al_2O_3, which were quite transparent to infrared transmission.

21-7 GLAZES AND ENAMELS

Alumina is a component of glazes and enamels, satisfying about the same functions as in glass. The properties are modified to compensate for adjustments related to the thinness of the applied layer, as for example volatilization of constituents, reactions with the body, and factors related to the fit of the expansion characteristics to those of the body. Watts (1958) based the control of glazes by the aid of published data on the eutectics in the systems Na_2O-Al_2O_3-SiO_2 and PbO-Al_2O_3-SiO_2. Good glaze compositions, resistant to acid and alkali attack contain about 12% Al_2O_3. The addition of Al_2O_3, CaO, and BaO in place of alkali is beneficial on resistance to attack (Lehmann and Bohme, 1958). Mehmel observed that glazes based on lithium aluminate have a high thermal expansion, while those based on β-eucryptite have a low thermal expansion. Budnikov and Shteinberg (1956) developed a glaze for porcelain with an Al_2O_3 content of about 11 to 29%, and small amounts of ZrO_2, CaO, MgO, Na_2O, and Fe_2O_3, the remainder being SiO_2.

Azarov and Chistova (1958) prepared vitreous compositions for enamels containing 10 to 20 mol. % each of SiO_2 and Al_2O_3, and 40 to 50% P_2O_5. Azarov and Serdyukova appraised the merits of using alumina gel to increase the stability of feldspar suspensions by making them thixotropic. Alumina introduced as feldspar opacifies enamels, but in excess imparts a mat finish (Vielhaber, 1940). Karmaus developed enamels with melting points below 725°C containing 19 to 36% Al_2O_3. An example consisted of $NaH_2PO_4 \cdot H_2O$ 66.3%, $NaNO_3$ 9.9%, H_3BO_3 21.2%, $Al_2O_3 \cdot 3H_2O$ 42.8%, TiO_2 7.8%, smelted at 1300°C. Every (1949) developed superopaque enamels of the ZrO_2 type containing 20 to 25% Al_2O_3. Alumina is necessary to opacify these enamels (Ref. Anon. Zircon needs alumina). Both require cryolite as a flux and as an opacifying agent (Maerker, 1957). Pavlushkin, Zhuralev, and Eitigon (1961) developed a satisfactory glaze for enameling decorative alumina ware, consisting of 50 wt % PbO, 25% SiO_2,

10% B_2O_3, 10% K_2O, 2% Li_2O, and 8% Na_2O. Various inorganic pigments could be used to give color in melts at 950°C for 2.5 to 3 hours. Amberg and Harrison (Exolon) developed an enamel for difficultly wettable substances such as graphite, carbon, silicon carbide, fused alumina, and their mixtures.

Farnham and Burdick presented data on enamels for aluminum. Enamels for aluminum may contain substantial amounts of alumina. Donahey (1953) prepared an enamel containing 18 to 20 mol. % Al_2O_3, 8 to 13% Li_2O, 25 to 30% Na_2O, 24 to 28% P_2O_5, 2 to 12% B_2O_3, 4 to 6% of an easily reduced oxide from the group CuO, CoO, NiO, and CdO, and 2 to 15% $(NaF)_2$. Bezborodov, Mazo et al.; Azarov and Chistova (1963) investigated the phosphate enamels for aluminum. Hüttig (1961) prepared the base layer of aluminum and its alloys for improved adhesion of enamel layers by treating the aluminum surface with boiling water containing some alkali (about 0.01% KOH for an aluminum alloy containing 1% Mg, 0.04% Fe, 0.08% Si, and 0.01% Cu); but 0.005% LiOH is recommended for cast aluminum (99.8%).

22 ALUMINA IN COATINGS

22-1 INTRODUCTION

Alumina finds applications as coatings on metals, ceramics, and other materials as evaporated films, vitreous glazes and enamels, chemical coatings, flame-sprayed coatings, etc. There are many purposes for the coatings, among which are: decoration, prevention of corrosion, and protection against erosion, abrasion, heat, and mechanical action. Coatings have become of prime interest in high temperature applications in jet engines, and rocket motors, and in supersonic applications, in which severe limitations are placed on conventional materials. Some references to coatings include the following: Machu (1952, Krier and Humenik (1963); Graziano (1962); Klopp (1961); Gangler (1963); Bergeron, Tennery et al. (1962); Huminik (1963); P.S. Payne (1964); High-Temperature Materials Conference, Cleveland, Ohio, 1957, 3-15 (Pub. 1959); and Plunkett (1964).

Coatings are used to protect high-temperature metals against oxidation. The metals of most interest and their melting points are niobium (2420°C), molybdenum (2620°C), tantalum (2995°C), and tungsten (3410°C). Each of these melts above the temperature for aluminum oxide, yet aluminum compounds have received consideration in their protection. Among the many coating methods examined for high-temperature protection are electroplating, electrophoretic deposition, flame and plasma-arc spraying, vapor deposition, and cementation processes (the transfer of a coating and diffusion into the substrate with the formation of new compounds). An example of the last is hot-dipping in molten aluminum (Bartlett et al., 1961; Lawthers and Sama, 1961; Jefferys and Gadd, 1961).

The more successful coating systems for the refractory metals niobium, molybdenum, and tantalum, at present, appear to be complex intermetallics containing silicon, chromium, aluminum, boron, or titanium. Protection for several hours at 1650°C is realized. Tungsten silicides promise the best protection for tungsten and its alloys at 1650 to 2200°C (Gangler, 1963). The pack process (immersion of the substrate in heated, granulated, or powdered, cementation coating materials) is favored for producing reliable coatings. Metallic and ceramic coatings show less promise.

Some semicommercial coatings that involve alumina for refractory applications are prepared as follows:
General Electric GE 300. A flame-sprayed coating of alumina on chrome-plated molybdenum provides protection to about 1650°C for several hours.
General Electric GE 400. A flame-sprayed coating of alumina on niobium or tantalum is sealed by a vitreous frit, and then

sintered at 1480°C. Protection to 1370°C for up to 100 hours
is provided.
Mond Nickel. An alumina diffusion layer is applied over
molybdenum. A coating of platinum over the alumina layer provides
protection at 1180°C for several hundred hours.

Douglas investigated the emissivities of ceramic coatings on
low alloy steels. Most dark refractories gave highly emissive
coatings. The best white refractory materials for use in low
emissive coatings at 600 and 815°C were found to be feldspar,
zirconium spinel, and Treopax (National Lead Co.), with
emissivities in the range 0.22 to 0.32. The comparable
emissivities of aluminum oxide (in 5% waterglass as a binder)
were 0.42 at 650°C and 0.35 and 815°C.

22-2 ANODIC COATINGS ON ALUMINUM

The naturally forming coating on aluminum, which effectively
retards oxidation of the metal, and anodic coatings formed under
applied voltages in specific solutions have been referred to pre-
viously (Section 3-6-3), in which it was found that the film is
amorphous, and porous. Certain electrolytic treatments have
yielded either eta or alpha alumina, with its inherently high
resistance to chemical attack. Mott (1904) produced electrolytic
coatings on aluminum in solutions of sodium hydrogen phosphate.
Flick (1924) discovered that a dense adherent coating of oxide
could be applied by making the aluminum an anode in a solution
of NH_4OH or NH_2S at a potential of about 220 volts. The films
had better corrosion resistance than the immersion in ammoniacal
solutions containing traces of silver, nickel, or cobalt (Pacz).
Bengough and Stuart developed an anodized treatment in chromic
acid (3%) under gradually increasing voltage to 50 volts. This
treatment was used particularly on aluminum-alloy airplane sur-
faces in marine service to reduce corrosion. Films in oxalic and
sulfuric acids were subsequently developed. Campbell (1952) des-
cribed a process in which an ac voltage was superposed on a dc
voltage during electrolysis. "Hard" anodic coatings can be pro-
duced quickly, but it is difficult to obtain continuous coatings
on some aluminum alloys, especially over aluminum-copper alloy
(3%) and aluminum-silicon alloy (7.5%). Thick, hard anodic
coatings provide durable abrasion resistant surfaces. They are
being used for wear resistance, and in architecture for aesthetic
effects.

For best resistance to corrosion and discoloration, anodic
coatings are sealed in boiling deionized water. Raether (1959),
Young (1959), and Holmes (1964) have offered explanations of the
nature of the anodic films and their conduction properties.

When aluminum is made the anode in certain electrolytes,

such as the borates, it acquires a film which is undirectional with respect to the passage of alternating current. The film can be subjected to potentials as high as 450 volts in some cases before its insulating ability becomes seriously impaired. Use is made of this property in electrolytic rectifiers. As the film has high dielectric strength and is extremely thin, another application is in electrolytic capacitors. The anodic film on aluminum sheets can adsorb a variety of organic dyes, and mineral pigments.

22-3 ENAMEL COATINGS

Enamel or glaze coats are applied conventionally to a base metal by dipping, spraying or painting a water slip of the fine-ground frit of glassy materials. The coating is then heated until the particles melt and merge to form an impervious glass. The adherence of the enamel depends on several factors, one of which is the fit of expansion characteristics. King, Tripp, and Duckworth (1959) cite other factors: (1) the enamel at the interface must be saturated with an oxide of the metal, (2) this oxide must not be reduced by the metal when the oxide is in solution in the glass, and (3) the heavy scale that forms during the heat treatment of firing the enamel in air must be dissolved in the glass.

Lauchner and Bennett (1960) investigated the mechanically and thermally induced stresses in ceramic-coated metal composites. Considerations of the interfacial structure of the composite indicated that the glassy phase was saturated with oxides of the base metal, accompanied by residual strain gradients mainly in the interfacial zone. The maximum induced strain (thermal or mechanical) which coatings could withstand without fracture was found to be related to the residual stress.

Harrison, Moore, and Richmond (1947) developed ceramic (enamel) coatings for mild-steel aircraft exhaust systems, consisting of protective frits of high refractoriness and high thermal expansiveness mixed with refractory fillers. Alumina A-1 (Alcoa) produced the most satisfactory filler for protection to about 680°C. Bennett (1950) developed ceramic coatings for ingot iron and 4140 alloy steel, good to 1090°C for 6 hours. Petzold (1958) claimed protection of ceramic coatings against lead bromide ($PbBr_2$) at 820°C, and against loss in strength to 1100°C. Bennett (1955) predicted wide acceptance of enamels for high-temperature resistance of metals.

Devrup (E. I. du Pont de Nemours) developed a vitreous enamel suitable for use on aluminum and its alloys. The enamel has a maturing temperature between 495 and 530°C, and is composed of the oxides of lead, lithium, sodium, potassium,

titanium and silicon in such proportions that the total
alkali metal content falls between 25 and 36 mol. %, and the
ratio of the sum of the silica and twice the titania to the
total alkali metal is between 1.8 and 3.0. A typical batch
contains 37.0 wt % red lead oxide, 24.1% flint, 5.1% lithium
carbonate, 14.4% soda ash, 11.1% potassium carbonate, and
8.3% titania. Andrus (Croname, Inc.) produced an anodic film
on the aluminum electrochemically (about 0.0002 to 0.00005 in.
thick),coated the film with a fusible vitreous material, and
heated to fuse the vitreous material.

22-4 FLAME-SPRAYED COATINGS

Dickinson (1954) described a flame-spraying technique
for applying refractory coatings of aluminum oxide onto
aluminum, magnesium, iron, steel, or titanium surfaces. Fine,
refractory powder is blown through a flame which melts it
and causes it to stick to the article if the coefficient of
thermal expansion of the coating matches the base material.
Wheildon (Norton Co.) in 1955 demonstrated the process of
spray-coating alumina (or zirconia) onto an iron base, com-
prising heating a rod of the stable oxide in a flame hot
enough to melt it (oxyacetylene), which instantaneously
atomized the molten oxide to form discrete particles. At the
same time, the molten particles were projected with a blast of
gas onto the heated base (about 430°C) before they could
congeal. The coating, designated "Rokide A" in the case of
alumina, could be applied to an iron backing to a thickness
of about 0.1 inch, and although the expansion characteristics
did not match closely, there was enough flexibility to
partially compensate the strain. The coatings are porous, and
do not give complete protection against oxidation, but even at
a thickness of only 0.025 inch, a temperature differential of
about 540°C is obtained when the face is subjected to a tem-
perature of 1980°C. Ault (1959) specified that the aluminum
oxide rod should have a porosity of 8 to 40% of open pores,
have a flexural strength above 2000 psi, and should contain
at least 95 wt % Al_2O_3. Curtis (1959), Westerholm (1959),
Meyer (1960), and Vasilos and Harris (1962) investigated the
preparation and process of flame-spraying.

Bradstreet (Armour Research Foundation) in 1959 des-
cribed a variation of the flame-spraying process in which a
powder of crystalline particles of an oxide (refractory at
1200°C) is injected into a gaseous stream being fed into a
continuous flame-generating device. A suitable powder consists
of 200 parts by weight of 60-mesh alumina and 20 parts MgP_2O_7
with 5 parts $Al(OAc)_3$. Improved results were obtained when
the surface of the base (steel) was pretreated with a solution
of H_3PO_4. The coatings were claimed to be useful for skid-
resistance for metal gratings and for refractory surfaces of

brick.

Eisenberg (1964) injected into one of the gas streams
entering the flame a solid powdered mix of the refractory
oxide, and a fluoride, and deposited the mixture on the
object to be coated. Another variation by Bradstreet and
Griffith (1956) comprised spraying a solution, which is
thermally decomposable to the refractory metal oxide, into the
flame. B. W. King (1962) concluded that cermets of the
graded type can be made by flame-spraying alternate layers of
an oxide and a metal. Most metals, as well as graphite,
glass, and various ceramics could be spray-coated. Aves and
Hart (1962) obtained improved high-temperature protection by
flame-spraying coatings of alternating metal and ceramic
layers, obtained by impregnating the coatings with vaporiza-
tion or sublimation materials such as tin, zinc, nickel,
cobalt, halides, silicone, furan, phenolic, or epoxy resins,
which upon heating pass from the solid to the gaseous state
without significant formation of liquid. The metallic layers
were selected from the group boron, niobium, iridium,
molybdenum, tantalum, and tungsten, alternating with ceramic
layers of metal oxides (Al_2O_3) or carbides.

