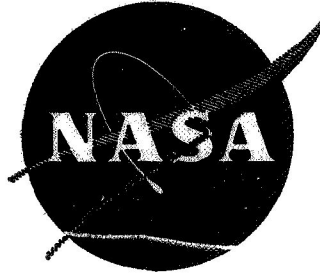


N71-23136

NASA-CR-72847

ADL 71965



APPLICATION OF YTTRIUM COATINGS ON  
CHROMIUM-BASE ALLOYS BY METALLIDING

By **CASE FILE  
COPY**

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA-LEWIS RESEARCH CENTER

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FINAL REPORT

APPLICATION OF YTTRIUM COATINGS ON CHROMIUM-BASE ALLOYS BY METALLIDING

By

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March 31, 1971

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## ABSTRACT

An attempt was made to form a dense, adherent yttrium oxide-chromium oxide coating on a high strength chromium alloy (Cr-7Mo-2Ta-0.09C-0.1(Y+La)), in order to protect the alloy from nitrogen embrittlement due to air exposure. Yttrium was deposited on the alloy surface electrolytically from a molten fluoride bath. Excess salt was removed by vacuum evaporation, and the mixed  $Y_2O_3$ - $Cr_2O_3$  was formed by preoxidation at 1500°F (1089°K) in  $H_2/H_2O$  gas mixtures. The coating failed to provide the necessary oxidation/nitridation resistance at 2100°F (1422°K), probably because of non-uniform coverage and lack of coherency.



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## I. SUMMARY

Chromium alloys are highly susceptible to pickup of interstitial impurities, especially nitrogen, at elevated temperatures. The successful application of chromium alloys in airbreathing engines with long life requirements is dependent on the development of coatings that will both prevent nitrogen embrittlement and improve high temperature oxidation resistance. Since nitrogen is virtually insoluble in oxides, a program was initiated to develop and evaluate a dense, adherent coating of yttrium oxide-chromium oxide on a high strength chromium alloy (Cr-7Mo-2Ta-0.09C-0.1 (Y+La)) as a means for protecting the alloy.

A three step coating procedure was used. Yttrium was deposited on the alloy surface electrolytically from a molten fluoride bath containing 77.8 wt % LiF and 22.2 wt % YF<sub>3</sub>. Optimum electrodeposition conditions, using an yttrium anode, were identified as 1740°F (1223°K) for 360 seconds at a current density of 0.825 A/in.<sup>2</sup> (1.28 x 10<sup>3</sup> A/m<sup>2</sup>). Excess molten salt was removed by vacuum evaporation at 1920°F (1323°K) for 600 seconds. The mixed Y<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> was formed by preoxidation at 1500°F (1089°K) in H<sub>2</sub>/H<sub>2</sub>O mixtures.

Coated samples were screened for oxidation/nitridation resistance in cyclic furnace tests at 2100°F (1422°K) in slow flowing dry air. Spalling was observed after 100-160 hours total time at temperature, and net weight gains exceeded 30 mg/in.<sup>2</sup> (0.0465 kg/m<sup>2</sup>) prior to the onset of spalling.

As received chromium alloy samples had a DBTT of approximately 625°F (602°K). Fused salt electrodeposition of yttrium usually increased the DBTT by at least 100°F (55°K), although several yttrium coated samples retained ductility at 650°F (616°K). All samples were brittle at 800°F (700°K) after the cyclic oxidation test.

The failure of the coating system developed to provide the requisite oxidation/nitridation resistance is ascribed to a lack of uniformity and coherency in the Y<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> formed.



## II. INTRODUCTION

Utilization of chromium alloys for jet engine components in long-time service applications (600-3000 hours) at temperatures between 2100°F (1422°K) and 2400°F (1589°K) is critically dependent on the development of oxidation/nitridation resistant coatings. High strength chromium alloys have been formulated with promising ductility in the as fabricated condition. However, these alloys are drastically embrittled by absorption of nitrogen during high temperature exposure. Furthermore, the oxidation resistance of the high strength alloys is inadequate above about 2000°F (1367°K).

The choice of coating materials that might inhibit nitrogen diffusion to a chromium alloy substrate is limited by the potential embrittling effects of the coating components. While the data in the literature is often conflicting, it has been reported that additions of titanium, nickel, aluminum, silicon, tantalum, manganese, beryllium, iron, tungsten (ref.1) and boron (ref.2) all raise the ductile-brittle transition temperature (DBTT) of chromium. Since coating components commonly diffuse into the substrate during high temperature service, elements that raise the DBTT of the substrate are to be avoided in environmental coatings for chromium alloys. It has been reported that additions of zirconium, yttrium, cesium and several other rare earths lower the DBTT of chromium, while gold and silver do not affect the DBTT (ref.2). The compatibility of copper with chromium alloys is uncertain (refs. 1 and 2), and recent data on silicon (ref.3) suggests that it may not have a severe embrittling effect.

The purpose of the present program was the development of a coating system for a high strength Cr alloy, Cr-7Mo-2Ta-0.09C-0.1(Y+La), which would provide oxidation/nitridation resistance for a minimum of 200 hours at 2100°F (1422°K) with consistent retention of ductility, and total oxidation-nitridation weight change of less than 3 mg/in.<sup>2</sup> ( $4.65 \times 10^{-3}$  kg/m<sup>2</sup>). The basic approach was to use an yttrium-chromium oxide coating to provide the necessary protection. Oxides are well-recognized as excellent diffusion barriers for nitrogen. It is almost impossible to sinter oxides in the presence of nitrogen, for example, since there is no mechanism by which nitrogen can diffuse out of closed pores (ref.4).

While the lack of ductility of oxides is a deterrent to their use generally, a thin dense layer of oxide, pore free, should provide the necessary barrier to nitrogen without seriously degrading the properties of the alloy such as the notch sensitivity, or the DBTT of the entire system.

The complex yttrium chromium oxide was selected as the best oxide for the current application, on the basis of the findings of Seybolt (ref.5) and others (refs. 6-8) with respect to the oxidation resistance of Y-containing chromium alloys. Seybolt provides good evidence that  $Y_2O_3$  dissolves in  $Cr_2O_3$ , and that  $YCrO_3$ , formed at the alloy oxide interface, effectively blocks diffusion of chromium. Even more important for our purposes, since we are primarily interested in  $YCrO_3$  as a barrier for nitrogen, is that the adherence of the complex  $Y_2O_3 \cdot Cr_2O_3$  oxide scale is vastly better than that of pure  $Cr_2O_3$ , probably as a result of a keying effect of  $Y_2O_3$  particles.

The method explored for forming the desired  $Y_2O_3-Cr_2O_3$  coating was based on a two step process involving first, electrolytic diffusion of yttrium onto the alloy in a fused salt bath, and then controlled low pressure oxidation in a nitrogen-free atmosphere to form the mixed  $Y_2O_3 \cdot Cr_2O_3$  protective barrier.

### III. EXPERIMENTAL WORK

#### A. Starting Material

We received 90 pieces of Cr-7Mo-2Ta-0.09C-0.1(Y+La) alloy from NASA, which was divided into three lots labeled A, B and C. Microscopic examination of this material showed that it contained a large number of inclusions in agreement with the results of Slaughter et al (ref.9). Figure 1 shows a photomicrograph of the alloy structure (lot C).

The DBTT of the alloy was found to be 600 to 625°F (589 to 602°K). Details of the DBTT measurements are given in section D below.

The alloy was cut into strips 2" (5.1 cm) long by 1/2" (1.3 cm) wide by about 1/16" (0.16 cm) thick by means of a fine silicon carbide wheel. A hole was drilled into one end of each strip by which it could be hung in the metallizing cell, and later in the oxidation furnace. Prior to use, the strips were carefully cleaned by scrubbing with detergent and dried with methanol.

#### B. Metallizing Procedures

A general view of the metallizing apparatus is shown in Figure 2 and a schematic diagram of the cell is given in Figure 3. The principle of the operation is similar to electroplating except that it is carried out at high temperature in a molten salt electrolyte, under conditions such that ions reduced at the cathode diffuse into its surface. All runs were carried out in an argon atmosphere except as noted.

Pre-boriding, abandoned early in the program, was carried out in a eutectic mixture of KF, LiF and NaF containing about 0.2 mole % boron added by bubbling gaseous  $\text{BF}_3$  into the molten salt. The anode consisted of 99.8% pure crystalline boron lumps, .2-21 in. (5-50 mm) in diameter, held in a copper mesh basket, 5" (12.7 cm) long and 1" (2.54 cm) in diameter. The mesh size is 12 wires/in. (471 wires/m). The chromium alloy, suspended from a 1/8" (0.32 cm) tungsten rod, served as the cathode. Two to six alloy samples are borided simultaneously. For the pre-boriding step, the cell was operated at 1650°F (1173°K) with a current density of 30 A/in.<sup>2</sup> (46.5 A/m<sup>2</sup>) for the initial 1-1/2 hours, and 20 A/in.<sup>2</sup> (31.0 A/m<sup>2</sup>) for the next 1.7 hours.



FIGURE 1: OPTICAL MICROGRAPH OF CROSS SECTION OF CHROMIUM  
ALLOY Cr-7Mo-2Ta-0.09C-0.1Y SHOWING INCLUSION CONTENT OF ALLOY  
Etched electrolytically in a Solution  
of Sodium Hydroxide. Magnification 62.5X



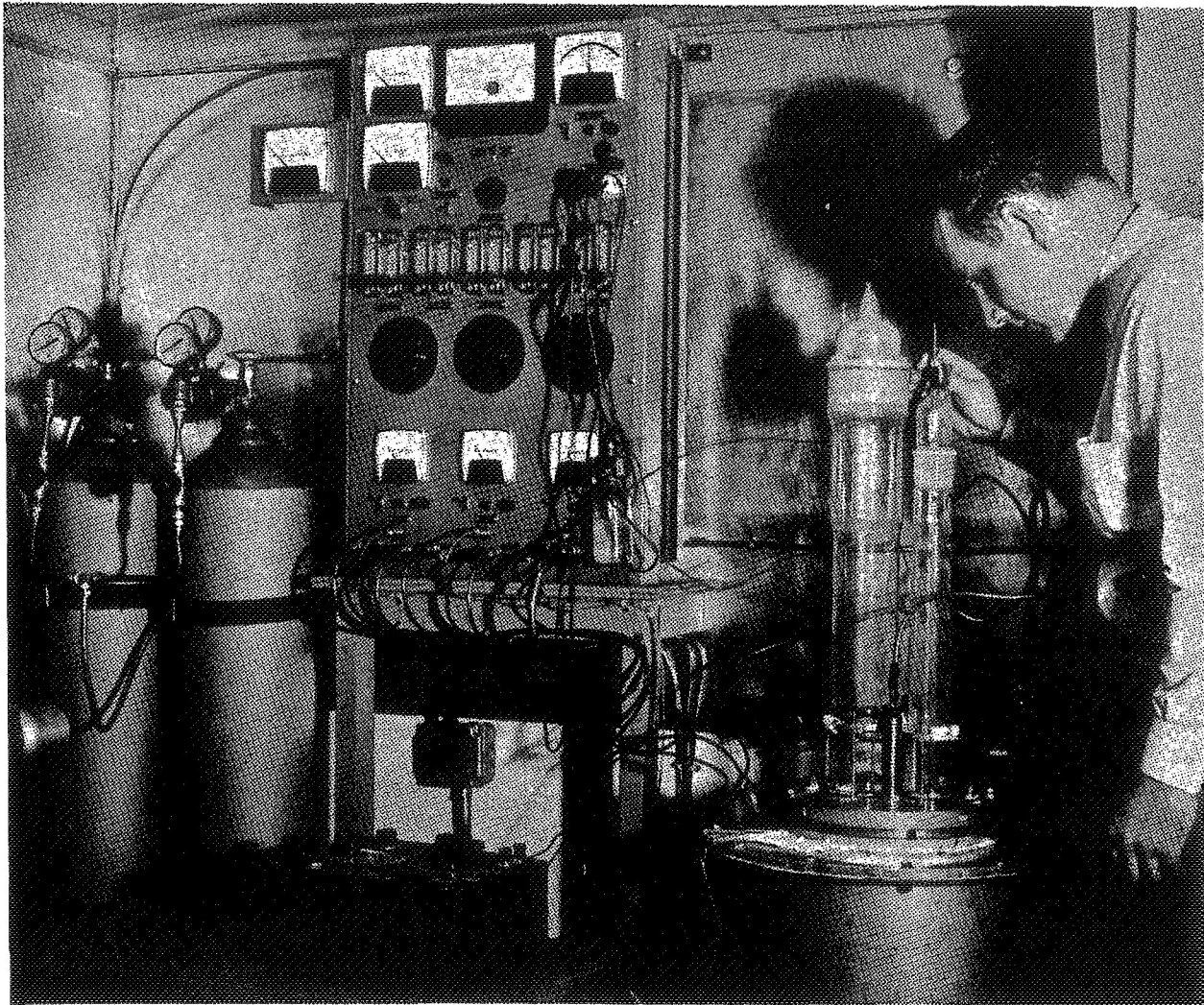


FIGURE 2: METALLIDING APPARATUS

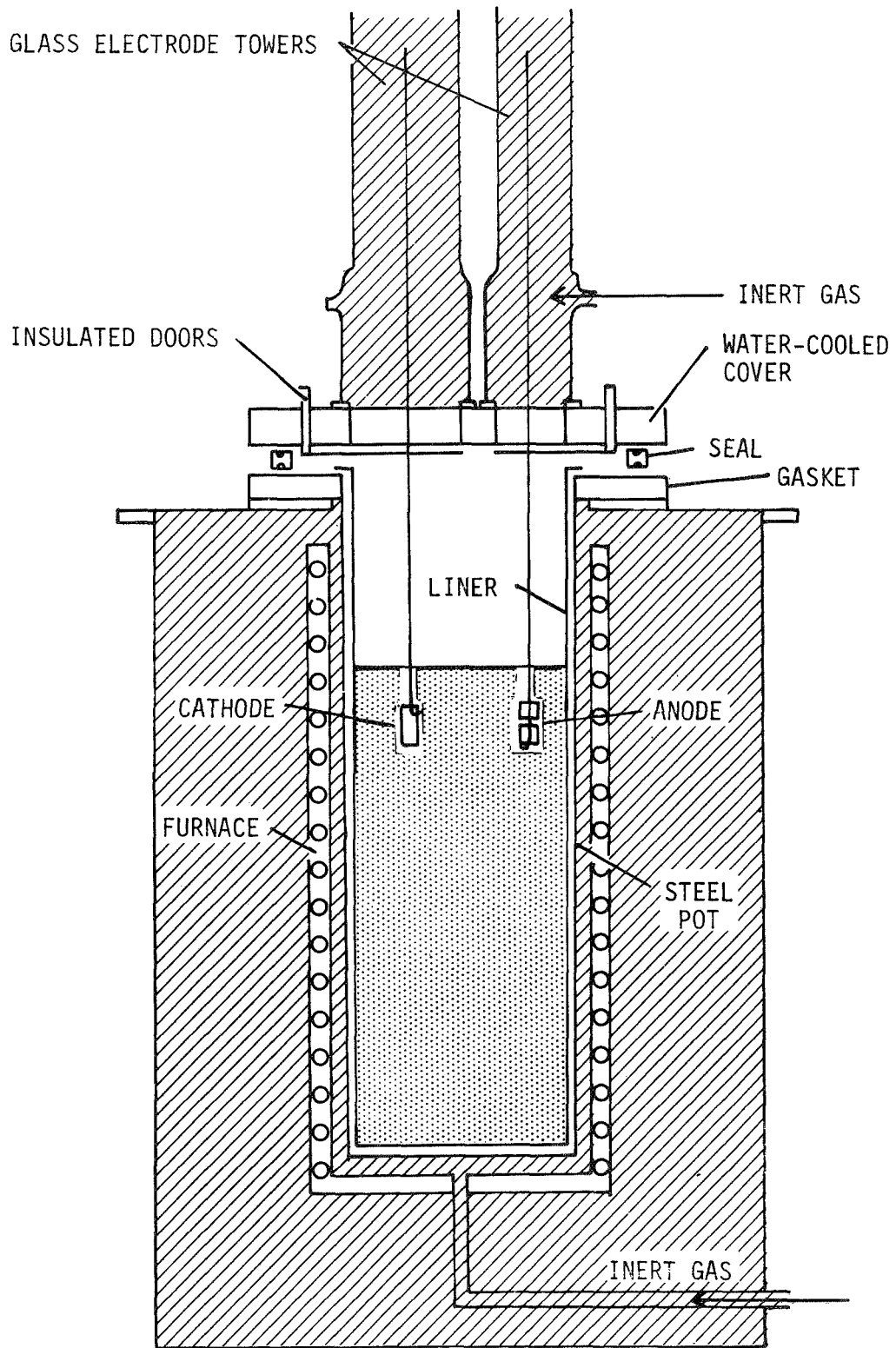


FIGURE 3 SCHEMATIC DIAGRAM OF METALLIZING CELL

during overnight operation. Except for a few preliminary runs which were accidentally made under nitrogen, an argon atmosphere was used. This procedure is essentially that of the Cook patent (ref.10) assigned to the General Electric Company.

The basic design of the yttriding apparatus was the same as that for boriding, except for a few minor modifications. A nickel screen was built to fit into the top part of the cell to hold yttrium chips, which can be used in this system for gettering the argon to assure ultra-clean conditions. The electrolyte is 77.8 wt % LiF and 22.2 wt % YF<sub>3</sub>. The anode consists of two pure 1" (2.54 cm) yttrium cubes, strung onto an 1/8" (0.32 cm) tungsten rod. The cathode is again the chromium alloy either as-received or borided. Before trying to yttride any of the chromium samples, a number of nickel cathodes were yttrided for cell clean-up purposes. In this operation impurities as well as yttrium are deposited on the nickel. Clean, stable operation is indicated when the measured gain in weight of the nickel cathode corresponds to the equivalent calculated from the charge flow in ampere-hours.

### C. Cleaning and Pre-Oxidation

One of the problems with the present yttriding process is the removal of the tightly adhering layer of solidified electrolyte which covers the sample surface after treatment. One way of removing this is to take advantage of the small but finite solubility of LiF in water. The coated samples were held in a large excess of hot water for a number of hours or sometimes overnight. This treatment softened the salt layer enough so that it could be scrubbed off with a steel brush. In many cases, however, no appreciable coating remained after this treatment.

Cleaning methods based on water soaking and scrubbing are open to the suspicion that any layer of deposited yttrium will be destroyed by the cleaning process.

A cleaning method which is free from this objection involves subliming off the fluoride salts at high temperature in a good vacuum. The vapor pressure of LiF is known to be 1 torr (133 N/m<sup>2</sup>) at 2100°F (1422°K), but we were

unable to find data on  $\text{YF}_3$ . Analogy with similar fluorides, however, suggests that its vapor pressure will be considerably lower than that of  $\text{LiF}$ .