The plasma arc is a powerful tool for obtaining temperatures
as high as 11,000°C, which can be sustained for periods of an
hour. Hedger and Hale (1961) described the use of the plasma
torch for the spheroidization of alumina powders. Orbach
(1962) cited various ceramic uses for the plasma jet.
Stackhouse, Guidotti, and Yenni (1958) substituted the plasma
torch for the oxyacetylene torch in flame spraying. Ten basic
coatings that could be melted and deposited as very dense pure
coatings were Ta, Pd, Pt, Mo, W, Al_2O_3, ZrO_2, and three com-
binations of W with ZrO_2, CrO_3, and Al_2O_3. Kramer and
Levinstein (1961) reported that all coatings from the group
Al_2O_3, Cr_2O_3, ZrB_2, and the carbides can be built up to thick
coatings on a graphite substrate. The materials deposit in
substantially the same form as the raw material. Westerholm,
McGeary, Huff, and Wolff (1961) compared the principal flame
and plasma spray methods. Sound coatings could be obtained
with alumina by these methods. H. Meyer (1962) drew attention
to the peculiarity that sprayed deposits of alpha alumina feed
deposited as gamma alumina from plasma temperatures as high as
16,000°C. Huffadine and Hollands (Plessey Company, Ltd, 1962)
were able to convert the gamma alumina (density 3.55 g/ml) into
alpha alumina (density 3.95) by flame-spraying onto graphite
at 1500°C. By transferring the assembly to a furnace at
1250°C, the graphite was oxidized, leaving the ceramic form.
Meyer (1963) determined the extent of the conversion by adding
chromia. Chromia dissolves up to 8 mol. % in corundum with
a red color, but in gamma alumina it is green. Huffadine
(1964) patented the chromia method of detecting the phase change
in aluminum oxide.

Ault and Milligan (1959) flame-sprayed alumina radomes over a removable form. The forms were claimed to be highly refractory, dense, strong, and impervious. Owing to the slight shrinkage in the final firing and the strength of the original flame-sprayed shape, distortion and cracking were reduced to a minimum. Huffadine and Allen (1964) commented on the advantages of flame-spraying as a means of fabricating dense bodies of alumina. By this method, porosities of only 8 to 12% at 0.125-inch thickness were attained, with an overall coating efficiency of 10 to 50%. Higher efficiencies and lower porosity levels were attained with metals than with ceramics. Spraying with alumina presents special problems because of the change from the low-temperature forms to stable alpha alumina. The normal spraying results in deposits of gamma alumina with about 10% porosity. At about 1000°C, these deposits shrink to alpha alumina. By keeping the temperature above 1000°C during spraying, cracking was markedly decreased. On parts of about 6 inches in diameter, porosity was reduced to 3.9% at a temperature above 1400°C. The average crystallite size was 4.6 X 2.9 microns. At the higher base temperatures cited, grain growth was considerable (12.2 X 4.2 microns).

Dittrich (1965) flame-sprayed self-bonding nickel aluminide coatings, which could subsequently be used to provide good adhesion for oxide coatings. The powder consisted of an aluminum core, clad with a nickel sheath. An exothermic reaction of these in the heating zone of the flame-spray gun forms nickel aluminide.

Montgomery et al. (Ohio State Research Foundation) flame-sprayed a sintered mixture of a metal from the group aluminum, iron, nickel, and cobalt with a metal oxide from the group alumina, magnesia, and zirconia. During spraying, the particles were heated to about 1150°C.

22-5 PAINTED, CAST, OR TROWELED COATINGS

The method of painting ceramic pastes on metals to form protective coatings is exemplified by the following procedures. Kleinert coated graphite or amorphous carbon electrodes with a slurry containing alumina, chromia, etc., stabilized zirconia, and silicone binders. The purpose was to prevent rapid burning of the electrodes. A protective coating for oxidizable metals may contain 20 to 50 wt % sodium metaborate, 20 to 40% plastic clay, and 5 to 40% alumina (Govan and Govan, 1957). Metallic castings and other shapes may be protected against excessive oxidation and loss of surface details in heat treatment by coating 1/64 to 1/32 inch-thick layers composed of 7 to 16 parts Al_2O_3, 29 to 60 parts SiO_2, and 3 to 7.5 parts sodium oxide. The coatings are applied by spraying, painting, or dipping from suspensions in water or glycerine (Cowles and Stedman, 1962).

Satterfield used suspensions containing 60% alumina in resin to form cup-shaped retainers for holding base-metal parts such as combustion-engine exhaust valves, while cladding with hard metal facings.

Blocker, Hauck et al. (1960) claimed that a metal-reinforced ceramic coating withstands temperatures of 1930°C when the refractory medium is phosphate-bonded alumina aggregate against stainless steel. Eubanks and Moore (1959) applied coatings of various refractory oxides with aluminum phosphate in thicknesses of 0.002 to 0.20 inch by spraying, brushing, or dipping. The heavier coatings were reinforced with expanded SAE 1020 carbon steel, spot-welded to the base material. Many phosphate-bonded coatings are possible, as for example, a 50:50 mixture of alumina and zircon, bonded with phosphoric acid and colloidal silica (Noble, Bradstreet, and Rechter, 1961). The phosphate-bonded coatings are porous, and do not protect against oxidation at high temperatures, hence are mainly used for thermal insulation.

Alexander (1963) specified conditions for bonding a re-fractory oxide coating to a cermet.

22-6 ELECTROLYTIC COATINGS

Grazen codeposited up to 50% by volume finely divided particles of aluminum oxide dispersed in nickel, copper, silver, cadmium and other metals by an electroplating process. The tough coatings greatly improved the life of gages, cutting tools, and other wear surfaces.

Ziegler and Ruthard (1958) produced coats of aluminum on copper, superficially converted to aluminum oxide, by electrolytic deposition from an organic solution containing an alkali metal halide, as for example, $NaF \cdot [Al(Et)_3]_2$.

22-7 EVAPORATED COATINGS

Deutscher (1961) deposited evaporated aluminum iso-propylate (235°C) in contact with nitrogen, ammonia and water vapor onto a ceramic substrate to obtain a coating of aluminum oxide. Oxley, Browning, Veigel, and Blocher (1962) vapor-deposited aluminum oxide on nuclear-fuel particles. Day and Stavrolakis (1962) evaporated aluminates of beryllium, strontium, yttrium, or lanthanum on molybdenum to form a coating to hold the cations on the surface of the article; they then oxidized the cations under controlled conditions to form a suboxide layer, and applied an oxide with heat to form a bond. Reichelt and Schmeken developed a heating element and holder for the vaporizing coating method consisting of 50 to 80% (wt) of a metal conductor (W, Ta, Mo, or Cr) with the

remainder a metal oxide of Al, Zr, Be, Th, or Mg, or a spinel such as MgO·Al$_2$O$_3$. These compositions had good wettability for the satisfactory evaporation of Fe, Co, Ni, Pt, Pd, and Al. In one example, 20% alumina and 80% molybdenum were mixed with an organic binder, were pressed into a shape having a recess to hold the material to be evaporated, and were sintered at a temperature below the melting point of at least one of the elements.

DaSilva and White (1962) found that aluminum oxide films prepared by the evaporation of aluminum with an oxygen pressure of 10^{-3} mm Hg had a dielectric constant of about 6 in vacuum or in nitrogen. On exposure to oxygen at 1 atm (23°C), the dielectric constant increased to about 12, comparable to that of bulk Al$_2$O$_3$. It was inferred that the original film was a suboxide. Schmidt, Brodt, and Lampatzer found that coating metal parts, especially steel sheet and strip alloyed with silicon, with the oxides or hydroxides of alumina in an inert or protective atmosphere for several hours at 900 to 1050°C resulted in a surface coating of from 2 to 3.5 microns in thickness.

22-8 DIP COATINGS, CEMENTATION COATINGS

A very effective method for prevention of oxidation of steel and the refractory metals is by immersion in a bath of molten aluminum. The surface of the aluminum is protected from rapid oxidation by halide salt fluxes. Aluminum baths are operated in the range 650 to 1150°C and for various time periods to allow for some diffusion of the aluminum into the surface. Subsequent treatments in an inert atmosphere or in vacuum may be applied to increase the amount of diffusion. With aluminum these periods may extend from 0.5 to 2 hours at 930 to 1150°C. Flame-sprayed coatings may be given a dip treatment in molten aluminum to seal the pores (Blanchard, 1954, 1955).

22-9 COATINGS ON ALUMINA AND OTHER CERAMIC BASES

The coating of ceramic alumina with metals is described in Section 25 as a metallizing prerequisite for forming seals. Only two examples are presented here. Cline and Wulff (1951) coated ceramic particles (alumina) with molybdenum deposited by hydrogen reduction of molybdenum pentachloride. Nickel was deposited by decomposition of nickel carbonyl. The particles in either case must be kept in motion by gas flow or by mechanical agitation during the coating process. In the presence of titanium carbide, the decomposition of nickel carbonyl proceeds abnormally, leading to the formation of carbon. In the second example, Luks (1961) applied a metallic

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coating to a refractory nonmetallic body by forming a molten mixture of a manganese component and a silica-containing glass capable of forming a flux with the manganese component at 700 to 1300°C. A ground frit prepared from this was mixed with nickel, cobalt, iron, or mixtures of them with molybdenum or tungsten. The mix was applied to the body and fired.

Methods for coating abrasive grain, so as to obtain firmer bonds in grinding wheels, are represented by the following: Amberg and Harrison (Exolon Co) produced ceramic coatings on difficultly wettable fused alumina by fusing on the surface of the grains a silicate melt, having a wetting agent present from the group: molybdenum, tungsten, uranium, vanadium, and their compounds. Walton and Bassett coated refractory grain with a glass of low melting point, and including molybdenum oxide to wet the surface of the grain. Masin and Tull (Monsanto Chemical Company) coated fused alumina grain with a substantially water-insoluble, unfused, unvitrified film, which bonds finely divided inert material to the grain surfaces. Aluminum, iron, and magnesium metaphosphates may be used as the film materials. The coated grains are calcined at a low temperature (550°C).

Robson and Tucker (1955) described a method for coating concrete articles with two vitreous coatings. The first coat, to fill the voids, is a glaze frit with 20 to 60 wt % of a refractory material (alumina) added. The frit contains 44.3% flint, 37.3% dehydrated borax, and 18.4% limestone. Alternatively it contains 36.1% flint, 30.4% borax, and 33.5% litharge. The firing range is from 540 to 820°C. A cover glaze coat containing pigments may then be applied.

Barnes and McCandless (1948) produced glossy surfaces on sapphire by applying a thin film of any oxide fulfilling one of the following requirements: having a melting point lower than sapphire; forming a eutectic with sapphire; forming a low-melting peritectic; and forming a solid solution. The film was then heat-bonded to the surface of the sapphire. Single-crystal silicon could be deposited epitaxially on sapphire by a process of reducing $SiCl_4$ with hydrogen at high temperature. The early stages of growth do not initiate the formation of monolayers but of very small nuclei. The silicon deposits are p-type and of high resistivity. Novak (1961) observed that alumina could be gasplated on quartz or silica articles by heating them in an atmosphere containing the vapor of a trialkylaluminum compound or a trialcoholate above the decomposition temperature of the aluminum compound. The plating pressure is preferably 7 to 7.5 mm; the aluminum compound vapor may be entrained in 1 to 6 times as much carrier gas (air or nitrogen) at about 70 to 600 cc/minute. Thin adherent coatings were obtained from aluminum ethoxide vaporized at 200°C, and decomposed at 800°C; or from aluminum

isopropylate vaporized at 177°C, and decomposed at 370°C with nitrogen and water vapor carrier. The process is useful for lining quartz tubes or crucibles to be used in handling semiconductor materials.

Attempts to evaporate quartz alone and deposit it upon a selective surface have usually been unsuccessful, owing to the difficulty in evaporating quartz. The difficulty is overcome by coating the entire quartz surface with aluminum (Ogle and Weinrich). The process of vaporizing aluminum onto glass and other surfaces for reflectors and astronomical mirrors has been described by K. Rose (1948).

Long and Furth (Solar Aircraft Co.) claimed the method of providing the surface of a metal, glass or ceramic article with a cermet coating having both a metal phase and a ceramic phase. The cermet coating consisted of 60 to 70 wt % of aluminum or aluminum base alloys and 30 to 40% of a smelted and fritted product consisting of $NaCaB_5O_9 \cdot 8H_2O$ (Gerstley borate) and Li_2O. The surface was heated at least to 670°C. Such coatings are useful on alloys such as Timken 1722-A(S) and General Electric Chromaloy, which are tempered at 677°C. The coating can also be used to seal woven glass fibers.

22-10 ALUMINA COATINGS FOR ELECTRICAL INSULATION

Alumina is used in compositions to insulate or fix in place electrical windings or heater elements. A recent example of this type of coating was disclosed by Larsh and Coppock (1962) for a slurry composition of density 35 to 60° Bé containing 50 to 75 parts of glass frit, fused at 760 to 870°C, 1 to 10 parts silica, and 1 to 10 parts tabular alumina, suspended in an organic liquid boiling at 10 to 38°C. The mixture is flowed over the electrical elements to be sealed, the vehicle is allowed to evaporate, and the part is then heated to the fusion point of the lower-fusing frit.

Junker (1962) used mixtures of alumina and a product which lowered the melting point, such as titania or silica, applied in the melted state by means of a sprayer, to insulate the electrical windings of copper-furnace bobbins. Marbaker (1945) described coatings for insulating wire-wound resistors. Alston and Strickland (1962) described the process of preparing insulating coatings of alumina on metals, in particular for coating the heaters for cathodes in electron tubes.

Vondracek (1963, 1964) examined the requirements for electrical insulation in space environments. Materials in which alumina serves to insulate include: paper coatings in motor slot liners, potting compounds, cements and adhesives, and anodized aluminum conductors.

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23-1 INTRODUCTION

The word "cermet" was coined by A. L. Berger, Wright
Air Field to designate structures composed of an intimate
mixture of a metal and a ceramic. The cermets were originally
investigated in the hope that the mixture of metals and ceramics
would develop the most desired properties of the two materials,
that is, the refractoriness and chemical inertness of the ceram-
ics coupled with the ductility and impact resistance of the
metals. The prime objective was a suitable structure for
airplane power plants. Although this has not been realized
very completely, the cermets have developed certain uses.
Alumina has figured conspicuously in the development of cermets
as the ceramic phase in various combinations with refractory
metals as well as with nonrefractory metals, including
aluminum.