Experiments were made by heating salt-covered, yttrided chromium alloy samples in a vacuum of  $3 \times 10^{-4}$  torr ( $4 \times 10^{-2}$  N/m<sup>2</sup>) for ten minutes at 1920°F (1323°K). The samples were heated by radiation from a graphite resistor and the furnace was evacuated with an oil-diffusion pump equipped with a water-cooled trap. The chamber was purged twice with argon prior to raising the temperature.

Pre-oxidation treatments were done for one hour at 1500°F (1089°K) in  $\text{H}_2/\text{H}_2\text{O}$  mixtures with hydrogen at air temperature flowing through water at 200°F (366°K). Work at Westinghouse (ref.11) had previously shown that pre-oxidation of Cr-0.22Y greatly improved the nitridation resistance of the alloy.

#### D. Ductile-Brittle Transition Temperature Tests

The apparatus used for performance of the DBTT test is shown, as it is mounted on the Instron, in Figure 4. It can be seen that the bottom support for the specimen is attached to the load cell. The bottom span is 1 inch (2.54 cm), with shoulders at the specimen surface of 0.050 inch (0.127 cm). Radius of curvature of the punch is 0.250 inch (0.635 cm) ( $\approx 4t$ ). Support rods to the crosshead and load cell are broken with Micarta inserts to reduce heat flow along the supports. In addition, the top and bottom supports are water cooled with soldered-on copper coils. The furnace is controlled by a controller which reads an iron-constantan thermocouple attached to the bottom specimen support about 1 cm from the specimen.

An important feature of the DBTT test is the "clam shell" opening of the furnace which allows specimens to be inserted in the lower jig and removed with ease. Approximately two specimens can be run per hour in the furnace; thus, many specimens can be tested each day. The highest operating temperature of the furnace is 1200°F (922°K). The highest temperature used in test evaluation of the chromium alloy is 1000°F (811°K). There should be no reason to test a material with a DBTT above this temperature.

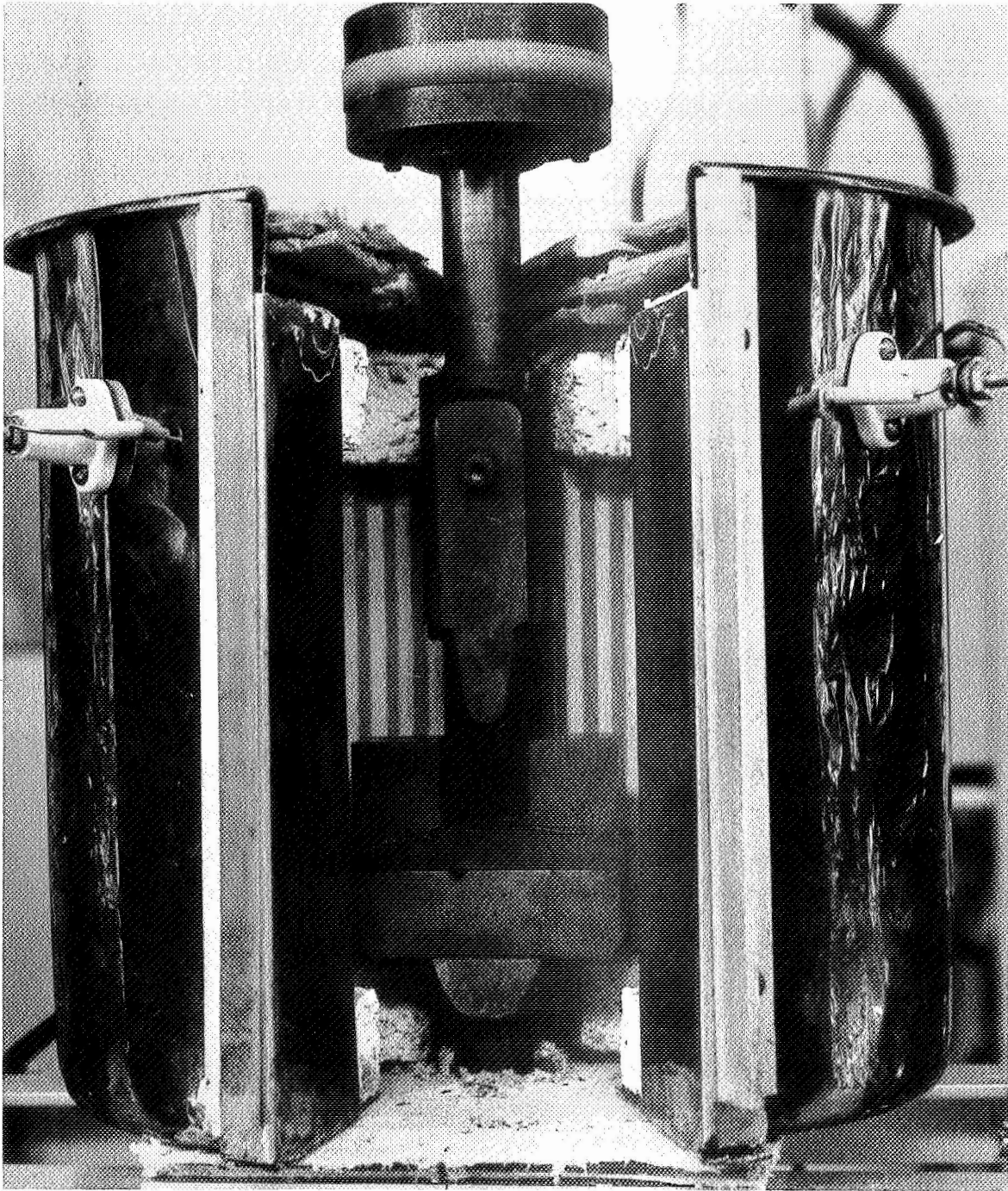


FIGURE 4 : APPARATUS USED FOR PERFORMANCE OF DBTT TEST

When a sample is put in the furnace it is not tested until it has been at the desired temperature for at least five to ten minutes. It is assumed that this time is sufficient for uniform temperature to be obtained in the sample region of the furnace.

During the DBTT test the crosshead speed is 2 cm per minute. This is as close to the suggested 1 inch per minute (0.42 mm/sec) given in the MAB specifications as can be achieved with the metric Instron at ADL. For convenience the chart speed used is 20 cm per minute, which means that 1 cm of chart travel corresponds to 1 mm of crosshead travel. It has been found that a setting of 100 kg full scale of the load cell is sufficient for the DBTT tests.

In the DBTT test, the sample is considered to be ductile if the crosshead travels 10 mm and the specimen is intact. With this travel the specimen bends to a 90° angle. As reported here, the DBTT is the lower test temperature at which this condition is satisfied.

In initial tests on three samples, an approximate value of the DBTT was obtained by pushing the samples 2 mm, then dropping the temperature in 50°F (28°K) intervals and pushing the same amount until the samples broke. It was subsequently found that the DBTT obtained by pushing a number of samples at unique temperatures is 25°-50°F (14-28°K) lower than that obtained by sequentially dropping the temperature of a sample after limited deformation. For this reason the preliminary technique was dropped in favor of obtaining the DBTT by deforming samples at unique temperatures. All DBTT's reported were obtained by the latter technique.

Typical load-deflection curves from the Instron for the alloy in the ductile and brittle conditions, irrespective of its initial condition, are shown in Figures 5 and 6. As seen in Figure 4, when a sample breaks, even in its most brittle condition, yielding precedes fracture, and about 1 mm of plastic deflection can occur. No samples broke in these tests in the absence of plastic deformation. When a sample does fracture, it is catastrophic, and the fracture cannot be arrested by stopping the Instron.

Representative test samples after ductile and brittle behavior are shown in Figure 7. It is seen that there is no ambiguity between ductile