Initially, there was a lack of basic data for many of the
chemical and physical properties involved in the general metal-
ceramic field (Westbrook, 1952). Some attempt was made to ex-
plain the interfacial reactions between various metals with
likely refractory oxides (Kingery, 1953, Economos and Kingery,
1953). Various types of cermets, oxide base, carbide, boride,
and intermetallic types were considered for high-temperature
applications (J. T. Norton, 1956). Murray (1960) pointed out
that oxide systems show little gain in strength, compared with
that of the oxide itself, but do show an intermediate improve-
ment in thermal shock resistance. The carbide cermets ap-
peared to be adequate for many high-temperature applications
in thermal shock resistance, but poor resistance to mechanical
shock was their main weakness. Tret'yachenko (1963) assessed
the factors affecting the resistance of brittle cermets to
thermal fatigue fracture. The sensitivity could be evaluated
in terms of two criteria, one for nonsteady-state heating and
the other for steady-state heating. J. T. Norton (Ref.
Hehemann and Ault, 1959, Chapter 8, page 119) stated that
cermets have found application in two important areas (1) tools
as cemented carbides, wire-drawing dies, rock-drills, and
cold heading tools, and (2) structural parts for high-tem-
perature service in which resistance to oxidation is the
important criterion. The future of cermets in the latter uses
was questioned, however. Lavendel and Goetzel (Ref. Hehemann
and Ault, page 149) stated that cermets are quite brittle, have
poor impact resistance unnotched (only 4 to 5 in.-lb) for a
cobalt-alloy infiltrated titanium carbide. Wambolt and
Redmond (same reference, page 125) found no failure for a
titanium carbide composition (K163B1) after 550 cycles of heat
shock at 1200°C. A chromium-alumina cermet failed after 234
cycles at 1100°C.

Maziliauskas (1960) described various developments in the preparation of cermets. Cermets, Eds. Tinklepaugh and Crandall (1960), is an attempt to present a cross-section of information published in the United States. Shevlin (1957) and Frechette (1956) discussed applications and uses of cermets.

23-2 CHROMIUM-ALUMINA CERMETS

In 1949, Blackburn, Shevlin, and Lowers investigated the mechanism of wetting and adherence of sintered alumina by the metals: nickel, cobalt, iron, chromium, and chromium-boron. The objective was to prepare well bonded cermets as a possible structural material for jet engines. The tests consisted of firing the metals on sintered alumina tiles in reducing and oxidizing atmospheres in the range 1480 to 1930°C. It was concluded from the tests that there is no inherent tendency of the cited metals to wet alumina below 1650°C. Wetting was observed in the case of chromium in a slightly oxidizing atmosphere by the formation of chromic oxide, which readily forms solid solution with alumina. It was concluded that wetting and adherence may be developed through thermochemical reactions involving glass-free interfacial compounds in which the oxide of the metal combines with alumina. This precludes a strongly reducing atmosphere. Consolidation depends on the amount of oxide formed, its rate of formation, and its rate of reaction with alumina.

Blackburn and Shevlin (1951) found an optimum composition containing 30% electrolytic chromium, dispersed in tabular alumina, both components being finer than 10 microns in particle size. Test bars were pressed from mixtures of the two components that had been dry-pressed with organic lubricants ("Ceremul C," paraffin, "Sterotex," or "Carbowax") at pressures of about 55,000 psi. The forms, designed for various physical tests, were fired at 1705°C on a 30-hr schedule in a flowing atmosphere of hydrogen and water vapor, controlled by the dissociation of hydrated alumina. The following data characterized the product:

Fired shrinkage 13-14%
App. porosity <0.5%
Sp.G. app. 4.60-4.65, true 4.68-4.72
Thermal expansion (25-800°C) 8.65×10^{-6}
　　　　　　　　(25-1315°C) 9.45×10^{-6}
Heat transfer - Slightly less than for sintered alumina
Thermal conductivity - 0.023 (cgs)
Resistance to thermal shock - excellent, cycled from 1315°C
Resistance to oxidation - excellent at 1510°C
Hardness 1100-1200 (Vickers pyramid number)
Modulus of elasticity 5.23×10^7
Impact resistance at 30°C　　　　1.05 in.-lb
　　　　　　　　　　　　　18.95 in.-lb/in.^{2}

Compressive strength at 30°C	320,000 psi
Bending strength	
30°C	55,000 psi
870	43,100
1090	32,800
1315	24,400
Tensile strength	
30°C	35,000
870	21,500
1090	18,400
1315	14,000

It was concluded that the strengths may be adequate for jet-engine parts at above 980°C. The stress-rupture curves were higher than those for any known high-temperature alloy, and fell off less abruptly with rising temperature. The strength was not adversely affected by a 100-hr test of oxidation in air at 1510°C. The resistance to thermal shock was greater than that of sintered alumina in cycling from 1316°C in air. The cermet was found to be extremely hard, but brittle, and the resistance to mechanical shock was very low.

Shevlin (1952) reported on a cermet composition containing 72% chromium-28% alumina, which also appeared very promising for aircraft turbine applications in comparison with the then potentially useful carbide-base cermets. A thermal shock record of 540 cycles of simulated burner blow-out, and a 1000-hr stress-rupture life of 15,000 psi in air at 980°C were achieved.

Conant and Gillies (1955), Kiyoura and Sata (1958), Onitsch-Modl (1955), and A. E. S. White et al. (1956) confirm the general findings on the chromium-alumina cermet. N. C. Moore (Plessey Company, Ltd, 1957) patented a combination of fused alumina, 10 to 70% metallic chromium, and up to 5% Cr_2O_3, obtained by mixing alumina, chromia, and carbon, and heating so that most of the chromia was reduced to the metal. Matsumoto, Yamauchi, and Nishiyama (1957) observed that the presence of chromium oxide in alumina aided in the diffusion and adherence between chromium and the alumina. The adhesion took place at a relatively low temperature. For optimum results, the sintering shrinkage of chromium should be as close as possible to that of alumina containing Cr_2O_3. This was accomplished by varying the amount of Cr_2O_3 added, changing the particle size distribution and compacting pressure, and by use of other additives.

Improvements were claimed by introducing molybdenum and chromium as the metal phase (Huffadine, Longland, and Moore), molybdenum, chromium, and titania, in addition to alumina (Frangos, 1958), and chromium and carbon (1 to 16 wt %) in alumina (Klingler and Dawihl, 1962). Conant (1957) claimed a cermet of improved thermal shock resistance and with very high

strength at elevated temperatures by the presence of a small amount of a partially reducible oxide (molybdenum or tungsten). The ceramic component, alumina, also may contain small amounts of another oxide (TiO_2, Nb_2O_5, or Ta_2O_5). One such mixture consists of 58 wt % Cr, 19% Mo, 1% Ta_2O_5, and 21% Al_2O_3. Conant (1959) coated chromium-alumina thermocouple protection tubes against molten metal penetration by applying a continuous metal oxide coating on the surface, consisting of alumina and chromia. The coating should have an electrical resistance of at least 100 megohms for the purpose.

Sata and Kiyoura (1959) hot-pressed chromium-alumina cermets containing about 20 to 70 vol % Cr at 1400 to 1470°C under a pressure of 2100 psi for 20 to 30 minutes in argon atmosphere surrounding graphite molds. An increase in the chromium content lowered the pressing temperature. The bending strength ranged from 78,000 to 100,000 psi for specimens 4 x 4 x 15 mm. Compared with cermets prepared in hydrogen, these had smaller corundum crystals (1 to 3 microns) and a rougher boundary between the Al_2O_3 and Cr phases.

Schatt and Schulze found that the structure of the fracture of chromium-alumina cermets indicated intercrystalline fractures, determined by electron microscopy.

23-3 (IRON, NICKEL, COBALT) - ALUMINA CERMETS

Jellinghaus and Shuin (1958) prepared cermets of iron or iron alloys with alumina from partially oxidized Fe-Al alloys with the addition of iron carbonyl and other metal powders. Up to 22 vol % Al_2O_3, the density is 95% of theoretical; at higher contents (around 50 vol %) the density falls off, but with further addition of alumina, it again rises to 95%. The material can be rolled with alumina contents as high as 22 vol %. Recovery and recrystallization take place, but grain growth is inhibited by the alumina. The ultimate tensile strength passes through a maximum between 3 and 5 wt % Al_2O_3. The oxide-rich cermets have poor impact strength, but resist scaling at elevated temperatures. The bending strength for an alloy containing 50.7 wt % Al_2O_3 at 800°C was 14,200 psi for at least 100 hours, and at 1000°C it was 7100 psi; the bending strength for an alloy containing 68% Al_2O_3 was 17,000 psi at 800°C, and at 1000°C it was 11,400 psi. This may be compared with a chromium-bearing cermet (35.3 wt % Al_2O_3) which sustained a bending load of 26,900 psi for 100 hours at 800°C. Siede and Metcalfe investigated the fineness of distribution of iron cermets by metallography, thermal analysis, and mechanical testing. Gatti (1959) used powder metallurgy techniques to produce iron-alumina cermets. He found that alloys containing up to 16 wt % Al_2O_3 are ductile. These structures have a higher yield stress and an improved creep resistance over that

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of pure iron.

Eisenkolb and Richter found no useful materials, technically, for mixtures of iron and flint. A small addition of the first iron powder to alumina improved the bending strength after sintering above the melting point of the iron. Larger additions of iron caused consolidation of the iron particles in drops. Matsumoto, Yamauchi et al. (1958) found that replacement of part of the alumina by iron oxide, lime, magnesia, manganese dioxide, chromia, titania, or silica reduced the contact angle, hence improved adherence between the iron and the alumina.

R. F. Thomson (General Motors Corp., 1958) composed a sintered-powder metal piston ring for an internal combustion engine, characterized by high wear resistance and formed of a sintered and worked mix of approximately 0.3 to 3% carbon, 1.5 to 6% crystalline alumina, and the remainder substantially all iron.

Baxter and Roberts concluded from comparison of the properties of the bonded carbides and of the metal-oxide cermets that a metal phase was needed to wet the nonmetal as well as to form a strong bond. The binary nickel (and cobalt) alloys were investigated but none was found to wet alumina effectively, although several formed high-strength bonds. Sintered compacts of the continuous alumina phase type were found to have increased thermal shock resistance but poorer strength compared with sintered alumina. Kiyoura and Sata (1956) found that a sintering temperature of 1670°C was necessary for various nickel concentrations in hydrogen. The oxide phase was continuous for metal concentrations to 70%, indicating that the properties of oxide cermets depend mainly on the properties of the oxide phase. This was believed to explain the superiority of cermets of the alumina series in mechanical strength and thermal shock resistance.

Cremens and Grant pointed out the necessity of obtaining very fine nickel powders (1 to 2 microns) and alumina (0.2 to 0.02 micron) in blended extrusions to produce strong cermets containing up to 45 vol % Al_2O_3. Creep-rupture tests at 700 to 980°C substantiate other investigations that still further strength improvements can be achieved if finer interparticle spacing is attained. Zwilsky and Grant attributed the increased stability of dispersion-strengthened composites to their resistance to recrystallization up to temperatures near the melting point of the base material. Dromsky et al. observed the growth of aluminum oxide crystals in a nickel matrix in the range 1170 to 1350°C. The instability of the dispersed alumina was independent of the crystal structure of the alumina. The activation energy for the growth of the dispersed alumina was 84.7 kcal. It was believed that the rate-controlling

mechanism is the solution of aluminum and oxygen into the nickel lattice, rather than diffusion.

Mayfield (1960) prepared a cutting tool composition with a continuous matrix of 80 wt % alpha alumina and a discontinuous metallic phase consisting of 0.1 to 7% nickel.

Burney (1958) attempted to reinforce an 80 Ni-20 Cr alloy by the addition of reactive TiO_2 and refractory Al_2O_3. Armstrong, Chaklader, and Clarke (1962) measured the interfacial energy of Ni-Ti and Ni-Cr powder mixtures on sapphire surfaces by the sessile drop method at 1500°C under a pressure of 10^{-4} mm Hg. Two basic mechanisms were believed to operate: (1) a segregation of solute metal at the interface, and (2) an interfacial reaction. X-ray diffraction indicated the formation of a Ti_2O_3.

Crandall and West (1956) used DTA, X-ray, and weight change in conjunction to derive the supposed mechanism by which oxidation proceeds in porous compacts of cobalt and alumina.

23-4 ALUMINUM-ALUMINA ALLOYS

The powder metallurgy of aluminum-alumina alloys was originated by Aluminium Industrie Actien Gesellschaft (AIAG) of Zurich, Switzerland, as a result of unusually high strengths observed in products wrought from milled aluminum powders. The product was called Sintered Aluminum Product (SAP). Alcoa Research Laboratories became interested in the product in 1948, and have designated the process Aluminum Powder Metallurgy (APM), and the alloys developed at present, XAP. While the properties of these materials are predominantly metallic, the materials are of interest ceramically as representing end members in the metal-ceramic series.

The high properties at elevated temperatures are due primarily to the dispersion-hardening effect of the aluminum oxide (Irmann, 1952; Lyle, 1952; Fisher, Hart, and Pry, 1953; Nock, 1953; Grant and Preston, 1957; Cremens, Bryan, and Grant, 1958). A Powder Metallurgy Symposium on the subject was held in London in 1954. During an International Conference held in New York in 1960 (Leszynski), progress in the development of the SAP process was discussed by Bloch and Hug. Bloch (1961) and Towner (1961) have provided comprehensive bibliographies on the subject.

The original products were prepared from flake aluminum powder (2-dimensional particles). Alcoa has developed four principal alloys of this type, three of which conform with SAP. A fifth alloy (XAP005) is a low-iron type for thin-wall tubing for atomic power applications. Types have also been developed

from atomized aluminum alloy powders (3-dimensional particles). Alcoa types M486, M643, and M457 contain 15% $FeAl_3$, 29% $FeNiAl_9$, and 3% $FeNiAl_9$, respectively, as the dispersed phase.

Data for some of the XAP alloys are shown in Table 16.

Table 16
Properties of Aluminum-Alumina Alloys (1)

	XAP001 (M257)	XAP002 (SAP 930)	XAP003 (SAP 895)	XAP004 (SAP 865)	XAP005 -
Principal Components (%)					
Al_2O_3	6.0	8.0	11.0	14.0	6.0
Fe	0.20	0.28	0.27	0.29	0.05
C	0.40	0.20	-	0.40	0.40
Si	0.08	0.10	0.10	0.10	0.08
Cu	0.00	0.01	0.01	0.01	0.00
Sp.G.	2.74	2.74	2.75	2.77	2.74
Thermal Conductivity (cgs)					
24°C	0.43	0.40	0.36	0.32	0.43
200	0.44	0.43	0.39	0.36	0.44
400	0.45	0.44	0.42	0.39	0.45
540	0.45	0.44	0.42	0.40	0.45
Coefficient of Thermal Expansion (°C X 10⁻⁶)					
20-100	21.6	21.2	20.7	20.2	21.6
20-300	23.6	23.2	22.5	21.8	23.6
20-450	25.0	24.8	23.4	22.5	25.0
Specific Heat (cal/g)					
20°C	0.213	0.212	0.211	0.210	0.213
100°C	0.225	0.224	0.223	0.223	0.225
Typical Mechanical Properties (psi) (1) Longitudinal Extrusions (2),(3)					
20°C					
Ultimate,psi	37,000	36,000		54,000	37,000
Yield,psi	27,000	21,000	-	38,000	27,000
Elongation,%	13	12		5	13
538°C					
Ultimate,psi	6,000	6,000		8,000	6,000
Yield,psi	5,000	5,000	-	7,000	5,000
Elongation,%	6	4		2	6

Notes:
(1) Source-Alcoa Green Letter "Alcoa's Aluminum Powder Metallurgy (APM) Alloys" September 1962.
(2) These properties are independent of time at temperature. Properties of specimens heated as high as 538°C revert to room-temperature values on cooling to room temperature.
(3) Extrusions measured transverse to direction of extrusion are about 13 to 15% lower in strength at 20°C.

The strengths of the flake-powder alloys decrease with increasing temperature but revert to the original room temperature values following heating at temperatures as high as 538°C. The maximum permissible soaking times at temperature of the atomized-particle type, M486, that will not cause a loss in strength, is 6 hours at 441°C, 1 hour at 468°C, and 0.1 hour at 510°C. The strengths longitudinal to extrusion are higher than those transverse.

The products can be formed by compacting, extruding, forging, impacting, rolling, drawing, etc. The applications are primarily in the aircraft, missile, automotive, and atomic energy fields.

Langrod (1959) investigated the compatibility of the alloy APM 257 with uranium dioxide; Friske appraised the general applicability for atomic energy uses. Lyle (1962) described the properties of commercial alloys. Modl-Onitsch (1961) discussed the necessary stability of the phases present to provide strength at high temperatures. Sherby (1962) compared the creep resistance of these alloys with other polycrystalline solids, and concluded that the creep strength is probably only of secondary importance. Myers and Sherby (1962) showed no apparent discontinuity in compressive creep behavior in the range 540 to 735°C (at the melting point of aluminum). The microstructure of the alloys is stated to be a honeycomb of alumina filled with and interpenetrated by aluminum.

Goetzel stated that the percent by volume of the dispersed phase, the size of the dispersed particles, and their spacing are the most important variables. Where the dispersed phase is the oxide coating (eta alumina),its size is near 0.02 micron.

The addition of certain alloying elements to both types of APM alloys can develop desirable properties. Nachtman (1958, 1960) claimed a metallurgical composition of aluminum or its alloys containing strengthening metals (iron, molybdenum, vanadium, titanium, tantalum, niobium, chromium, manganese, nickel, cobalt, tungsten, boron, beryllium, thorium, iridium, or the rare-earth elements) with aluminum oxide or mixtures with various aluminates. The composition was sintered at a temperature between 370°C and the melting point of aluminum. Lenel discussed the dispersed phases in powder metallurgy as being primarily Al_2O_3 in aluminum. Wolf (1960) devised a method for assuring an aluminum oxide content of 6% in the powder, making it particularly suitable for the production of sintered bodies of high tensile strength and hardness at elevated temperatures.

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23-5 MISCELLANEOUS CERMETS

Johnston, Stokes, and Li showed the effect of alumina particles on the nucleation and growth of cracks through a silver chloride matrix. Fibrous cracking could be promoted under notch-impact conditions at temperatures at which silver chloride alone shows brittle cleavage. Baxter and Roberts found that alumina particles coated with cuprous oxide and bonded with silver act as a "model system" in which the metal phase actually wets and bonds to the nonmetal. Specimens of the continuous metal-phase type gave high bond strengths and a linear stress/strain relation.

Jackson (1961) found that the porosity of hydrogen-sintered bodies composed of $MoSi_2$ and Al_2O_3 was affected by grain size and alumina content of the cermet. Oxidation-resistant bodies could be made with grain sizes not over 10 microns, but the bodies were not strong. Specimens sintered in dissociated ammonia rather than in hydrogen corroded more easily, probably because of the formation of Si_3N_4 during sintering.

The use of metallic aluminum powder in ceramic protective coatings for refractory linings has been mentioned (Schurecht, 1939). Powdered aluminum has also been recommended for use in ceramic binders for abrasives (The Carborundum Co., Ltd., 1954; Cantrell; Degg; and Nobes, 1957).

German patent 873,674 (1943) covers the production of metal-ceramics, which comprises heating formed silica articles for 5 hours at 900°C in molten aluminum, whereby a complete transformation of the silica articles into (Al,Si)-Al_2O_3 occurs, owing to the exothermic reaction with aluminum. Such articles were intended for measuring electrical resistance. Walton and Poulos (1959, 1960) prepared cermets by the thermitic reaction of powdered aluminum with the oxides: Co_3O_4, Cr_2O_3, Fe_2O_3, MnO_2, MoO_3, NiO, SiO_2, TiO_2, V_2O_5, and ZrO_2. The temperatures required to ignite the compositions ranged from 560°C for MoO_3 to 980°C for Fe_2O_3. A third component, clay, alumina, or magnesia was added to moderate the reaction. Metallic silicides and borides as the metallic phase of a cermet were produced from the appropriate silicates or borates, or metal oxides with silica or boric acid. $ZrSi_2$ was formed by the reduction of either $ZrSiO_4$ or ZrO_2 and SiO_2.

Meyer-Hartwig (1961) prepared a chromium-alumina cermet by the thermitic reaction of powdered aluminum and chromia. Fleming and Johnson (1963) heated Al-U_3O_8 compacts above the melting point of aluminum to produce a cermet containing about 65 wt % U_3O_8. At the ignition point, 816°C, the reaction

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was violent, the calculated maximum energy release being 1.2 megawatt-seconds/kg of reactant. The sintered compacts contained α-Al_2O_3, UO_2, UAl_2, and UAl_3, but the relative amounts of each compound differed greatly from sample to sample.

Cronin (1951) investigated cermets as likely refractory materials for thermionic cathodes in electron tubes. Unlike other cathodes, cermet bodies can be brought to elevated temperatures by impressing a voltage directly across the terminals. Resistivity can be altered by processing changes and control of the composition. Satisfactory cermet bodies were developed having low vapor pressure, good chemical stability, adequate thermionic and secondary electron emission, and high hot strength.

24 ALUMINA IN AIRBORNE CERAMICS

24-1 INTRODUCTION

Active interest in the United States in sintered alumina as an airborne ceramic material received an impetus from the reports of ceramic developments in Germany prior to 1945 (Watt el al., 1945; Keller and Herberger; de Witt; Kistler; and Schilling). These developments related mainly to ceramics in turbine blades and in jet propulsion accessories for hopefully prospective use at temperatures as high as 1200°C. High-temperature metal alloys were scarce in Germany during 1940 to 1945, and ceramic materials were being substituted wherever possible. Blackburn (1946); McRitchie; King; Graff;Hursh; and Slyh et al. (1946) reported on early progress in ceramic coatings for gas engine tubes, cermets of alumina, with nickel or chromium, and the testing of refractories for rocket motor liners and nozzles. Duckworth (1948) and Bressman (1948) described the potential lines of development as consisting of (1) solid ceramic shapes for high-temperature parts, and (2) ceramic coatings to protect the high-temperature metals from corrosion. Besides the refractory oxides, BeO, Al_2O_3, ZrO_2, ThO_2, MgO, and CaO, German developments using powder metallurgy of mixtures of metals and ceramics were mentioned, including Brown-Boveri disclosures of cermet compositions for turbine blades having a highly ceramic tip and increasing metal content toward the root.

24-2 GAS-TURBINE ACCESSORIES

Although the inherent mechanical shortcomings of oxide ceramics and cermets with respect to impact, thermal shock, and lack of ductility were realized early in the investigation of these materials for airborne applications, the gains to be realized by successfully circumventing these problems encouraged further investigation. The application of sintered alumina and alumina cermets as a complete substitution for refractory metals in the fabrication of gas turbine blades has been discussed in the following references: Geller (1948); Bole (1949); Bobrowsky (1949); Ault and Deutsch (1950); Duckworth and Campbell (1950); Rotherham et al. (1952); Carruthers and Roberts (1952); Thielke (1953); Richardson (1954); Waeser (1955); Puri (1959); Blakeley and Darling (1957); and Bragdon (1958). Flock and Halpern (1952) collected a bibliography of books and published reports on gas turbines, jet propulsion, and rocket power plants.

Bobrowsky stated that both ceramic and ceramic-metal compositions have operated as blades in gas turbines at temperatures above those in service use with alloy blades, although speeds were lower. The life of the ceramic materials was short, primarily because of mechanical design problems that could not be

anticipated prior to research evaluation. Tacvorian and Levecque (1957) claimed that a cermet containing 56% Al_2O_3, 4% Cr_2O_3, 30% Cr, and 10% Mo, pressed at 28,000 psi, and sintered at 1700°C, was especially suitable for turbine blades or nozzles of jet power plants.

Lavendel and Goetzel (1957) found that failures occurring during engine testing of cermet buckets for high-temperature gas turbine use were generally located in the upper 25% of the airfoil section or in the neck of the root. In an attempt to correct difficulties with ductility in these regions, they investigated a "graded" cermet (variable in metal content). The cermet selected for this test contained no alumina, but was a titanium carbide skeleton infiltrated with Inconel-X. The test results indicated a substantial improvement in ballistic impact strength and in thermal shock resistance.

The use of ceramic materials as coatings for aircraft power plants and in high-temperature applications in general has been discussed by the following: Koenig et al. (1950), Schell and Neff (1951), Holland (1952), Garrett and Gyorgak (1953), Lynch et al. (1958), Graham and Zimmerman (1958), Miller and Wheeler (1958), Levy (1963), and Merry and Vondracek (1963).

Some of the coating applications for high-temperature metals appear more promising at present than the complete substitution of metals by ceramics in airplane power plants. Koenig found that Inconel and Haynes Stellite metals, coated with $BaO-Al_2O_3-SiO_2$ glass, were protected to 1000 to 1150°C. These coatings would not adhere to other high-temperature alloys and stainless steels. Lynch, Quirk, and Duckworth (1958) investigated 34 ceramic materials, including three alumina coatings on stainless steel, as nozzle liners in a laboratory rocket motor. The motor was operated with a 4:1 volume ratio of hydrogen to oxygen to give a combustion temperature of about 2480°C at 200 psia. The functional life of the motor with the various experimental nozzles ranged from less than 15 seconds to 107 seconds. The alumina coatings on stainless steel lasted 15 to 30 seconds, in comparison with over 60 seconds for complete nozzles of recrystallized silicon carbide, zirconium boride and beryllia. It was noted that the erosion in the case of the coated alumina probably resulted from melting of the stainless steel because of lack of thermal insulation from the coating. The alumina coatings provided an adherent refractory layer.

Cermets have found application as pump seals in rockets and in nuclear power plants in uses where their resistance to corrosive liquid metals makes them valuable (Graham and Zimmerman).

Truesdale, Swica, and Tinklepaugh investigated the use of

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molybdenum metal fibers as reinforcing for alumina ceramics. The main difficulty was that the metal fiber reinforcing did not shrink with the alumina during firing; the fibers opposed both the forming pressure and the sintering. Hot-pressing was the only likely solution, but this method affords only a few simple shapes. Cracks were not observed for alumina ceramics containing only 5 wt % molybdenum fibers, but fine cracks developed for 10 and 20 wt % loadings. There was some evidence of increased resistance to failure by thermal shock cycling, as determined by changes in flexural strength and modulus of elasticity. Atlas (1958) investigated metal reinforcing by the use of wire screens, sheets, and plates in sintered alumina for the prospective application as a ceramic radome. The structures were produced by hot-pressing at 1275 to 1450°C with sintering additives. Inconel alloys, stainless steels, titanium, molybdenum, and mild steel were investigated as the metallic components. Phosphate-bonded laminates were also formed from tabular alumina, bubble alumina and P_2O_5-H_2O, with different high-temperature metal components. Wetting of the alumina was accomplished by a light coating of titanium hydride in combination with dry hydrogen for brazing operations. Flexural loading caused failure at lesser loads than for an equal thickness of the homogeneous ceramic. The test bars, however, retained a significant integrity of form. The most significant advantage of metal reinforcing was shown by impact tests. The impact absorption of the reinforced specimens (Charpy pendulum) depended on the thickness and type of metal, but in some cases was 10 times or more that of the ceramic alone.

H. B. Porter (1955) appraised the applications of ceramics in rocket refractories meeting temperatures of 2200 to 2770°C (above the melting point of Al_2O_3), reached within a second after ignition. Although the general conditions are more severe with solid fuels, erosion and corrosion were stated to be more severe with liquid propellants. In addition to aluminum oxide, the hard metal aluminide, Mo_xAl_y was considered a possible rocket material. Its resistance to oxidation is good, but its strength and thermal shock resistance is poor, and it is hard to fabricate.

24-3 RADOMES AND ROCKET EQUIPMENT

When the speeds of aircraft approached Mach one, the plastic radomes for enclosing radar antenna equipment began to encounter difficulties with air friction and impact from dust and raindrops in the atmosphere (Wahl, 1957). It was claimed that velocities of 733 ft/sec (500 mph) cause serious damage to plastics. Raindrop impacts at velocities of about 6600 ft/sec do not significantly abrade sintered alumina surfaces, but can fracture sintered alumina surfaces. Engel (1960) estimated

that plates of sapphire or hot-pressed alumina 0.125 inch thick can be expected to survive collision with a 0.2 cm water drop without damage at a velocity as high as 11,000 ft/sec (Mach 10).

The choice of materials for transparent windows for enclosing radar equipment in aircraft and guided missiles narrowed to a few sintered ceramic materials (mainly high-alumina) and special refractory glasses (Pyroceram). The size requirements and the necessity for close tolerances on the dielectric constant, wall thickness and shape of the radomes imposed new problems in their fabrication (Smyth, 1957). The problems related to forming, firing, and surface-machining techniques.