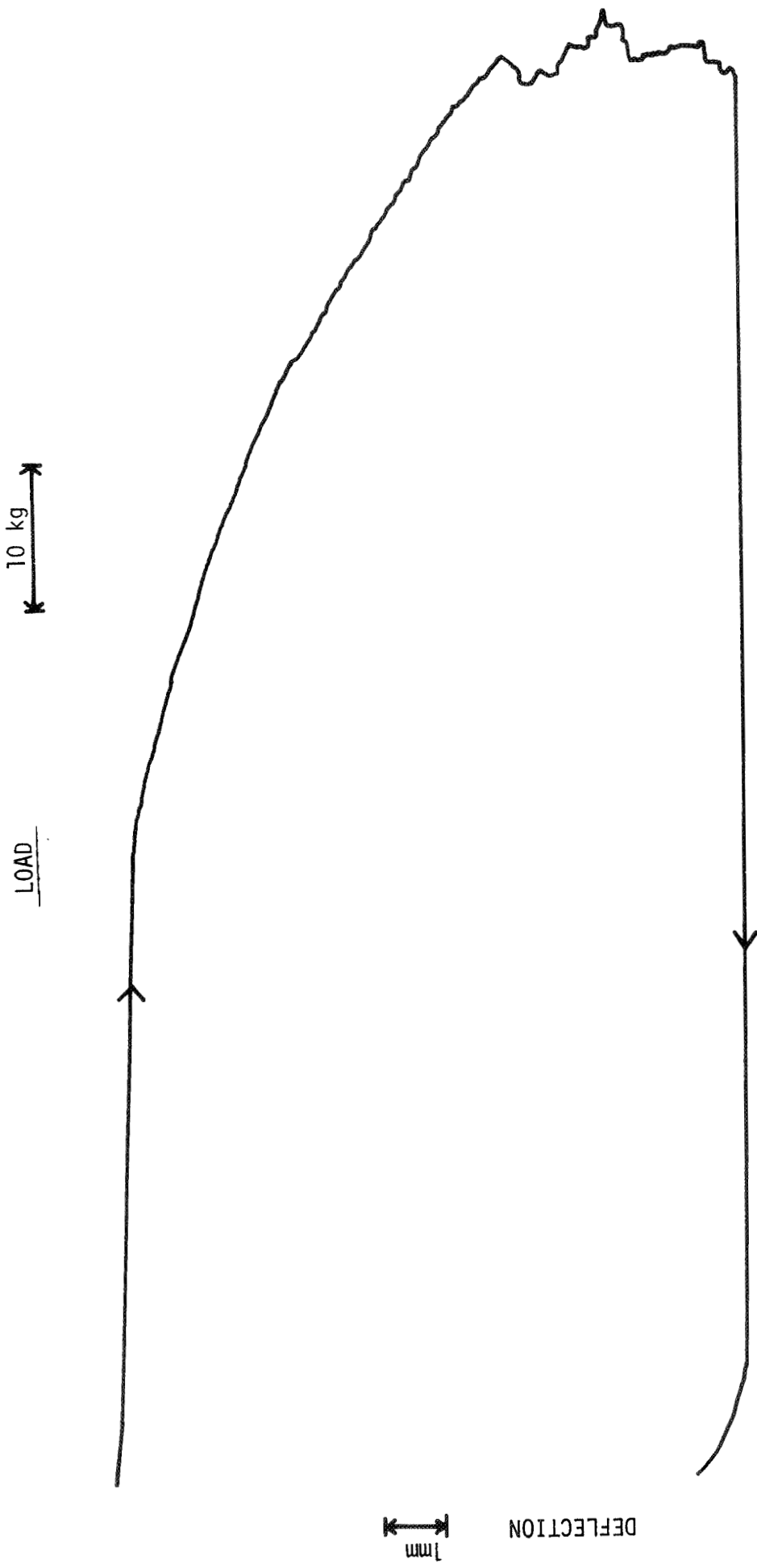


FIGURE 5 LOAD-DEFLECTION CURVE OF A DUCTILE CHROMIUM ALLOY SPECIMEN  
 (As Received Alloy, 650°F (616°K) Test, Specimen 9)

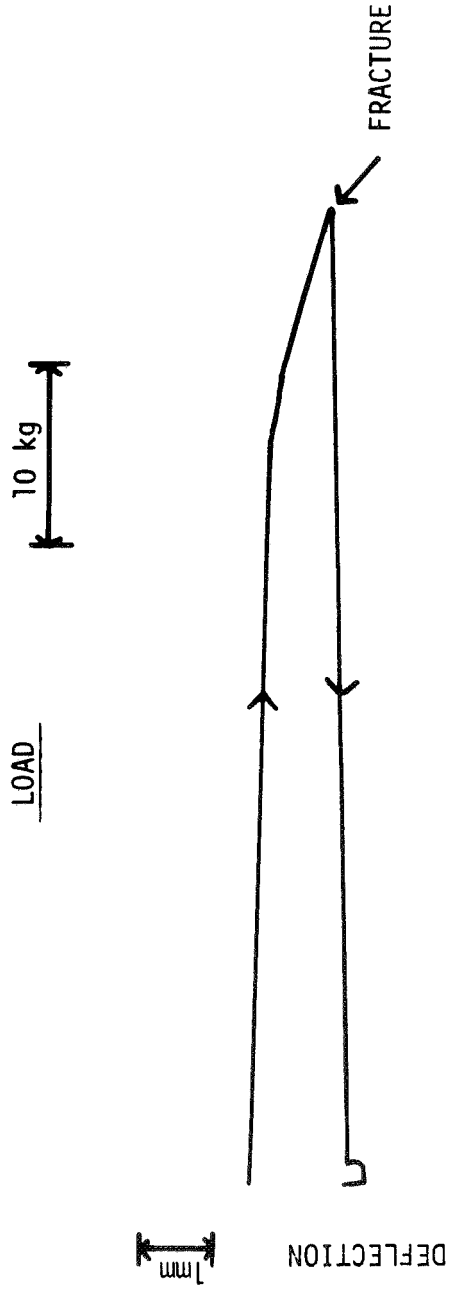


FIGURE 6 LOAD-DEFLECTION CURVE OF A BRITTLE CHROMIUM ALLOY SPECIMEN  
 (As Received Alloy, 550°F (561°K) Test, Specimen 5)



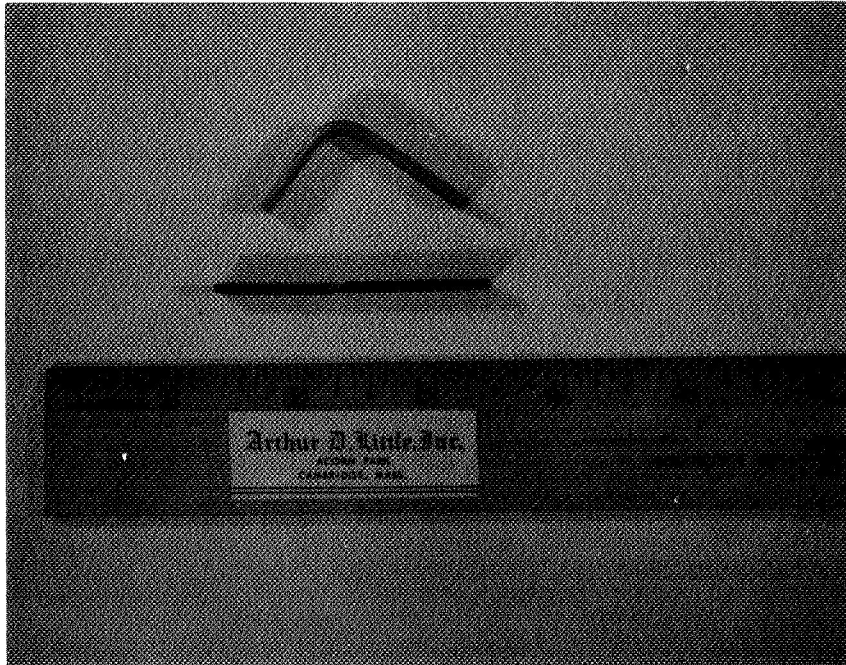


FIGURE 7 : PHOTOGRAPH OF DUCTILE AND BRITTLE CHROMIUM ALLOY SPECIMENS (SPECIMENS 9 AND 10)

and brittle samples. When a sample fractured, the fracture was always in line with the axis of the punch. Fracture was not seen around the hole used to support the samples in the metallizing cells, since the hole is too far from the stressed region to influence fracture.

#### E. Oxidation Testing

Oxidation screening tests were carried out on a selected set of optimally coated samples. The specimens were suspended on a stainless steel jig and inserted into a pre-heated Mullite tube, surrounded by a Globar (silicon carbide) furnace. Air from a compressed air tank was dried over potassium perchlorate and Drierite, and was flowed slowly past the samples at one atmosphere pressure. A schematic diagram of the test apparatus is shown in Figure 8. For the first twenty hours, samples were repeatedly heated at 2100°F (1422°K) for two hours, air quenched to room temperature and weighed, then reheated. For the next 180 hours, or until failure, twenty hour heating cycles were used.

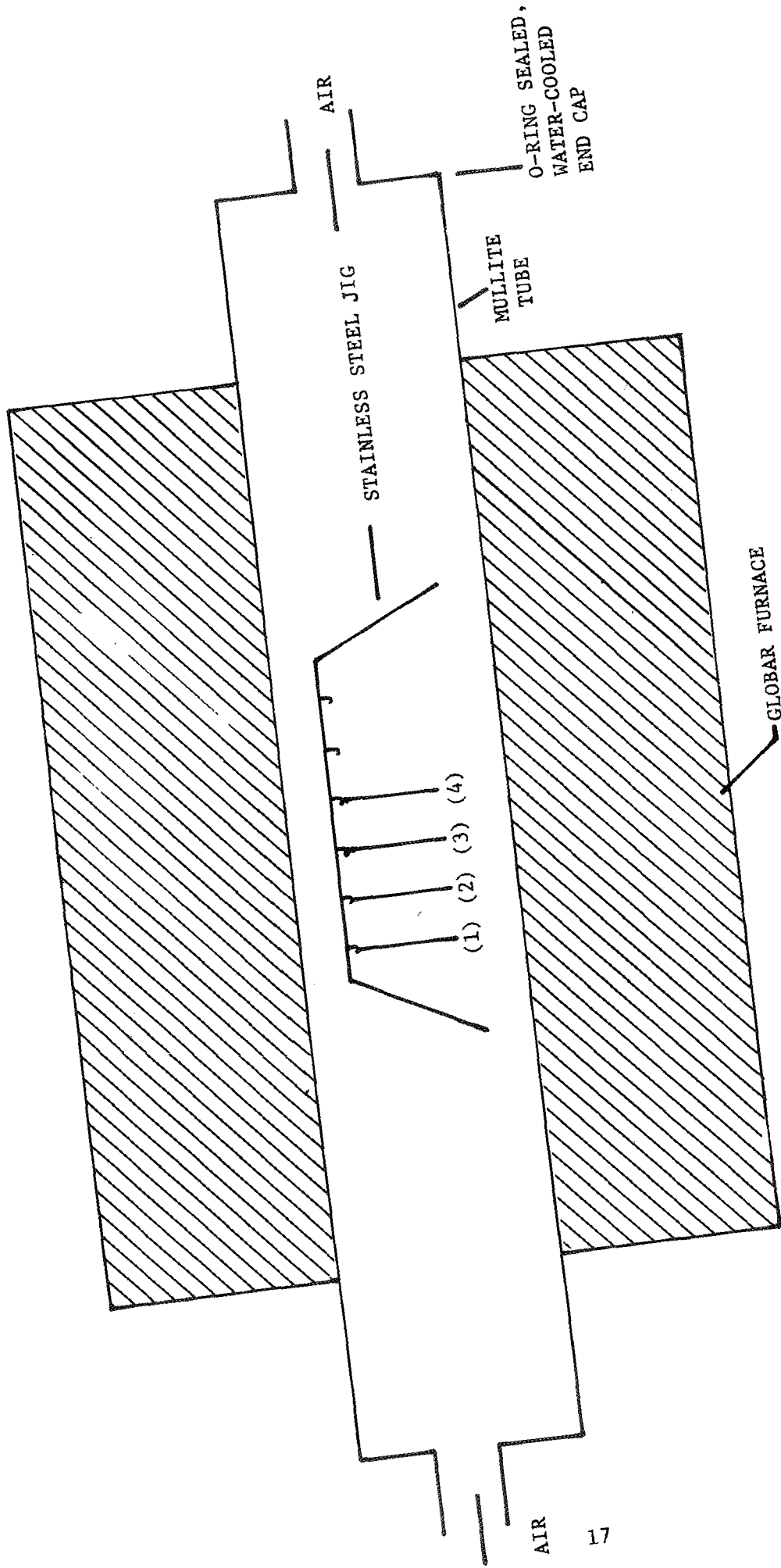


FIGURE 8: SCHEMATIC DIAGRAM OF OXIDATION TEST APPARATUS



## IV. RESULTS

### A. Metallizing

It was recognized very early in the program that the low solubility of yttrium in chromium and the absence of intermetallics in the Y-Cr binary system precluded the possibility of forming an yttrided diffusion layer on the chromium alloy surface by the metallizing process. It did seem possible, in principle, to enrich the alloy surface in yttrium by pre-treating with boron or nickel. Yttrium forms intermetallics with both these elements. The experiments summarized in Table I were done to assess the feasibility of the pre-treatment approach. Figure 9 shows the microstructure of the borided alloy.

Yttriding of the borided chromium alloy samples (Runs 11310 and 11413) resulted in a weight gain which was only 15% of that which would have been observed if all the yttrium arriving at the surface diffused into the samples. X-ray diffraction of a borided sample after yttriding shows only  $\text{CrB}_2$  to be present. The boriding pre-treatment results in the formation of  $\text{CrB}_2$  by diffusion of boron into the alloy surface. Although there is every reason to expect that yttrium can be metallized on boron, with the formation of one or more yttrium boride phases, yttrium apparently cannot readily be electrochemically diffused into  $\text{CrB}_2$ . Since all borided specimens showed an unduly high DBTT (cf. IV., B.) the pre-boriding approach was not pursued further.

Three alloy specimens from lot "A" were electroplated with nickel to a depth of 0.5 mil (.01 mm) (runs 31339, 31340 and 31641). The plated samples were yttrided at  $1740^\circ\text{F}$  ( $1223^\circ\text{K}$ ) and a current density of  $0.4375 \text{ A/in.}^2$  ( $679 \text{ A/m}^2$ ) for times of 1, 3, and 6 minutes, to achieve various depths of yttrium penetration. X-ray analysis clearly identified the presence of several nickel-yttrium phases. The DBTT was of the order of  $750\text{--}775^\circ\text{F}$  ( $672\text{--}686^\circ\text{K}$ ). Preliminary experiments with these samples indicated that the coating tended to blister in water despite attempts to diffuse the nickel into the base alloy by annealing in the metallizing bath for about an hour before yttriding. All the nickel plated samples were brittle at  $700^\circ\text{F}$  ( $644^\circ\text{K}$ )



← CHROMIUM  
BORIDE  
LAYER

FIGURE 9: OPTICAL MICROGRAPH OF CROSS SECTION OF CHROMIUM ALLOY Cr-7Mo-2Ta-0.09C-0.1Y SHOWING CHROMIUM BORIDE LAYER Etched Electrolytically in a Solution of Sodium Hydroxide. Magnification 250X

and one at 800°F (700°K). Nickel pre-plates of 0.2 and 1 mil ( $0.5 \times 10^{-2}$  and  $2.5 \times 10^{-2}$  mm) offered no advantage over the 0.5 mil ( $1.3 \times 10^{-2}$  mm) plate.

Since the pre-treated samples of Table I all exhibited an increase in DBTT as compared to the as-received alloy, it was of interest to determine the effect of yttriding per se on ductility. Run 11312 was made with an as-received sample under the yttriding conditions of run 11310, where the sample has been pre-borided. While no significant amount of yttrium was deposited in either case, the as-received sample remained ductile.

The remainder of the program was directed towards optimization of the yttriding parameters for as-received alloy specimens. If yttrium could not be diffused into the alloy, there was still a possibility that yttrium might be plated out onto the surface, although fused salt electroplating in general results in dendritic or powdery deposits.

As indicated in Table II, the as-received chromium alloy samples were initially yttrided at 1700°F (1200°K) for 5-1/2 minutes at a current density of 131 A/in.<sup>2</sup> (2030 A/m<sup>2</sup>) (ref.12). X-ray diffraction revealed an unknown cubic phase on the surface which was subsequently shown by X-ray fluorescence to contain yttrium. This yttrium may have been due to residual salt, since a metallographic section indicated that there was no diffused layer present.

An as-received chromium alloy sample from Lot C, 1/2" x 2" (1.27 cm x 5.08 cm), was yttrided at 1775°F (1238°K) for 180 minutes at a current density of 0.163 A/in.<sup>2</sup> (252 A/m<sup>2</sup>) (Run No.13023). After yttriding, the sample was scrubbed in hot water to remove the fluoride salts on its surface and from its appearance was clean. This sample was then examined by X-ray diffraction and X-ray fluorescence. Yttrium was not detected by fluorescence and the only elements noted were those of the substrate. X-ray diffraction showed the presence of the compound Cr<sub>23</sub>C<sub>6</sub> on the surface. Apparently, the alloy has picked up carbon in the cell. The presence of carbon in the salt bath as YC<sub>2</sub> was confirmed by X-ray diffraction, and some evidence was found for sulfur and nitrogen impurities as well. Since the metallizing process demands a very clean system, anhydrous HF was bubbled through the salt bath for 1-1/2 hours at 1775°F (1238°K) in an attempt to remove the impurities as volatile C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, and NH<sub>2</sub>. After the clean-up procedure with HF, a chromium alloy

TABLE I. - YTTRIDING OF PRETREATED ALLOY SPECIMENS

Run No.	Alloy Lot	Pretreatment	Pieces	Temp °F °K	Time Sec.	Current Density A/in.2 (A/m <sup>2</sup> )	Analytical Data - X-ray Diffraction	DBTT °F (°K)	Remarks
11310	A	Borided	1	1700 1200	336	1.31 (2030)	CrB <sub>2</sub>	Brittle at 700 (644)	
11413	C	Borided	1	1700 1200	444	1.0 (1550)	--	Brittle at 800 (700)	
20324	A	0.2 mil Ni plate	2	1775 1240	1800	0.4375 (679)	Ni + Ni <sub>9</sub> Y	Brittle at 700 (644)	
31339	A	0.5 mil Ni plate	1	1740 1225	180	0.4375 (679)	Ni <sub>3</sub> Y; Ni <sub>5</sub> Y; Ni <sub>2</sub> Y; Ni	Brittle at 700 (644)	
31340	A	0.5 mil Ni plate	1	1740 1225	60	0.4375 (679)	Ni <sub>5</sub> Y; Ni <sub>3</sub> Y; YN	Brittle at 700 (644)	
31641	A	0.5 mil Ni plate	1	1740 1225	360	0.4375 (679)	Ni <sub>2</sub> Y; Ni <sub>3</sub> Y; Ni <sub>5</sub> Y		
31742	A	1 mil Ni plate	2	1740 1225	60	0.4375 (679)	--	Brittle at 750 (672)	
11312	C	--	1	1700 1200	336	1.31 (2030)	Trace of Y	Ductile at 700 (644)	Compare to 11310



TABLE II. - YTTRIDING OF AS-RECEIVED ALLOY SPECIMENS

Run No.	Alloy no. of Lot Pieces	Temp. °F	Temp. °K	Time Sec.	Current Density A/in. <sup>2</sup>	Current Density (A/m <sup>2</sup> )	Analytical Data	DBTT °F (°K)	Remarks
11312	C 1	1700	1200	330	1.31	(2030)	Trace of Y	Ductile at 700 (644)	
13023	C 1	1775	1240	10,800	0.163	(252)	Cr <sub>23</sub> C <sub>6</sub>	---	
30634	A 1	1830	1275	10,800	0.163	(252)	Cr <sub>23</sub> C <sub>6</sub>	---	After HF cleanup
30937	A 1	1830	1275	10,800	0.163	(252)	YN before cleaning; nothing after	---	After 5 yttriding runs with chrome plated steel cathodes
30938	A 1	1830	1275	10,800	0.163	(252)	---	---	
31038	A 1	1830	1275	10,800	0.163	(252)	---	---	
31640	A 1	1830	1275	10,800	0.163	(252)	---	Brittle at 700 (644)	
40143	A 1	1830	1275	1800	0.163	(252)	Y <sub>2</sub> O <sub>3</sub> + YOF	Ductile at 650 (616)	Velvety black coating
40344	A 6	1830	1275	14,400	0.163	(252)	YF <sub>3</sub> + YOF	Brittle at 700 (644)	
40645	A 1	1830	1275	1800	0.163	(252)	Y <sub>2</sub> O <sub>3</sub> + YOF	Brittle at 700 (644)	Spotty coating
40746	A 1	1830	1275	1800	0.163	(252)	---	Brittle at 950 (783)	
41049	A 1	1830	1275	10,800	1.5	(2320)	---	---	Heavy, granular, non-adherent deposit

specimen from lot "A" was yttrided at 1740°F (1223°K) for 3 hours at a current density of 0.163 A/in.<sup>2</sup> (252 A/m<sup>2</sup>) (Run No.30634). X-ray diffraction analysis still showed the presence of a chromium carbide phase Cr<sub>23</sub>C<sub>6</sub> at the surface. A series of five yttriding runs were carried out under similar conditions with one mil chromium plated steel cathodes, 2" x 6" (5.1 x 15.2 cm), to remove the residual carbon. Finally, four chromium alloy specimens from lot "A" were yttrided in like manner, and were found to be free from carbide. Unfortunately, no yttrium appeared to have diffused into the alloy on the basis of X-ray evidence.