Smoke (1957) described the fabrication of dense ceramic radomes by casting. Dorsey (1958) and Ault and Milligan (1959) described flame-spraying methods. The former claimed that silica, alone, or with additions, was the only material that could be fabricated to a dense deposit. The latter prepared thin, dimensionally controlled alumina radomes by flame-spraying a coating of potassium chloride over an aluminum form, by flame-spraying a coating of alumina over the salt, by dissolving the salt to facilitate removal of the alumina shell, and by firing the shell to an impervious structure. Isostatic forming either over or within a nonyielding mandrel, appears to be a more favored method of forming at present.

Ward and Passmore (1960) described diamond-grinding techniques for finishing sintered alumina radomes. Thomas (1963) stated that a single machine has been developed to perform all the grinding operations, except finishing the outer diameter on alumina ogival nose cones. The surface, chamfer, inside diameter, contour and plunge grinding and core drilling operations were described, with details of feed rates and speeds. The claimed accuracy was 0.0005 inch for size and contour shape from piece to piece.

Smoke and Koenig (1962, 1963) developed high-alumina radome bodies containing 94 and 96% Al_2O_3, that had excellent engineering properties when matured in the range 1430 to 1540°C. The favorable maturing conditions were ascribed to a presintering process in which the fluxing agents were more homogeneously distributed than in usual one-fire processes. Magnesium carbonate and magnesium fluoride were the sources of magnesia. Substitution of aluminum oxide-oxychloride for the alumina resulted in a very high-density body (Smoke et al., 1962). Atlas (1958, 1960) prepared very high purity alumina from 99.999% aluminum in order to control the electrical properties of radomes made from it.

Metzger (1957) designed light-weight radomes, in one of which a half-wave wall construction, electrically homogeneous was proposed. A sandwich construction was used (dense skins,

light cores). The radome wall thickness is related to the wavelength of the radar frequency by the expression:

$$d = \frac{n\lambda}{2(\epsilon - \sin^2\theta)^{1/2}} \quad , \text{ in which d = the approximate}$$

mechanical thickness, n = an integer, ϵ = the dielectric constant, θ = the effective angle of incidence of the radiation, and λ = the wavelength of the radiation.

Poulos, Elkins et al. (1962) investigated fused silica as a radome structural material. Fused silica has the advantage of a very low coefficient of thermal expansion (less than one-tenth that of sintered alumina), but is inferior in strength, refractoriness, and hardness.

During the Seventh Symposium on Electromagnetic Windows, Ohio State University, 1964 (Ref. Slonin), Guarini stated that supersonic velocities to mach 6 force designers to high-density, thin-walled, brittle ceramics. High-Q environments prohibit the use of most half-wave refractory walls, because of thermal shock. Two rain-erosion sled tests (NOTS and Sandia) showed that sintered alumina (Coors AD-99) survived the rain impact well beyond the peak velocity used in the tests. Competitive structural materials were not as satisfactory. Guarini concluded, however, that none of the structures, whether ceramic or reinforced plastic, could survive high-velocity flight (greater than 2.0 mach), unless the radome shape was sufficiently sharp.

Wheeler, Winslow, and Gates (Ref. Slonin) recommended sintered alumina for matching to niobium, but zircon and mullite for matching to molybdenum, in the design of slot closures for an antenna operating at 1370°C. The favored forming method was by spraying the alumina onto the mandrel from an alcohol vehicle containing an organic binder.

Loyet and Yoshitani (Ref. Slonin) described sandwich types of radomes in which the skins have either a higher (A-type) or a lower (B-type) dielectric constant than the core. Type A radomes have been developed at Interpace (International Pipe and Ceramics Corp.), that appear to be more suitable than any single-structure form that has been so far developed (Caldwell, 1962; LeClercq, 1962; Caldwell and Gdula, 1962).

Dense alumina is mandatory for the resistance to rainfall. The electrical and thermal properties are also better than those of the devitrified ceramics.

N. F. Dow (1961) showed that 25-micron filaments, 2 inches long, dispersed in a ceramic matrix of the same modulus of elasticity, require a bond strength 1/8000 the tensile

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strength of the fibers. B. D. Coleman (1958) demonstrated that the strength of a group of parallel filaments is determined by the variation of individual strengths about the average. From statistical considerations, a bundle of filaments with individual variations 30% of the mean could support a load of only 60% of the average strength. If the filaments are not completely parallel, the reinforcement is still further reduced. Lockhart (1965) had difficulty in dispersing alumina whiskers in initial attempts at reinforcement of alumina ceramics matured at 1427°C to over 80% of maximum density by use of MnO_2 or $MgTiO_3$ used as sintering aids. The filament-loaded, slip-cast bars cracked severely during air-drying, and later failed in bending tests. High shear stresses between the matrix and filaments were obtained, however, at 50 vol % fiber loadings in the ceramic.

Aves (1959) claimed that the most satisfactory protection for backup plates of rockets for re-entry at 2760°C was alternate layers of flame-sprayed molybdenum and alumina. Trout (1960) compared these coatings with other prospective types. A. V. Levy (1959) recommended flame-sprayed or troweled alumina for insulating airborne power plants. Pellini and Harris (1960) gave detailed requirements and possible solutions to the problems involved in thermal protection of heat sink systems, ablation, sublimation, transpiration, and radiation systems in flight in the thermosphere. Grindle and Rosenbery (1964) simulated re-entry conditions at mach 3 to 7 velocities in a plasma arc re-entry tunnel using nitrogen and oxygen as the operating gas. Miller and Wheeler (1958) described the potential applications of ceramic materials for airframes. Ramke and Latva (1963) presented the favorable properties of ceramics for nose cones, leading edges, and insulation. Nowak (1961) discussed the material property requirements and test methods for ceramic materials for leading edges of hypersonic aircraft.

M. Levy (1963) found that flame-sprayed alumina was successful in preventing erosion of titanium and aluminum rocket nozzle components for at least one firing. B. W. Lewis (1961) found an alumina cermet was one of the least affected of 22 refractory materials investigated to withstand a mach 2 jet at a stagnation temperature of 2095°C.

Bradstreet (1961) reviewed the problems encountered in attaching ceramic coatings for high-temperature service. The "tailoring" of protective coatings for refractory metals was suggested. Cavanaugh and Sterry (1961) suggested ablative protective coatings against thermal shock for radomes on an advanced interceptor). Blome and Kummer (1964) described the use of alumina in the glide-re-entry vehicle ASSET (McDonnell Aircraft Corp.). In one antenna, a 99% alumina ceramic (Coors AD-99) was used, metallized and brazed to a Kovar retainer.

Vincent (1960) described the testing and operation of Avco ceramic re-entry vehicles on the Martin Titan ICBM. W. H. Wheeler (1963) evaluated the properties of low-density ceramic foams, laminated composites, and high-density, high-strength materials as heat shields. High emissivity is required to keep wall temperatures within practical limits. Merry and Vondracek (1963) found three specific uses for flame-sprayed alumina coatings: as electrical insulation on an aircraft generator, a mounting bar for an edge-wound resistor, and a tube furnace.

Wilkins, Lodwig, and Greene collected the free energy functions for 47 gases and 9 condensed species containing the chemical elements, lithium, boron, and aluminum, free and in combination with hydrogen, oxygen, nitrogen, and fluorine. The theoretical flame temperatures and the primary metallic chemical species in flames containing these metals were determined because of their relation to rocket propulsion.

25 SEALS, METALLIZING, WELDING

Polycrystalline alumina and sapphire forms are subjected to joining operations of the types: alumina to metal, alumina to itself or other crystalline ceramic, and alumina to glass. The development of sintered alumina envelopes for high-wattage electron tubes, cutting tools, the potential use of cermets in gas turbines, and the application of sapphire windows to thermionic converters and other devices, are examples of equipment requiring rugged seals, capable of holding impermeable to leakage and at increasingly high temperatures.

The German firms, Siemens and Halske, Telefunken, and AEG had begun investigations on ceramic sealing about 1934, and had developed disk seals by means of thin metal interfaces by 1943. A symposium on ceramics and ceramic-metal seals was held at Rutgers University in 1953 to discuss problems related generally to electron tubes. Metallizing and metal-to-ceramic seals have probably drawn the greatest attention. Palmour reviewed the high-temperature metal-ceramic seal literature prior to 1955; Van Houten surveyed the art in 1959.

Burnside classified bonding with an intermediate layer into nine divisions: (1) bonds produced by firing a metal oxide on the ceramic surface, and reducing it to the metal; (2) bonds produced by firing laminates bearing metal and ceramic powders in varying proportions; (3) bonds produced by hot-pressing, for example at 1000°C, 3000 psi in nitrogen or vacuum; (4,5) bonds produced with active metals, active alloys, or active metal hydrides; (6) bonds produced using glazes in an oxidizing atmosphere; (7) bonds produced using glazes and metal powders in a reducing atmosphere; (8, 9) bonds produced using refractory metal powders with or without manganese for continuity, copper or nickel for build-up, and solder for the final bond.

Bonding techniques in use circa 1959, according to Van Houten included the Mo-Mn, the hydride, and the active metals processes. The Mo-Mn process is generally ascribed to Pulfrich (1939), although Vatter (Siemens and Halske, 1935) also claimed the process. The Vatter patents describe vacuum sintering of the ceramic after coating with iron, chromium, nickel, or tungsten, with or without additions of manganese. After metallizing, the ceramics could be joined to gold, silver, copper, or their alloys. The Pulfrich disclosures describe painting a layer of molybdenum, rhenium, or tungsten (in a suitable binder) onto a nonporous ceramic surface in a controlled atmosphere to obtain a platable or solderable surface. Nolte and Spurek (1950) substituted manganese powder for iron. The British Thomson-Houston Co. (1951) included nickel, and fired in a vacuum. The Mo-Mn process

is claimed to be relatively insensitive to small changes in the process, hardly the case with the Ni-Fe-Mo process (Telefunken). This latter process has been modified by the substitution of tungsten for molybdenum, additions of iron or manganese, or the use of MoO_3, reduced directly on the ceramic. Coatings of nickel or copper are placed over the molybdenum to aid wetting by the silver. The method was performed in hydrogen (Bender, 1955).

The hydrides of titanium and zirconium were found particularly active in producing low-temperature bonds with ceramics (Bondley, 1951). A metallizing and bonding patent was issued to F. C. Kelley in 1951 for TiH_2-ZrH_2-Cu bonds that could be developed at only 400°C. The decomposition of the hydrides liberates active hydrogen which is effective in cleaning the surface to be bonded. A typical reference to use of a hydride involves the low-melting eutectic (878°C) composed of 72 wt % copper - 28% titanium hydride. Strong bonding is possible by the method, using silver, copper, lead, or other solders.

Active metal films of titanium or zirconium are easily welded to glass. Vapor deposition of metal films of chromium, titanium, and silicon had been deposited by spraying the volatile chlorides onto the work, and molybdenum, tungsten and tantalum films were deposited by reduction of the volatile chlorides (Van Houten).

Cronin (1956) discussed trends in the design of magnetrons and the transition from glass-bonded, through glass-bonded ceramic, to ceramic-to-metal seals. Hynes (1956) described the forming, firing, and grinding requirements of alumina for use in ceramic-to-metal seals. The sandwich-type seal was designed primarily for the construction of output windows for magnetrons. The hydride-glass seal and sinter-type processes were used (Pryslak, 1955).

Knecht (1954) reviewed the Air Force projects on electron-tube, metal-ceramic structures, and cermets for gas turbines at different laboratories. Gallup and Dingwell described some low-temperature lead borosilicate glasses (70% PbO) for low-temperature electron-tube solders. Cole and Hynes concluded that higher seal strengths could be attained by closer control of firing temperature and flux content, and that the glass content is of prime importance in obtaining good seals. Denton and Rawson investigated the chemical reactions involved in metallizing high-alumina ceramics by two refractory-metal methods, the Mo-Mn and the MoO_3. They found that minor constituents in the ceramic are important, acidic oxides, such as SiO_2, being of great importance in the Mo-Mn technique, and basic oxides, such as MgO, being of more significance in the MoO_3 technique. Best results were obtained with fine crystal

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size.

Sterry investigated the brazing of alumina to titanium and molybdenum with silver and copper-silver eutectic. Brazed joints develop higher strengths than clamped or pinned joints. Suitable ceramics include, among others, alumina, calcium aluminate and germanate glasses, sapphire, phosphate-bonded composites, and Pyroceram. In the nuclear and missile fields, most radio tube assemblies use high-alumina ceramics, and the brazing is best accomplished, by the Mo-Mn or the active alloy method (Lerman, 1961). In the former, the ceramic is cleaned, coated with the metal, sintered, cooled, and nickel plated before assembly with the metal component. In the active alloy method, titanium or zirconium is contacted with the two ceramic parts, or one ceramic and one metal part in a vacuum or neutral atmosphere, and heated. The active metal reduces some of the ceramic oxide. Cole and Sommer (1961) claimed that the glassy phase in the high-alumina ceramic migrates into the interstices of the molybdenum-based coating when using Mo-Mn, Mo-Ti, and pure Mo metallizing agents on 94 and 99% Al_2O_3 compositions.

Pincus (1954) concluded that the experimental evidence on molybdenum-alumina interactions point to the need for a controlled amount of oxide on the metal, available at the metal-ceramic interface, as an essential step in the establishment of strong ceramic-to-metal bonds. When molybdenum metal is used as the starting material, adherence is not satisfactory until a sufficiently high temperature has been reached to cause dissociation of oxide of the ceramic. When molybdenum oxide is used as the initial coating, adherence and interpenetration occur at lower temperature, and more uniformly. Floyd investigated the mechanism of adherence of 80 Mo-20 Mn powdered metal to a high-alumina ceramic containing glass, and concluded that the weakest bonds were caused by formation of a modified $MnAl_2O_4$ spinel at the metal-ceramic interface. Greater bond strength was observed as the spinel was moved from the interface into the voids of the metal coating. The metal-alumina reaction theory and the glass-penetration theory were both believed to apply.

Some patents of interest include the following: KLG Sparking Plugs (1954) applied an oxide film to the bonding metal. Dijksterhuis and Hovingh (1957) added a thin layer of a metal such as Ag, Au, Cu, Ni, Fe, Co, or Mn, or alloys of these to the active-metal process, which dissolves part of the titanium or zirconium, when melted. Cohen, Herbst, Jenkins, and Wilkinson (1960) join titanium or zirconium to a suitably matching ceramic by brazing in an inert atmosphere with Cu, Ag, or Au, and other metals may then be brazed to the titanium or zirconium. Louden and Homonnay (1963) stacked in sequence an alumina backup ring, a thin titanium washer shim, an end cap,

another shim, an alumina tube, and another assembly of shim, end cap, shim, and alumina backup ring. The end caps consisted of an Fe-Co-Ni alloy in approximately 48-26-26 proportions. The stacked parts were heated in a nonoxidizing atmosphere at 955 to 1060°C to obtain a sealed device. Ross bonded polycrystalline alumina shapes with Nb, Ti, Pt, Ta, Mo, W, Ni, Cr, or stainless steel by using a powdered glass consisting of equal parts of alumina and calcia. The assembly was heated above the melting point of the glass, but below the melting points of metal and the ceramic. Elms (1964) sprayed the surface of 99.5 to 99.9% Al_2O_3 bodies with a mixture containing from 5 to 40 wt % powdered TiN or TiC, the remainder being powdered molybdenum, suspended in a resin, gum, wax, or nitrocellulose lacquer base material. The assembly was fired at 1450 to 1900°C in hydrogen (dew point > 4°). The metallized layer was then nickel plated and brazed. Mackey (1963) sintered a paint coating on vacuum-tube elements to be joined, consisting of 1200 parts powdered molybdenum, 200 parts powdered manganese, ground in petroleum solvent containing manganese stearate 200 parts, and titania (100 g per gallon of ball mill capacity). Beggs (1958) inserted a metal shim (titanium, zirconium, hafnium, thorium, or an alloy of more than one metal of the group) between the ceramic surface and the other metal member to be joined, selected from the group: copper, nickel, iron, molybdenum, chromium, platinum, cobalt, and alloys of others in the group. The stack was heated in a nonreactive atmosphere to a temperature at least equal to the melting point of the eutectic alloy of the metal member and the metal shim member.

Mesick formed gas-tight seals between the ceramic and a metal surface by applying a thin coating (less than 15 mg/cm²) of an oxide selected from the group, molybdenum, tungsten, and mixtures of these. The coated assembly was fired in a reducing atmosphere. Umblia (1958) applied a layer of powdered mixture, 60 to 95% from the group: molybdenum, tungsten or rhenium, 5 to 40% of an easily deoxidizable metal from the class: nickel or cobalt, and 0.05 to 0.5% of an oxide from one of these metals. The member and layer were heated to 1200 to 1350°C in an inert atmosphere. Luks and Powell (1958) coated the ceramic, refractory body with a metallic glass consisting of 5 to 30 wt % of a powdered metal (molybdenum or tungsten), 40 to 85% of a powdered heavy metal (nickel, cobalt, or iron), a powdered manganese component not exceeding 35% as elemental manganese, and 5 to 30% powdered glass. The glass was fused to the body at 815 to 1260°C, and soldered for subsequent bonding. Nolte (1959) metallized pure alumina bodies with a powder containing 20% Cr and 80% Mo, and fired at 1625°C for high heat-shock uses. Rhoads and Berg (1961) silk-screened a uniform layer of powdered molybdenum, tungsten, molybdenum-copper, or molybdenum trioxide, fired to sinter the material, silk-screened a second mixture of powdered nickel or copper, dried the second layer, applied another layer of a hard solder and pressed the metal member

into contact, and finally heated to seal the members together.
B. R. Smith metallized the ceramic by applying a coat of
powdered tungsten, molybdenum, or manganese, and by firing in a
reducing atmosphere at about 1700°C until the ceramic was bonded
and all binders, vehicles and plasticizing agents were de-
composed.

LaForge metallized vacuum tube envelopes by coating the
ceramic with a metal molybdate or a metal tungstate, firing
in an oxidizing atmosphere at 1125 to 1040°C for 2 to 20
minutes to produce a glassy surface, and by firing in a
reducing atmosphere at 1300 to 1225°C to provide an outer
surface of metal integrally united with and overlying the glassy
surface. Woerner (1962) coated the alumina ceramic with a
suspension containing at least 1% finely divided borosilicate
glass, free from materials reducible in hydrogen, and manganese
oxide molybdenum oxide, and optionally tungsten oxide. The
bond is matured at 1600°C in a hydrogen atmosphere. Omley
obtained a hermetic seal between sintered alumina and a solid
pin of nickel-iron-cobalt alloy by use of an alloy having the
approximate composition: 60% silver, 27% copper, and 13%
indium.

McDonald and Whitemore metallized with a carbide (major
portion tungsten carbide, minor portion titanium carbide).
The film was fired in a hydrogen atmosphere. A metallized sur-
face of nickel, cobalt, or iron was formed on the surface
for brazing. Grattidge (1958) formed a metal surface on a high-
alumina body by applying one or more layers of a mixture of
alumina and an oxide of iron or chromium, the alumina consti-
tuting 30 to 90%, then applying a layer of either platinum or
iridium and heating in an oxygen-containing atmosphere to 1200
to 1600°C for platinum and 1200 to 1750°C for iridium to obtain
a bond between the body and the applied metal layer.

Some more recent investigations are as follows:

Cowan (1964) described the bonding of tungsten to sintered
alumina containing from 0.05 to 2% yttria. Yttria was substi-
tuted for glassy fluxes in sintering alumina to be used for
thermionic converters because of the attack by cesium vapor. At
a metallizing temperature of 1600 to 1800°C, tungsten powder
coatings in a mixed atmosphere, 96% hydrogen, 4% water vapor,
developed bond strengths of 4,000 to 10,000 psi.

Bristow (1964) used active alloys such as TiN_3 to seal a
thermionic converter at 700 to 900°C. Leaks were unsatisfactory
above 600°C because of continued reaction of the sealing alloy.
The alumina-nickel bond, sealed by TiN_3 deteriorates to a weaker
bond above 900°C.

Fox and Slaughter observed that metallizing is unsatis-
factory in nuclear environments. Most sealing operations

require pre-metallizing - then brazing. Two experimental brazing alloys were developed, Ti 48 wt %-Zr 48%-Be 4%, and Ti 49%-Cu 49%-Be 2%. The latter provides good brazing-bonding to sintered alumina and uranium dioxide in a vacuum or inert atmosphere. The 5% beryllium in the alloy reduces the melting point of zirconium below 900°C. The fabrication of a synthetic sapphire Hall cell was demonstrated.

Mattox produced active-metal seals (chromium and titanium) on sintered alumina (Coors AD-99) by first applying a dc gas discharge at about 5000 ev to clean the surface and to ionize a portion of the metal atoms. The required time was about 20 minutes for cleaning and 20 minutes for deposition. Bond strengths of 3000 to 7000 psi were claimed.

Fulrath and Hollar sealed molybdenum to a 99% Al_2O_3 body by the use of a glass having the composition 50% MnO, 20% Al_2O_3, and 30% SiO_2, and a coefficient of thermal expansion of about 7.0×10^{-6} (20 to 600°C), between that of the molybdenum (5.9×10^{-6}) and that of alumina (7.2×10^{-6}). By proper adjustment of the concentration of molybdenum powder, tensile strengths of about 8000 psi were achieved. The addition of the glass to the metallizing solution allowed sealing to sapphire. Some devitrification to galaxite was observed.

Williams and Nielsen, and Sutton and Feingold used the sessile-drop method to appraise the wetting obtainable by coatings and brazing solders during metallizing.

Tentarelli and White (1964) developed a low-temperature ceramic seal applicable to 99.5% Al_2O_3 bodies, using a metallizing paint of MoO_3-MnO_2 suspended in a butyl alcohol-butyl acetate-naphthenic acid mixture. A Cu-CuO braze was applied at 1100°C in a wet ammonium hydroxide atmosphere at 900 or 1150°C (not at 1000°C). Tensile strengths as high as 17,000 psi were attained.

Reed and McRae found that molybdenum can be evaporated onto 94% Al_2O_3 bodies and sapphire to provide vacuum-tight seals having about 20,000 psi tensile strength for 94% Al_2O_3 compositions and 10,000 psi for sapphire. The seal was resistive to potassium vapor at 550°C. L. Reed (1964) stated that the factors affecting the integrity of a ceramic-to-metal seal include sintering, surface energy, thermal expansion of the components involved, strength of the crystalline phase, and devitrification of the glassy phase. Crystallites precipitate from the glassy phase above 1100°C. Glassy phase disappears from the high-alumina compositions. The active metal sealing types include Ti, Zr, V, Be, generally alloyed with Ni, for example, Ni-Ti. Brittle alloys are formed, as for example by the equation: $BeO + Ti = Be + TiO_x$
The refractory metal metallizing method uses glass bonding,

for example, the system $Al_2O_3-Al_2O_3 \cdot SiO_2-M_x$, to provide tensile strength of about 5000 psi. Sapphire requires a paint (a glass melt for molybdenum). The metallizing paints consist of MnO, SiO_2, etc.

Anderson and Stepp (1962) described the fabrication of glass-to-sapphire end-window seals capable of holding 2×10^{-6} mm Hg vacuum with no noticeable effect of attack when exposed to sodium vapor at 400°C for 4 hours. Reinhart (1961) collected a review of American and European literature on ceramic-to-ceramic and ceramic-to-glass seals. Hokansen, Rogers, and Kern (1963) presented details on the welding of alumina to alumina, tungsten, molybdenum, niobium, and Kovar by the electron beam. Kessler described a novel method for sealing glass by pressing aluminum foil between the surfaces to be joined at high pressures and at a temperature lower than the melting point of the aluminum and the softening point of the glass. Diffusion of aluminum atoms appears to replace silicon atoms in the glass structure.

An example of an early spark plug porcelain seal between the ceramic and the electrode is a lead borosilicate glass around a nickel-iron-cobalt alloy (Bosch, 1942). More recent examples of seals for high-alumina spark plugs are the following: Schwartzwalder and Somers (1958) mixed from 50 to 90 parts by weight of calcium aluminate with 20 to 60 parts of phosphoric acid (25 to 75 wt %). The exothermic reaction that ensues should not be allowed to go above 21°C (70°F). The mixture can be stored for several hours at about 4°C, or for longer periods at -12°C. Somers and Schwartzwalder (1959) described a cement consisting of 3 parts calcium aluminate and 2 to 2.5 parts sodium silicate containing 50 to 65% water and having a ratio $Na_2O:SiO_2$ of 1:1.5 to 1:2.5.

26 FIBERS, WHISKERS, FILAMENTS

26-1 INTRODUCTION

Much interest has developed in applications of ceramic fibers, in particular synthetic continuous fibers and whiskers, because of their high tensile strengths. Fiber-reinforced structures are probably the solution to some problems in hypersonic aircraft and missiles. Since methods have been found to produce aluminum oxide both as single-crystal and polycrystalline fibers (Section 3-9), it is a likely contender in these applications directly. It also is involved in high-alumina-silica glass fibers for the more general large-volume applications of the special glasses in textiles, insulation, and reinforced plastics, an industry that totaled over 1.2 billion pounds in 1963 (Ref. "Glass," Chem. & Eng. News).

McCreight, Rauch, and Sutton (1965) have compiled a current report on the state of the art of ceramic fiber production. The following data, Table 17, taken from Figure 1 of that report (page 4) show the comparative tensile strengths for virgin glass fibers (S-glass and E-glass of Owens-Corning) and alpha alumina fibers (Brenner, 1962). Also included are data for Houze glass No. 29 (Ceramic Industry, April 11, 1964, p. 108).

Table 17
Tensile Strength of Ceramic Fibers (1000 psi)

Temp., °C	α-Al$_2$O$_3$	S-Glass	E-Glass	Houze No. 29-A
20	900	700	500	680
250	880	600	450	670
500	800	450	270	630
800	750	130	-	410
1000	570	-	-	
1500	300	-	-	
1900	150	-	-	

26-2 ALUMINA FIBERS

Brenner (1962), from theoretical considerations, concluded that the upper limit of the strength of alumina (S_f) as a function of the modulus of elasticity is $0.17E$, and has found about $0.16E$ experimentally. The lower limit, because of

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plastic deformation is about 0.03E, or an average Sf of about
0.1E. The conventional determination of tensile strength on
rods is usually as low as 0.001E. His experimental room-
temperature values for alumina fiber were about 0.099E. Room
temperature values for different fiber types, assembled by
McCreight et al., show only 0.018E to 0.055E for strong glasses,
0.081E for fused silica, 0.005E to 0.021E for metals of the
continuous filament types, 0.002E to 0.066E for metals of the
discontinuous (whisker) type, and 0.036E for graphite.
Competitive ceramic fibers, including BeO at 0.47E, B_4C at
0.013E, and SiC at 0.024E, were also weaker than alumina.
The best compositions for fabrication purposes have the lowest
density/$E^{1/3}$ values and the highest use temperatures. Alumina
falls in a favorable position in this respect, in comparison with
other potential ceramic materials.

General references to the state of the art of fiber and
whisker production and the progress in fiber metallurgy are
discussed in the following: C. Z. Carroll-Porczynski,
Refractory Fibers, Fibrous Metals, and Composites, 1962; Baskey
(1962); Anon. "Developments to Watch," 1964; Accountius (1963);
Bradstreet (1964); Bartlett and Ogden (1965); Krock and Kelsey
(1965); and McClure (1965).

Several methods have been found to produce single-crystal
alumina fibers from the vapor state, among which are the
following: the oxidation of an aluminum halide and nucleation
on a powder substrate by either batch or continuous process
(W. B. Campbell, Lexington Laboratories, 1963); the vapor
deposition at 1370 to 1510°C onto a cooled substrate (Wainer
and Cunningham, Horizons, Inc., 1963); and by vapor de-
position from aluminum chloride in a controlled mixture of CO_2
and H_2 at reduced pressure (Brisbin and Heffernan, 1963). Vapor
deposition onto a heated resistance wire (W, Ni, Ti, Mo),
produces composite filaments containing a core surrounded by a
polycrystalline (or amorphous) coating (Davies et al. (1965).

Fibers produced by vapor deposition are almost devoid of
flaws. Webb, Wissler, and Forgeng (1961) reacted aluminum or
an aluminide of Zr, Hf, V, Nb, Ta, Cr, Mo, or W at 1300 to
2050°C in hydrogen-water vapor atmosphere, and condensed fibrous
single crystals of alpha aluminum oxide onto an aluminum oxide
substrate. The claimed tensile strengths are around one
million psi or higher. The tensile strength is found to be
dependent upon size, due to the greater probability of flaws with
increasing size (Brenner, 1956, Regester 1963). Brenner (1962)
claimed that sapphire whiskers develop high tensile strength,
averaging about 900,000 psi at room temperature, but falling

with increasing temperature. However, the fibers were found to be stronger at 20° below the melting point than bulk sapphire at room temperature. Lynch, Valdiek, and Robinson concluded that impurities appear to be necessary to obtain good whisker growth, since they were able to grow whiskers from less pure grades of alumina containing SiO_2 and Fe_2O_3 as major impurities under conditions which failed to produce fibers from pure grades of alumina. Additional references to apparatus for producing whiskers, and their growth on various substrates were furnished by Hoffman (1958), Hargreaves (1961), Edwards and Happel (1962), Mazer and Straughan (1963), Coleman (1964), and Gatti (1964). Soltis (1964) found that the mechanical behavior of sapphire fibers was anisotropic, being weaker in the c-axis direction, than in a_1, $\langle 11\bar{2}0 \rangle$, or a_{11}, $\langle 1\bar{1}00 \rangle$.