Continued effort did result in some yttrium deposition at the alloy surface, although as indicated in Table II results were highly non-reproducible. Runs 40143, 40645, and 40746, for example, were made under nominally the same conditions, but the appearance of the coatings and the extent of embrittlement of the substrate were very different.

The runs summarized in Table III were made to determine the effects of time, temperature, and current density on coating quality. Runs 41553, 41451, and 41350T were made at three different temperatures under conditions of constant current density and time. All coatings were spotty and non-uniform, and the DBTT was of the order of 100°F (55 °K) higher than that of the as-received alloy for all coated specimens. Thus, no important effects of temperature were observed. Runs 41452T and 41452B were designed to evaluate the effects of high current density-short time conditions and low current density-long time conditions. Both conditions led to more severe embrittlement than the previous intermediate time-current density conditions. Run 41350B, made with nickel plated specimens also resulted in serious embrittlement.

From the experiments summarized in Table III, it was impossible to identify optimum yttriding conditions. None of the coatings were uniform in appearance; all seemed to embrittle the substrate. Furthermore, four samples from Run No. 41451 failed catastrophically within four hours in the cyclic oxidation test as described in III., E. Results were so much poorer than those obtained previously from Run No. 40143, made under normally similar conditions, that we felt the salt bath must have become contaminated.

TABLE III. - EFFECT OF TIME, TEMPERATURE, AND CURRENT DENSITY ON  
YTTRIDING OF AS-RECEIVED CHROMIUM ALLOY SPECIMENS

<u>Run No.</u>	<u>Alloy Lot</u>	<u>No. of Pieces</u>	<u>Time °F</u>	<u>Time °K</u>	<u>Time Sec.</u>	<u>Current Density A/in.<sup>2</sup></u>	<u>Current Density (A/m<sup>2</sup>)</u>	<u>Analytical Data</u>	<u>DBTT °F (°K)</u>	<u>Remarks</u>
41553	C	6								
41553	C	6	1560	1125	1800	0.163	(252)	---		Brittle at 700 (644) Ductile at 800 (700)
41451	A	6	1650	1175	1800	0.163	(252)	---		Brittle at 700 (644)
41350T	A	6	1740	1225	1800	0.163	(252)	---		Brittle at 700 (644) Ductile at 800 (700)
41452T	A	6	1650	1175	18000	0.016	(24.8)	---		Brittle at 900 (755)
41452B	A	6	1650	1175	360	0.8	(1240)	---		Brittle at 800 (700)
41350B	A	6	1650	1175	60	0.4375	(689)	---		Brittle at 800 (700) 0.5 mil (.01 mm) Ni plate

Numerous attempts were made, as summarized in Table IV, to clean up the cell and to obtain an optimized yttrium deposit. Yttrium nitride was found fairly consistently on the surface of yttrided samples, although the cell was continually purged with argon during operation, and attempts were made to remove nitrogen from the bath by adding HF and  $Y_2O_3$ . The latter, it was thought, would release as  $NH_3(g)$  any nitrogen held as  $NH_4F$ , and indeed alkaline fumes were detected after the oxide additions. Incorporation of a gate valve, to prevent back-diffusion of nitrogen, was beyond the scope of the program. The presence of YN on the surface apparently did not embrittle the substrate alloy. A sample from Run No. 52862 proved to be ductile at 650°F (616°K) in spite of the surface nitride. This result is not too surprising, since the gettering of nitrogen by yttrium at the surface of the alloy could actually prevent the diffusion of nitrogen into the base metal. A thin brittle surface layer, furthermore, need not necessarily embrittle the system.

It can be seen from Table IV that the vacuum evaporation step used to remove residual salts resulted in surface oxidation. This is of course a result of the relatively poor vacuum used (about  $10^{-4}$  torr) ( $1.3 \times 10^{-2}$  N/m<sup>2</sup>). In a number of runs, yttrium borates were found after vacuum evaporation. Intensive cleaning removed the source of difficulty.

Optimum deposition conditions were identified as 1740°F (1223°K) for 6 minutes at a current density of 0.825 A/in.<sup>2</sup> (1280 A/m<sup>2</sup>). These conditions gave the most consistent results and the best adherent deposits. Although yttrium was successfully plated on the chromium alloy surfaces, the deposits were for the most part non-uniform, thin, grey, and probably not coherent. In no case was any identifiable diffusion coating formed on the chromium alloy.

## B. Ductility

### 1. As-Received Chromium Alloy

The three preliminary samples from lot "C" referred to above gave a DBTT of approximately 625°F (602°K). On samples pushed at single temperatures, the DBTT obtained was 600°F (589°K). Data for these tests are given

TABLE IV. - EFFECT OF CLEANUP PROCEDURES ON THE QUALITY OF YTTRIDED DEPOSITS

Run No.	Pieces	Temp °F	Temp °K	Time Sec.	Current Density A/in. <sup>2</sup> (A/m <sup>2</sup> )	Analytical Data	DBIT °F (°K)	Cleanup Procedure	Remarks
51457	1	1560	1125	1800	0.163 (252)	YN		0.050kg HF added to cell	
52260	1	1560	1125	1800	0.163 (252)	YN		Three cleanup runs*	
52862	4	1560	1125	7200	0.163 (252)	YN before vac evap; Y <sub>2</sub> O <sub>3</sub> -Cr <sub>2</sub> O <sub>3</sub> after	Ductile at 650 (616) after vac evap.	Two more cleanup runs*	
70166	1	1740	1225	1800	0.163 (252)	Cr <sub>23</sub> C <sub>6</sub>		Another 0.226kg of Y <sub>2</sub> O <sub>3</sub> added to cell	
70669	2	1740	1225	1800	0.163 (252)	YN + Cr <sub>23</sub> C <sub>6</sub>			
70670	6	1740	1225	1800	0.163 (252)	YN		Cleanup run*	
70871	1	1740	1225	57600	0.013 (20.2)	--			
70971	4	1740	1225	1800	0.163 (252)	Y <sub>2</sub> O <sub>3</sub> -Cr <sub>2</sub> O <sub>3</sub> after vacuum evap.			
70972	2	1740	1225	360	0.825 (1280)	YOF-Cr <sub>2</sub> O <sub>3</sub> after vacuum evap.			
71092	2	1740	1225	360	2.5 (3880)	YN after iding;			Preoxidized for 2 hrs at 1500°F(1089°K) in H <sub>2</sub> /H <sub>2</sub> O before iding
271501	2	1740	1225	360	0.825 (1280)	YB <sub>3</sub> after vac evap.			
271503T	1	1740	1225	1800	0.163 (252)	YB <sub>3</sub> after vac evap.			
271503B	1	1740	1225	1800	0.163 (252)	Cr <sub>2</sub> O <sub>3</sub> , YOF, YB <sub>3</sub> after vac evap			
280909	1	1740	1225	360	0.825 (1280)			Four cleanup runs*	
281013	2	1740	1225	360	0.825 (1280)	Y		Two cleanup runs*	
281113	2	1740	1225	360	0.825 (1280)	Y	Brittle at 700 (644) after 4 hrs oxid.		
281917	1	1740	1225	360	0.825 (1280)	Y, YOF, YN		Cleanup run*	
282019T	6	1740	1225	360	0.825 (1280)	Y, YOF, YN		Cleanup run*	
282019B	2	1740	1225	180	0.438 (679)	Ni <sub>2</sub> Y, NiY, Y			0.01 mm(0.5 mil)Ni plate
282121T	4	1740	1225	360	0.825 (1280)	Y (trace); YN			
282121B	4	1740	1225	360	0.825 (1280)	Y (trace); YN			
282123	3	1740	1225	360	0.825 (1280)	Y (trace); YN			

\* A cleanup run involves yttriding of chromium plated stainless steel at 1173°K for 180 min. at a current density of 0.125 A/in.<sup>2</sup> (194 A/m<sup>2</sup>)

in Table V. In this table the amount of crosshead deflection after yielding and the presence or absence of fracture is noted.