Brenner (1962) proposed the use of alumina fibers for producing whisker metal composites of high strength at elevated temperatures. Sutton (1962, 1963, 1964), Sutton and Chorne, and Sutton and Feingold investigated the bonding of high-strength, heat-resistant metals and alloys for space vehicle applications. Silver, reinforced with sapphire whiskers, is 20 times stronger at 760°C in tension than pure silver under similar conditions. The strengthening was retained to large extent to within about 20°C from the melting point of silver (960°C). Other alumina fiber-metal composites were investigated by Price and Wagner, Ellis (1964), Wagner (1964), Salkind, Morley, and Sicka et al. (1964). Wagner (1963) described techniques for reinforcing ceramic matrices with metal filaments as well as the reinforcement of a metal with ceramic whiskers. Hill discussed the theory of the mechanical properties with respect to the elastic and inelastic behavior of the composite. Sutton, Rosen, and Flom found that reinforced epoxy resin (14 volume % alumina whiskers) developed tensile strength of about 140,000 psi, and Young's modulus of 6×10^6 psi. The original plastic had a tensile strength of about 12,000 psi and Young's modulus of 0.4×10^6 psi. Short-fiber-reinforced plastics usually develop about 50,000 psi tensile strength, but with continuous fibers, about 250,000 psi. Milewski also investigated whisker-reinforced plastics, and Schuster and Scala their interaction mechanically with a birefringent plastic, to develop the strain behavior.

Lockhart (1964) reported on the use of whisker alumina in the fabrication of an electromagnetic window in an environment of 1370°C. At high fiber loading in the ceramic matrix (50 vol %), the shear stress between the matrix and filament reached high values near the broken filament values. In a previous report, it had been observed that the critical diameter was about 50 microns; below this size cracks were rare.

Polycrystalline fibers could be grown by extrusion of

alumina pastes through spinnerets. Wainer and Beasley, and
Beasley and Johns (1963) spread colloidal suspensions of
alumina in thin layers on a nonsticking base, and evaporated the
moisture rapidly to form gels that cracked into fiber structures
of rectangular cross-section. The tensile strength of such
polycrystalline structures is low, particularly if the crystal
size approaches the fiber diameter in magnitude. Bugosh (1963)
used colloidal fibrous boehmite in producing fibers of gamma
alumina at 300 to 850°C, without change in the particle size
or shape, and to alpha alumina above 1000°C.

26-3 GLASS FIBERS

The chemical compositions of some ceramic and glass fibers
are shown in Table 18.

Ceramic fibers for refractory applications may contain
about 50% Al_2O_3. Fiberfrax, a product of the Carborundum
Company, is based on the investigations of J. C. McMullen.
The optimum mix consists of 50 parts Bayer alumina, 50 parts
flint, and 1.5 parts borax, melted and poured at 1870°C. Short
and long staple fibers in diameters less than 3 to 40 microns
(average 10 microns) have a maximum use temperature of 1260°C
(2300°F), coarser fibers around 80 microns, about 870°C (1600°F).
The tensile strength is about 180,000 psi (Straka, 1961).
Kaowool, a product of Babcock and Wilcox, contains about 45%
Al_2O_3, derived from clay minerals, and has a claimed use tem-
perature of at least 1200°C. Both have good insulation value
in the form of loose wool or batts. The material is available
also as short fibers, yarns, rovings, felts, papers, and coating
cements. Blocks, boards, and castables can be prepared from
the fibers. At a hot-face temperature of 1100°C, a 2-inch
thickness of the Fiberfrax forms assures a cold face tempera-
ture of about 220°C for the bulk wool, 400°C for the paper,
180°C for the blanket, and 190°C for the block. The bulk and
blanket form have been used in preheating and stress relief of
large units during welding, in jet-engine acoustical dampers,
and in furnace back-up insulation (Straka). The retention of
resilience at high temperatures reduces the mechanical dete-
rioration of the brick overlay in rotary kilns.

Walworth (1957) suggested several thermal, acoustical, and
electrical insulating applications, and uses in filters, gaskets,
and packings. Basic properties were listed, as well as those
for the different forms. First, Graham et al. prepared a
graded-fiber filter of 4, 8, and 20 microns fiber diameter,
providing 99% efficiency at 760°C in filtering a specific
aerosol. Filter performance data were used to solve other
filtration problems.

Lambertson, Aiken, and Girard (1961) performed melting

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and fining of refractory glass compositions, and the drawing
of continuous-filament, ceramic fibers in a dry inert-atmos-
phere glovebox, which permitted the use of refractory metals,
graphite, and boron nitride as crucible and heater materials,
and prevented the adsorption of moisture by the filaments.
Refractory glasses in the $BaO-Al_2O_3-SiO_2$, $CaO-Al_2O_3-SiO_2$, and
$MgO-Al_2O_3-SiO_2$ systems were successfully drawn into continuous
filaments. Tensile strengths as high as 138,000 psi at room
temperature and 132,000 psi at 815°C were obtained.

Analytical data on a few glass fiber types are shown in
Table 18.

Table 18
Types of Ceramic Fibers

Ref. Types	(1) E	(2) 29-A	(3)	(4) "Fiberfrax" (charge)	(5) "Kaowool"
Analysis (%)					
Al_2O_3	14.0	35.0	52.8	49.3	45.1
SiO_2	54.0	46.8	0-12	49.3	51.9
Na_2O,K_2O	-	2.5	5.4	0.4	0.2
MgO	-	10.5	4.1		-
CaO	22.0		20.1		0.1
B_2O_3	10.0		0-5	1.0	0.08
ZnO					
ZrO_2		4.1	5.1		
TiO_2		0.09	3.3		1.7
BaO		-	9.2		
Fe_2O_3		0.88			1.3

(1) Tiede
(2) Provance, 1962
(3) Machlan, 1959
(4) Straka, 1961
(5) Babcock & Wilcox Circular 12-62

The glass fibers also represent an application of alumina
since some of the most successful types have fairly high Al_2O_3
contents, added as Bayer alumina. The major markets for glass
fibers are in insulation, textiles, and reinforced plastics.
Soda-lime-borosilicate glass is the leading insulation type,
since it is fireproof, heat-resistant, inert, and a better
insulator than mineral wool. Since Fiberglas (Owens-Corning)
was introduced commercially in the early 1930's, research has
aimed at stronger and finer fibers. In 1945 more than 4000
forms of fibers for hundreds of different applications had
developed (Ref. Anon. Research Responsible for Fiberglas).

A list of glass fiber manufacturers includes Owens-
Corning Fiberglas Corporation, Johns-Manville Fiber Glass
Division, Pittsburgh Plate Glass Company, Gustin-Bacon

Manufacturing Company, Ferro Corporation, and Modiglass Fibers, Inc., as some of the leading suppliers (Ref. Anon. Fiber Glass Manufacturers). DeDani (1955) described the manufacturing processes.

Alumina enters significantly into the compositions of the special fiber types: beta yarn, E, S, and M glasses. Beta fiber, aluminum borosilicate glass, is used for textiles, for curtains, and drapes. E-glass fibers (low-soda) develop high tensile strength (around 450,000 psi), but S-glass fibers, alkaline earth-aluminosilicate, develop tensile strengths as high as 750,000 psi. Hollow glass fibers with single filaments have an outside diameter of 15 microns, and an inner diameter of 9 microns, but some strength has been sacrificed for lightness and flexibility.

The primary area of uses for high-strength fibers is in composite-reinforcement of metals and plastics. The continuous ceramic fibers are only 10 to 20% as strong as the best whiskers in tensile strength, their usable strengths are about equal to those of glass fibers, and, additionally, provide an increase in elasticity several times that contributed by fiber glass. The greatest gains in fiber-reinforcement of metals with continuous fibers has apparently been the combination silica fiber-aluminum, as applied by Rolls Royce Ltd (Arridge, 1964). This, however, required the development of coatings for the silica fibers to reduce the thermitic reaction between them and molten aluminum. Cratchley and Baker (1964) obtained about twice the tensile strength for silica-reinforced aluminum as for a high-strength aluminum alloy RR-58, and even a greater superiority in comparison with 10% S.A.P. alloy. The strength of all three materials decreased beyond 300°C, but the reinforced aluminum retained its superiority in about the same relative ratio.

The glass fibers (and others) do not retain their pristine strength properties for several reasons. McCreight et al. (1965) classified the factors involved into four types: compositional, processing, structural, and testing. Compositional factors are corrosion, abrasion, atomic bonding, and the time-dependent properties, creep, stress-rupture, and stress-corrosion. The processing factors are those affecting surface perfection, degree of crystal size, if polycrystalline, etc. Structural factors relate to size and shape of the fiber, internal stresses, and defects. Testing methods vary and may themselves affect the results.

Based on theoretical estimates the tensile strength of glass should approach 3×10^6 psi. In bulk, the value may be about 10,000 psi. Anderegg (1939) presented data to show that strength increases with increasing fineness of the fibers. More recently, Otto (1955) and Thomas (1960) show no agreement

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with this over a wide range of fiber diameter (5 to 15 microns).
The values were not affected very markedly by variation in
the drawing temperature.

Flaws and chemical contamination of the fiber surfaces
reduce the strength, but the damage can be largely reduced
by chemical cleaning of the glass rod prior to drawing
(Holloway). It seems imperative to prevent abrasive contact
between the fibers. Low-alkali glasses do not necessarily
have higher tensile strength than high-alkali glasses, but
they resist abrasion relatively better. Coatings applied to
the fibers as soon as formed aid in preventing abrasion, but
at the expense of some loss in strength (Morrison et al.,
1962). There appears to be little choice between chemical bond-
ing and physical bonding, as by a resin, in protecting the sur-
face of the fiber.

Rapid cooling was believed to explain the difference in
strength between massive glass and fiber glass. Anderson(1958)
deduced simplified equations for the cooling time of the fibers
to show that the cooling time is about the same as the Maxwell
relaxation time of the glass at about 900°C. Otto and Preston
(1950) concluded that the glass fibers contracted equally in
all directions, hence the so-called Griffith flaws cannot be
oriented in any one direction.

Moisture was found to be a potent effect in causing a slow
decrease in strength of the fibers. The rate of deterioration
and the loss in strength increased with increasing temperature
(Holland, 1964).

27 MISCELLANEOUS CERAMIC APPLICATIONS OF ALUMINA

Specific applications of alumina not given extensive consideration in the preceding sections, have been collected under the general classification, "Miscellaneous Ceramic Applications of Alumina." Some of these applications involve no very significant consumption of alumina, and are merely representative of the wide range of uses that are dependent on the properties of the different alumina phases.

Thread Guides. Ceramic forms in the shape of loops are used for changing the direction of textile threads during forming or weaving. The wear of these pieces is considerably accelerated by additives to synthetic organic fibers such as titania, added to opacify or to dull and roughen the surface. Sintered alumina has high resistance to wear and chemical reaction of acid and alkaline solutions of synthetic fiber-formers. Ryshkewitch (1960) stated that flame-polished synthetic sapphire is less satisfactory than smooth, but not highly polished, polycrystalline alumina, because a too complete contact with the thread increases the friction. Acceptable surfaces should have small, rounded elevations. Alumina porcelain guides are satisfactory but inferior to pure sintered alumina. The service life is over 100 times that of the formerly used porcelain guides. Thurnauer (1945), and West (1964) described sintered oxide textile guides containing titania to increase the electrical conductivity in order to conduct off static electricity generated by thread friction. Ultraviolet irradiation might be used for a similar purpose.

Frictional Members. Herron (1955) and DuBois (1956) explored the field of frictional devices as applications of ceramics and cermets for service temperatures above 425°C. The desired characteristics in brake and clutch linings are: sufficient mechanical strength to withstand the operating stresses; a high and constant coefficient of friction with different speeds, loads, and temperatures; a low wear rate; low tendency to score the opposing surfaces; and smooth engaging characteristics. Thermal shock resistance is also a factor, since gradients as high as 800°C are possible. Thomson (1958) described a highly wear-resistant, sintered composition comprising up to 15% aluminum oxide particles dispersed in copper or copper-base alloy. Moore and Huffadine (1959) claimed a composition containing up to 40% aluminum oxide dispersed in a molybdenum-chromium alloy having substantially the same coefficient of thermal expansion as the alumina. Huntress (1963) dispersed the alumina in sintered powdered nickel or molybdenum aluminide, bonded with nickel.

Wear-Resistant Ceramic Articles. Erickson (1958) described applications of both hot- and cold-pressed ceramics for plug and

ring gauges, thread plug gauges, and various wear applications. Meyerson et al. (1960) described alumina gauge blocks of superior stability. Wheildon (1963) presented data on the use of sintered alumina and flame-sprayed oxide coatings for mold linings, mold arbors, mill linings, hammer protection, extrusion dies, etc. Twells (1950) produced gauges containing 90% Al_2O_3, and fired at 1680°C, from slip-cast compositions.

Sandmeyer (1959) recommended a fused-cast mill liner consisting of alumina and zirconia in the approximate ratio 5:4 (wt), bonded with a glassy matrix containing 1 to 2.5% alkali oxide, 0.1 to 0.5% B_2O_3, and 15% SiO_2. Such compositions show improved resistance to corrosion and erosion.

Ryshkewitch (1960) stated that sintered alumina was not satisfactory in use as air blasting nozzles because of its low impact resistance. A high-alumina composition containing a vitreous phase and manganese oxide was found more resistant to erosion by impingement of refractory grains, however, than steel.

Besides jewel bearings, gauges and mortars and pestles are prepared from synthetic sapphire (Anon. Sapphire Mortar; Anon. Sapphire Plug Gauge). Mortars and pestles are also made from formed polycrystalline alumina. Sapphire ball bearings in small sizes have been used, although their poorer load-bearing properties relative to steel and anisotropic wear have been a disadvantage. Sintered alumina has been used in fabricating gyros to precisions in parts per million for airborne directional controls.