To determine if the temperature and time used for boriding might influence the DBTT, several samples were vacuum annealed at 1650°F (1173°K) for nineteen hours under the temperature-time conditions used for boriding. The samples from lot "C" with as-received surfaces were sealed in evacuated quartz tubes and then annealed. It was noted that these samples were slightly darkened after the anneal, indicating that they picked up oxygen. The test results are given as Samples 15 and 16 in Table V. At 700°F (644°K), Sample 15 was not far from being ductile. Possibly at a test temperature of 725°F (658°K) this sample would have been ductile. Although the indicated DBTT is about 100°F (55°K) higher than that of the as-received alloy, it is thought that the oxidation of the sample during annealing has raised the DBTT, rather than the annealing treatment. It will be noted later that the DBTT of the borided samples is about 300°F (422°K) higher than that of the as-received samples with the same condition of time and temperature. Thus, it would appear that annealing, per se, during the boriding treatment has little or no influence on the DBTT.

## 2. DBTT of the Borided Chromium Alloy

Test results on DBTT of the borided lot "C" chromium alloy are shown in Table VI. The lowest temperature noted to obtain a ductile sample was 950°F (783°K). This means that the DBTT of the borided samples is 900-950°F (775-783°K), about 300°F (422°K) higher than that of the as-received samples. The exact DBTT has not been obtained, but there is no doubt about the serious increase in DBTT caused by boriding.

It was found that the borided samples oxidized during the DBTT test. A dark coating formed on the samples indicated poor oxidation resistance. In contrast, the as-received alloy samples showed no evidence of discoloration at test temperatures as high as 800°F (700°K). Possibly the poorer oxidation resistance of the borided samples contributes to their considerably higher DBTT.

To determine if a better surface before boriding would improve the DBTT, one sample was polished on 600 grit before boriding. This sample,

TABLE V. - DBTT OF THE AS-RECEIVED CHROMIUM ALLOY

<u>Specimen Number</u>	<u>Condition</u>	<u>Test Temperature °F (°K)</u>	<u>Crosshead Travel - mm/s</u>	<u>Fracture</u>
5	Lot C, as received surface	550 (561)	1	yes
6	Lot C, as received surface	575 (575)	3	yes
7	Lot C, as received surface	590 (583)	5.5	yes
4	Lot C, as received surface	600 (589)	8	no
9	Lot C, as received surface	650 (616)	10	no
16	Lot C, as received surface, vacuum an- nealed 900°C for 19 hours	650 (616)	0.2	yes
15	Lot C, as received surface, vacuum an- nealed 900°C for 19 hours	700 (644)	4	yes

TABLE VI. - DBTT OF THE BORIDED CHROMIUM ALLOY

<u>Specimen Number</u>	<u>Initial Condition Before Boriding</u>	<u>Test Temperature</u>		<u>Crosshead Travel - mm/s</u>	<u>Fracture</u>
		<u>°F</u>	<u>(°K)</u>		
8	Lot C, as received surface	650	(616)	0.4	yes
10	Lot C, as received surface	700	(644)	0.6	yes
11	Lot C, as received surface	800	(700)	1	yes
12	Lot C, as received surface	900	(755)	5	yes
14	Lot C, as received surface	950	(783)	10	no
-----					
13	Lot C, surface polished 600 grit	800	(700)	1	yes
-----					
17	Lot A, as received surface	750	(672)	1	yes



No. 13 as shown in Table VI, was brittle at 800°F (700°K). Apparently, the high DBTT of the borided samples cannot be improved appreciably by surface treatment.

One sample from lot "A" was also borided (see Table VI, No. 17) and was found to be brittle at 750°F (672°K). Thus, the initial quality of the chromium sample also does not lead to significant improvement of the DBTT after boriding.

### 3. DBTT of Yttrided Samples

The ductility data on all the yttrided samples are summarized in Tables I-IV. The borided samples were brittle at 800°F (700°K) and below. The samples which were nickel-plated before yttriding were brittle at 700°F (644°K). One sample was brittle at 800°F (700°K). The load-deflection curves indicate that most samples would have a DBTT of the order of 750-775°F (672-686°K).

The samples which were yttrided as-received were, for the most part brittle at 700°F (644°K), an increase of the DBTT of at least 100°F (55°K). Some were brittle at 700, 800, and 900°F (672, 700, and 755°K).

Two samples (40143 and 52862) were found to be ductile at 650°F (616°K). The reason for these favorable results is not known. It is possible that the embrittlement is caused by pickup of nitrogen in the cell during treatment. If this is the case, there is no obvious reason why these two samples failed to pick up nitrogen.

### C. Oxidation

The yttrided sample, No. 40143, which had a dense, adherent, velvety black coating, and which had retained ductility up to and including the vacuum evaporation step was cyclically exposed at 2100°F (1422°K) in slow flowing dry air with the results given in Table VII. This sample failed to meet the goal of no more than 3 mg/in.<sup>2</sup> ( $4.65 \times 10^{-3}$  kg/m<sup>2</sup>) weight gain in 200 hours.

TABLE VII. - CYCLIC OXIDATION TESTS OF SAMPLE NO. 40143  
 (Yttrided at 1650°F(1173°K) for 30 minutes  
 at 0.163 A/in.<sup>2</sup> (252 A/m<sup>2</sup>))

	<u>Time at Temperature, Hrs.</u>	<u>Weight Gain</u>	
		<u>mg/in.<sup>2</sup></u>	<u>(kg/m<sup>2</sup>)</u>
	2	--	(---)
	2	1.4	(2.17)
	2	0.6	(0.93)
	2	0.7	(1.09)
	2	0.2	(0.31)
	2	1.1	(1.70)
	2	0.7	(1.09)
	2	0.4	(0.62)
	2	0.2	(0.31)
	2	0.4	(0.62)
	20	2.9	(4.5)
	20	1.9	(2.92)
	20	2.9	(4.5)
	20	1.5	(2.32)
	20	1.7	(2.63)
Total	120 hours	16.6 mg/in. <sup>2</sup>	(25.6 kg/m <sup>2</sup> )
	20	45.9 spalling	(71.0)

One of the four samples comprising run 52862 was tested for ductility immediately after removal from the salt bath, and proved to be ductile at 650°F (616°K) like the untreated alloy. The three remaining samples were soaked in water for several days and vacuum heat treated to remove residual salts. One of the treated samples was preoxidized for one hour in flowing 5% O<sub>2</sub>-95% Ar at 1650°F (1172°K). A heavy oxide coating resulted which spalled badly. Subsequent preoxidation treatments were done at 1500°F (1089°K) in H<sub>2</sub>/H<sub>2</sub>O mixtures with hydrogen at one atmosphere flowing through water at 120°F(323°K). A second treated sample was cyclically oxidized in slow moving air at 2100°F(1442°K), together with an untreated control specimen. Weight gains were lower for the yttrided sample, but were still too high for practical applications. Neither sample was ductile at the end of the test. The results are given in Table VIII.

One sample from each of the lots 281011 and 281113, and two samples from 281013 were cyclically oxidized in slow flowing dry air at 2100°F (1422°K), with no preoxidation. The 281113 sample was tested for ductility after two 2-hour exposures and proved to be brittle. The other samples were carried through the 200 hour oxidation/nitridation test, and showed higher weight gains than the desired 3 mg/in.<sup>2</sup> (4.65 x 10<sup>-3</sup> kg/m<sup>2</sup>). Test results are summarized in Table IX.

Four samples from lot 282121T were preoxidized in hydrogen-water vapor as described above, and subjected to cyclic oxidation testing. Three samples from lot 282123 were tested similarly. Both sets of results are given in Table X.

While all of the weight changes are unacceptably high, it is clear from Tables IX and X that the magnitude of the weight change increases from position (1) to position (4) in the furnace. The temperatures at these four positions were originally measured in a static system and were found to be fairly uniform, 2090°F (1416°K) at (1), 2100°F (1422°K) at (2) and (3), and 2086°F (1414°K) at (4). The gas flow altered the temperature distribution considerably to 2060°F (1400°K) at (1), 2092°F (1417°K) at (2), 2112°F (1429°K) at (3), and 2119°F (1432°K) at (4). Hence the increasing weight change with position corresponds to increasing temperatures.

TABLE VIII. - CYCLIC OXIDATION TESTS OF SAMPLE NO. 52862  
 (Yttrided at 1560°F(1123°K) for 120 min. at 0.163 A/in.<sup>2</sup>)  
 (252 A/m<sup>2</sup>) and an Untreated Control)

<u>Time at Temperature (hrs)</u>	<u>Weight Gain of Yttrided Sample</u>		<u>Weight Gain of Untreated Control</u>	
	<u>mg/in.<sup>2</sup></u>	<u>(kg/m<sup>2</sup>)</u>	<u>mg/in.<sup>2</sup></u>	<u>(kg/m<sup>2</sup>)</u>
2	4.6	(7.14)	2.9	(4.5)
2	2.6	(4.04)	2.6	(4.04)
2	0.9	(1.39)	1.7	(2.64)
2	0.3	(0.465)	2.2	(3.42)
2	0.4	(0.62)	1.9	(2.95)
2	0.6	(0.93)	2.1	(3.26)
2	1.4	(2.18)	2.0	(3.10)
<hr/>				
Total 14 hrs	10.8 mg/in. <sup>2</sup>	(16.8 kg/m <sup>2</sup> )	15.4 mg/in. <sup>2</sup>	(23.9 kg/m <sup>2</sup> )

TABLE IX. - CYCLIC OXIDATION TESTS OF SAMPLES  
 YTTRIDED AT 1740°F(1223°K) FOR 6 MINUTES AT 0.825 A/in.<sup>2</sup>(1280 A/m<sup>2</sup>)  
 (NO PREOXIDATION)

Time at Temperature	Weight Gains, mg/in. <sup>2</sup> (kg/m <sup>2</sup> )					
	281011		281013		281113	
Furnace Position:	(1)	(2)	(3)	(4)	(5)	(6)
2 hrs.	1.6 (2.5)	3.5 (5.4)	3.7 (5.7)	6.1 (9.5)		
2	0.2 (0.3)	0.9 (1.4)	1.3 (2.0)	2.7 (4.2)		
2	3.2 (5.0)	3.9 (6.0)	3.6 (5.6)	DBTT		
2	0.6 (0.9)	1.0 (1.5)	1.6 (2.5)			
2	0.8 (1.2)	1.1 (1.7)	1.7 (2.6)			
2	0.7 (1.1)	1.3 (2.0)	1.7 (2.6)			
2	0.9 (1.4)	1.6 (2.5)	2.3 (3.6)			
2	0.0 (0.0)	0.1 (0.15)	0.4 (0.6)			
2	0.3 (0.5)	0.4 (0.6)	0.5 (0.8)			
2	0.2 (0.3)	0.5 (0.8)	1.0 (1.5)			
20	5.0 (7.8)	10.2 (15.8)	14.3 (22.2)			
20	4.4 (6.8)	8.8 (13.6)	11.3 (17.5)			
20	2.6 (4.0)	5.3 (8.2)	9.7 (15.0)			
20	2.1 (3.3)	6.2* (9.6)	-33.2 (-51.5)			
20	2.2 (3.4)	11.3*(17.5)	-62.3 (-96.5)			
20	6.6 (10.2)	-16.1 (-25)	-27.6 (-42.8)			
20	2.8* (4.3)	-20.1 (-31)	-19.2 (-29.8)			

\* Spalling

TABLE X. - CYCLIC OXIDATION TESTS OF SAMPLES

YTRIDED AT 1740°F(1223°K) FOR 6 MINUTES AT 0.825 A/in.<sup>2</sup> (1280 A/m<sup>2</sup>)

Weight Gains, mg/in.<sup>2</sup> (kg/m<sup>2</sup>)  
Sample No.:

Time at Temperature	282121T				282123		
	(1)	(2)	(3)	(4)	(1)	(2)	(3)
Furnace Position:							
2 hrs.	4.1 (6.4)	7.8 (12.1)	9.8 (15.2)	12.5 (16.4)	4.2 (6.5)	5.8 (9.0)	7.8 (12.1)
2	3.7 (5.7)	3.8 (5.9)	4.7 (7.3)	2.1 (3.3)	3.4 (5.3)	4.4 (6.8)	8.8 (13.6)
2	1.4 (2.2)	1.6 (2.5)	2.3 (3.6)	2.1 (3.3)	3.8 (5.9)	3.6 (5.6)	4.1 (6.4)
2	0.4 (0.6)	0.9 (1.4)	1.8 (2.8)	1.8 (2.8)	1.2 (1.9)	1.6 (2.5)	2.6 (4.0)
2	1.4 (2.2)	1.6 (2.5)	2.6 (4.0)	2.1 (3.3)	0.6 (0.9)	1.4 (2.2)	1.3 (2.0)
2	1.0 (1.5)	1.5 (2.3)	2.7 (4.2)	2.3 (3.6)	1.0 (1.5)	1.4 (2.2)	1.2 (1.9)
2	0.7 (1.1)	1.3 (2.0)	2.6 (4.0)	2.5 (3.9)	1.3 (2.0)	2.0 (3.1)	2.0 (3.1)
2	1.1 (1.7)	1.5 (2.3)	1.6 (2.5)	2.2 (3.4)	0.2 (0.3)	0.6 (0.9)	0.6 (0.9)
2	0.6 (0.9)	1.0 (1.5)	1.8 (2.8)	1.4 (2.2)	0.1 (0.15)	0.6 (0.9)	1.0 (1.5)
2	0.5 (0.8)	0.7 (1.1)	0.8 (1.2)	0.3 (0.5)	0.5 (0.8)	0.9 (1.4)	1.4 (2.2)
20	10.2 (15.8)	6.7 (10.4)	loss	DBTT	DBTT	7.9 (12.2)	13.1 (20.3)
20	2.8 (4.3)	loss	loss	-	-	14.7 (22.8)	4.8* (7.4)

\*Spalling

## V. DISCUSSION

The basic concept of using a dense adherent  $Y_2O_3-Cr_2O_3$  coating as a nitrogen diffusion barrier to prevent embrittlement of chromium alloys remains, we think, a valid one, although we were unable to form such a coating under the present program. We did electrodeposit Y or YN on the surface of a chromium alloy, and we did form  $Y_2O_3-Cr_2O_3$  in many cases. However, neither the yttrium containing surface layer, nor the mixed oxide was deposited as a uniform, pore-free, coherent coating which might be impenetrable to nitrogen.

Due to the insolubility of yttrium in chromium, or in any of the components of the alloy, and the absence of Y-Cr intermetallics, the metallizing cell could not be operated in the usual diffusion mode. Instead, conditions were sought for electroplating of yttrium. The history of electroplating from fused salt media, dating from the time of Michael Faraday, is almost exclusively a dismal description of the formation of powdery or dendritic deposits. Only the refractory metals, aluminum-manganese alloys, and iridium have been electroplated as coherent deposits from molten salt baths, and even for these materials, success was not achieved easily. One of the necessary, but not sufficient, requirements for electroplating in salt baths is meticulous cleanliness. Thus, a gate valve system to permit introduction of chromium alloys into the salt bath in the total absence of air would certainly be mandatory if the work were to be pursued. The persistent nitrogen contamination in our experiments almost certainly contributed to the poor quality of the deposits. The successful fused salt plating of the refractory metals depended in part on precise control of the average valence of metal ions in solution (ref.13). However, the refractory metals are commonly multi-valent; yttrium is not.

The non-uniformity of the yttrium deposit obtained in the metallizing cell was reflected in non-uniform oxide coverage in the preoxidation and subsequent cyclic oxidation experiments. The oxides formed were porous, flaky, and variable in color over the surface of a single specimen.





## VII. RECOMMENDATIONS

There are methods other than metallizing and preoxidation by which an yttria-chromia diffusion barrier with the desired physical characteristics might be achieved. Ion plating of yttrium onto chromium, for example, could provide a well-adherent true diffusion layer which might subsequently be oxidized to a protective  $Y_2O_3-Cr_2O_3$  film. In ion plating an argon gas discharge would be struck between a chromium alloy cathode and a heated yttrium anode. Vaporizing yttrium atoms, some of which would be ionized in the plasma, could strike the chromium surface with sufficiently high energy to penetrate the surface with the formation of a stable diffusion zone. One of the great advantages of ion plating, particularly for active metal substrates, is that sputter cleaning precedes and accompanies the actual plating process, so that surface impurities are effectively eliminated.

Another possibility might be to deposit  $Y_2O_3-Cr_2O_3$  directly onto the alloy surface by chemical vapor deposition. Hydrolysis of a mixture of  $YCl_3(g)$  and  $CrO_2Cl_2(g)$  might produce the desired product, although not necessarily as an adherent coating. Alternatively, yttrium might be chemically vapor deposited by hydrogen reduction of  $YCl_3(g)$  at the chromium alloy surface, and subsequently oxidized. Adhesion again would be the major problem, since chemical vapor deposition, unlike ion plating, will not give a diffusion type interface if the coating is insoluble in the substrate and forms no compounds with it.

All things considered, the ion plating approach appears to be most promising. Adherent, fully dense, pore-free coatings are obtained even at thicknesses of the order of .08 mil (2000 Å). In order to promote formation of the mixed oxide,  $Y_2O_3-Cr_2O_3$ , some chromium might be ion plated simultaneously with the yttrium, from a separately powered source.



## VI. CONCLUSIONS

1. We have been unable to produce any yttrium-containing diffusion coating on the alloy Cr-7Mo-2Ta-0.09C-01Y by the metallizing process, despite the fact that free yttrium has been found by X-ray diffraction on the alloy surface after treatment.
2. The presence of nitrogen in the cell electrolyte appears unavoidable with the present experimental equipment. Some nitrogen from the air appears to enter the cell during operation, despite the use of yttrium chips over the electrolyte as a getter for O<sub>2</sub> and N<sub>2</sub>. We do not consider the presence of nitrogen in the cell to be the cause of the failure of diffusion. However, yttrium electro-deposited on the alloy surface often appeared as YN. The presence of the surface nitride did not embrittle the substrate.
3. The failure of the diffusion process appears to be due to the inherent properties of the system. The alloy is already saturated with yttrium in solution and chromium forms no intermetallic compounds with yttrium.
4. We have succeeded in producing surface layers containing Y<sub>2</sub>O<sub>3</sub> and YOF on the alloy surface by oxidizing surface layers of plated-on material. These coatings, however, do not enhance the oxidation/nitridation resistance of the base alloy, and do not meet the goal of 3 mg/in.<sup>2</sup> (4.65 x 10<sup>-3</sup> kg/m<sup>2</sup>) weight gain in 200 hours.
5. Pretreatment of the alloy surface by boron diffusion formed CrB<sub>2</sub> which did not permit the subsequent diffusion of yttrium into the surface. Since boron raises the ductile-brittle transition temperature (DBTT) of the alloy to an unacceptable degree, this approach was not pursued.
6. Plating the alloy surface with nickel permitted the diffusion of yttrium with the formation of nickel-yttrium intermetallic compounds. Preliminary experiments, however, showed that this layer tended to flake off the base alloy and the yttrided samples were brittle. A more effective diffusion step prior to yttriding may overcome this problem.



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