Welding Rods for Steel. A welding rod compound to improve the weld quality of high-strength low-alloy Cr-Mn-Si-Ni steel contains a fused flux of 21.7 to 24.9% Al_2O_3, 23.8 to 28.8% SiO_2, 14.4 to 18.4% CaO, 9 to 11% MgO, 20 to 22.5% CaF_2, and 1.8 to 2.2% MnO (Makara et al., 1959). This was intended specifically for the peripheral welding of thin-walled tubes.

Nuclear Fuel Elements. A nuclear fuel element composition of the refractory oxide type contains a 50:50 mixture (wt) of coarser than 325-mesh particles of uranium dioxide (92% U^{235}, 8% U^{238}) and calcined alumina. During pressing, surface coatings consisting of 99% fine-ground calcined alumina and 1% of a mixture of $CaCO_3$, MgO, and SiO_2 are applied on both surfaces. The composite is fired for 15 hours at 1750°C and for three hours at 1700°C before cooling (Norton Grinding Wheel Co.,1960). Sheath failures caused by expansion of uranium dioxide fuel elements on melting have been reported by Pashos.

Aluminum Borates. Scholze (1956) and Berry (1963) describe the formation of fibrous aluminum borates. Scholze found that $2Al_2O_3 \cdot B_2O_3$ forms at 1000°C, while $9Al_2O_3 \cdot 2B_2O_3$ is formed at

1100°C, the latter having marked similarity to mullite. Berry found the ratio of length to width of the flexible fibers to be at least 10:1, and the length at least 0.7 mm. Recommended applications were for thermal insulation and filter media, in the form of felted mats, and as reinforcing agents for plastics, ceramics, and metals. Knapp (1962) recommended lithium borate as a pore-sealing agent for sintered alumina articles, when melted on the surface at 800 to 930°C.

Light Guide. The use and calibration of synthetic sapphire rods, for use in light-guide radiation pyrometry, have been described by Vollmer (1959).

Ozone Storage. Streng and Grosse (1961) describe the storage and transportation of gaseous ozone under pressure in a container packed with hollow porous alumina spheres, to prevent explosions and to increase the stability against decomposition.

Oil-Well Fracturing. Tabular alumina sintered balls have been used for "fracturing" plugged oil wells.

Color Modifiers. Alumina is used as a diluent in reducing the color of ceramic stains. It serves as the host, directly or in the form of an aluminate of beryllium, magnesium, calcium, strontium, barium, zinc, or cadmium, as a phosphor with various activators : manganese, chromium, gallium, iron, silver, or cerium (Crosby et al., 1959).

Fillers. Hydrated alumina and calcined alumina are used as fillers in epoxy resins and other organic resins and cements. The dielectric properties depend greatly on the shape and chemical composition of the filler (Dobrer, 1962). Applications are in potting electrical equipment. Calcined alumina is also used in thermosetting resins in wear-resistant journals and bearings.

Aluminum Oxide Films. The preparation of thin alumina films for electron tube windows, infrared transmission, and electron microscope specimen supports have been described by Walkenhorst (1947), Pupko (1949), and others. Amorphous disks as large as 2 to 3 inches in diameter have been prepared from aluminum foil, about 10 microns thick. Walkenhorst oxidized, anodically, pure aluminum foil in 3% ammonium citrate, and separated the film by dissolving the aluminum backing in 0.25% mercuric chloride solution. No structure could be observed in the film up to heating temperatures as high as 600°C, at magnifications of 40,000 times. The film thickness is linear with voltage, being 70 Å at 75 volts, and 275 Å at 200 volts. Pupko prepared the films by degreasing ordinary aluminum foil, anodized in an electrolyte of 1 part HNO_3 (density 1.35-1.40) and 2 parts methyl alcohol for 10 to 15 minutes at 0.3 to 0.35 amp/cm²,

4.0 to 4.5 volts, and 20°C. The specimens were withdrawn under the current, were washed, immersed in 4% H_3PO_4 (75%)- Cr_2O_3 (2%) solution, and again washed, dried, and anodized for 15 to 20 seconds. The foil disk was then immersed in saturated mercuric chloride to separate the film from the metal. Amorphous films about 100 to 300 Å thick were obtained.

Harris and Piper(1962) measured the tranmission and reflectance of aluminum oxide films in the far infrared.

Alumina in Greases. Marsden and Berstein (1960) thickened lubricating oil with a mixture of pyrogenic alumina and colloidal silica to form high-body greases. The pyrogenic alumina was prepared by the flame hydrolysis of an aluminum halide.

Analytical methods for appraising the structure of calcined alumina and sintered alumina are of ceramic interest. The literature on the analysis of alumina compositions, however, is too voluminous to be covered in this survey except for a few references. Wet chemical reaction methods depend on quick methods for dissolving alpha alumina under conditions in which the composition of the sample has not been prejudiced by excessive pickup of impurities during sample preparation or by loss of volatile constituents. For example, Jackson (1950) dissolved calcined alumina in hydrochloric acid in a sealed tube at 200°C for the complete solution of sodium ion. Archibald and McLeod (1952) found this method too time-consuming, as was also the case with the classical J. Lawrence Smith method (ignition with NH_4Cl and $CaCO_3$ in platinum). They claimed that sintering with boric acid or boric oxide provides a rapid method for bring the soda into solution; but sodium combinations with boron are among the most easily volatilized of sodium salts. Schmidt, and Koehler, and Schmidt (1959) found that, although corundum is not completely dissolved by heating with concentrated sulfuric acid (as it is by fusion with Li_2CO_3 and B_2O_3), the alkali content is quantitatively dissolved, making the solution adequate for the determination of alkali by flame photometry. Dawihl and Kuhn (1964) determined the sodium content of corundum by dissolving it in 80% H_2SO_4 solution at 220°C, and by applying flame photometry. Incomplete solubility was considered to indicate the presence of another alumina phase which is not soluble, but from which the acid extracts all the soda.

Many present methods are designed to simplify the analysis routinely for control of plant operations in the Bayer process. Rapid volumetric methods were demonstrated by Snyder (1945), for aluminum in the presence of from 1 to 10% Ca, Cu, Cr, Fe, Mg, Mn, and Zn; by Burkard (1943), and by Bushey (1948) for differentiating NaOH from $NaAlO_2$ by the sodium fluoride conversion; by Watts and Utley (1953, 1956) for determination of carbonate, hydroxide and alumina in sodium aluminate solutions, and for the direct replacement of both tartrate and barium in aluminum titrations by sodium gluconate; and by Watts (1958) for the direct determination of aluminum in the presence of Fe, Ti, Ca, Si, and other impurities, by precipitating the Ca with oxalate, and reacting the alumina with a fluoride, to release an equivalent of the Al as NaOH, which can be titrated with standard acid.

Reich and Grabbe (1957) improved a photoelectric colorimetric method for the rapid determination of alumina in refractory materials, using Eriochrome cyanine (mentioned by Giessen, Glemser, and Raulf), by refining the operations in the photometer,

by applying a correction for TiO_2, separately determined, by sequestering small amounts of Fe_2O_3 with thioglycolic acid, and by using the reagents in the proper aged condition.

Pranter and Konopicky (1948) recommended the direct determination of Al_2O_3 in refractory brick by decomposition with sodium peroxide and precipitation with oxine (4% oxyquinoline acetate) from a solution containing tartaric acid. Kassner and Ozier (1950) determined aluminum by precipitating with 8-hydroxyquinoline in ammoniacal solution containing tartrate, cyanide, and hydrogen peroxide.

Standard analytical methods for refractory materials have been developed by the American Society for Testing Materials (ASTM Std., 1961, Part V, pp 453-82).

Rapid quantitative and semiquantitative spectrographic methods for alumina and impurities in alumina have been devised by Churchill and Russell (1945), Steinberg and Belic (1949), Black and Lemieux (1957), Voinovitch and Vilnat (1957), Fitzgerald (1963), and Ryan and Ruh (1964), among others. The accuracy and reproducibility of quantitative spectrographic analysis of Al_2O_3 and SiO_2 in aluminosilicates were found to compare favorably with those of the traditional chemical methods. Ryan and Ruh restricted the influence of the cyanogen bands in the carbon arc emission by use of an argon-oxygen arc ambient.

Pfundt (1964) described the quantitative analysis of aluminum oxide by means of X-ray spectroscopy. X-ray fluorescence spectra covering the oxides of Ca, Fe, Si, Ti, V, Cr, Zn, enabled the estimation of trace elements as low as 0.003% in a sample containing about 99.2% Al_2O_3. The apparatus used was a Norelco Autrometer with 24 channels, equipped with an X-ray tube that can be loaded to 100 kv and 2.5 kw., a scintillation counter, a transmitting counter, and a 6-channel high-impulse discriminator. Calibration curves are obtained from standard samples in suitable concentrations for the concentration ranges of a given element in the sample.

The American Society for Testing Materials has provided X-Ray Powder Data File: Sections 1 to 5, Revised, containing the relative intensities of the interplanar spacings that are used for indexing 2095 cards in the inorganic section, for identification of the compounds in this section.

Wiele (1955) observed that in the determination of Al in alumina hydrates, differences had been found in the values calculated from loss on ignition. Careful tests with products made from pure aluminum showed a continuous decrease in weight of the substance with temperature. After calcining at 1400°C, the material was still hygroscopic and contained water. In

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technical alumina, the weight is constant only after calcining for one hour at 1500°C. The hygroscopic remanence was ascribed to the presence of gamma alumina and probably a sodium aluminum silicate. But residual soda also shows a tendency to slow volatilization. Milner and Gordon (1960) claimed that although other investigators have shown by thermogravimetric analysis of alumina precipitates that constant weight can be reached below 700°C, their evidence indicated the safe minimum temperature to be 1200°C for obtaining constant weight.

Jaeger (1953) determined the amount of beta alumina in fused corundum by fine grinding the material and separating the alpha form (d = 4.0) and beta form (d = 3.33) by flotation in methylene iodide (d = 3.33) or a saturated solution of $BaI_2 \cdot HgI_2$ (d = 3.57). This method would hardly be suitable in the case of Bayer alumina because of the intimacy of mixture of the two phases. Reichmann (1936) determined the extent of crystallization of calcined aluminum oxide by determining the intensity of coloring in an alizarine red dye suspension in water. Balkevich and Gol'dberg (1958) based the control of calcination of technical alumina on the change in bulk density, which in turn depends on the change in specific gravity and densification of the different grains. Adachi and Takahashi (1957) determined the degree of calcination by determining the amount of water required for "hydration," as measured by titrating with a normal solution of HCl the free alkali released on addition of sodium fluoride to the suspension in water. The free alkali, obtained by the reaction:

$6NaF + Al(OH)_3 = 3NaOH + 3NaF \cdot AlF_3$, represents aluminum hydroxide supposedly formed when water is chemically absorbed by calcined alumina. A more direct appraisal of the degree of calcination is by determination of the amount of water adsorbed under equilibrium conditions from a water vapor atmosphere saturated to some standard humidity. In technical alumina this method is influenced to a slight extent by the residual alkali and the form in which it is held in the alumina.

The determination of pore volume, crystal structure and crystal size of sintered alumina ceramics is of concern as a ceramic problem in production control.

Allen and Friedberg (1948) applied replica techniques to the study of ceramic surfaces with the optical microscope. Rigby, Thin-Section Mineralogy of Ceramic Materials (1948), Baumann, "Microscopy of High-Temperature Phenomena," Insley and Frechette, Microscopy of Ceramics and Cermets (1955)

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describe methods and techniques for making topographic studies of aluminum oxide. Frechette and Sephton (1949) described a method for determining particle size in the subsieve range, which included the dispersion of the sample in warm raw Canada balsam, the classification of individual particles with respect to Martin's diameter by means of an external scale which is visible through the camera lucida (Abbe' drawing camera), and examination of the mount at three successive magnifications. The respective particle counts were reduced to the same basis as percentage of the total sample either by a micrometer-driven stage or by an internal standard. Smith and Gutman (1953) described the measurement of internal boundaries in three-dimensional structures by random sectioning. Dillingham (1956) investigated the structure of sintered high-alumina surfaces, polished with 14, 6, 3 and 1-micron diamond abrasive, to show the appearance of the specimen at various stages of polishing. Polishing with 1-micron diamond grit leaves scratches that are generally visible by chemical etching methods (Elyard). Angelides (1961), and Swan (1963) described the use of diamond polishing powders for the relief polishing of high-alumina ceramics.

Ryshkewitch (1960), p 208, stated that polished sintered alumina shows no surface structural details unless it has been etched. Aqueous mineral acids do not attack rapidly enough, so it is more practical to use sodium hydroxide or acidic melts ($KHSO_4$, KHF_2, etc.). McVickers, Ford, and Dugdale (1962) etched in concentrated H_2SO_4 for 5 minutes at 270°C; H. D. Taylor (1963) used boiling H_2SO_4 for up to one minute on 92 to 99% Al_2O_3 sintered alumina, but 1 to 2% HF for 85 to 90% Al_2O_3 alumina; Bassi and Camona (1963) etched in a mixture of $KHSO_4$ and HBF_4 at about 130°C. Alford and Stephens (1963) and Tighe (1964) also used chemical methods.

Bierlein, Newkirk, and Mastel (1958) etched by ion bombardment, a method similar in almost all respects to the ion etching of metallic specimens. Beauchamp (1960) "flash" etched by raising the temperature of the specimen to the flame-polishing temperature (about 1900°C) with a slightly reducing oxyacetylene flame, and by holding for about 2 to 5 seconds at the temperature. Elyard claimed that both these latter methods were superior to chemical etching in producing much cleaner specimens. Thermal etching is easier to apply, and can be performed at 1600°C in air within a period of five minutes. Krokhina et al., etched by ionic bombardment in an inert gas at about 2.5 kv, 1 milliamp/cm², and for 5 to 7 hours to obtain sufficient structural definition.

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13. ABSTRACT

This comprehensive survey has been compiled to provide a sourcebook for aluminum oxide ceramic technology. The features and characteristics of high-temperature, transition and hydrated aluminas are presented in detail and are adequate for both engineering and scientific reference. Subjects discussed include nomenclature, natural occurrence and associations, beneficiation and preparation techniques, crystallographic features and mineralogical properties. Mechanical, thermal, sonic, electrical, magnetic, optical, radiation (nuclear), chemical, and colloidal properties are critically reviewed. The aspects of grinding, forming and sintering pertinent to production of refractories, and applications including uses in cement, glass, cermets, electrical insulation, thermal coatings and airborne equipment are given. An extensive bibliography is provided.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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