

The changing landscape of carbonyl iron and nickel powder production

Until recently, much of the global production of carbonyl metal powder was centred on manufacturers in Europe and North America. Although China has produced these powders since the 1960s, the last ten years or so has seen a rapid increase in the volume of both carbonyl nickel and carbonyl iron powders produced in this region. In this report, Jun Shu and Lou Koehler describe the production processes and look at the changing landscape of carbonyl metal powder production.

Carbonyl nickel refining was first commercialised in 1902 by the Mond Nickel Company Ltd, with carbonyl iron powder production being developed in 1925 by Germany's BASF (formerly I G Farben). Today, carbonyl nickel powders are widely used in Powder Metallurgy, battery and fuel cell electrodes, hardmetal binders, welding rods, high-temperature filters, conducting additives, electronic materials, anti-seize lubricants, chemicals and catalysts (Fig. 1). Typical applications of carbonyl iron powders include Metal Injection Moulding (MIM), magnetic cores, hardmetal binders, radar absorption materials, magneto-rheological fluids for shock/vibration damping, precision polishing, industrial diamond synthesis and health supplements.

Global carbonyl nickel powder production capacity has reached around 37,000 metric tons per year, with the main producers being Vale in Canada and Wales, China's Jinchuan and Norilsk in Russia. Carbonyl

iron powder production capacity is reported to be around 29,000 metric tons per year, with BASF being the largest manufacturer. However, nearly half of the current carbonyl iron powder capacity is represented by recent additions from China.

Carbonyls of nickel and iron, of molecular forms $Ni(CO)_4$ and $Fe(CO)_5$,

were discovered by Dr Ludwig Mond and his colleagues in 1890 and 1891, respectively [1, 2]. Subsequently, carbonyl nickel refining, or the Mond process, was first commercialised in 1902 by the Mond Nickel Company in Clydach, South Wales, to produce high-purity nickel pellets [3]. Carbonyl nickel powder



Fig. 1 Commercial applications of discrete carbonyl nickel powder

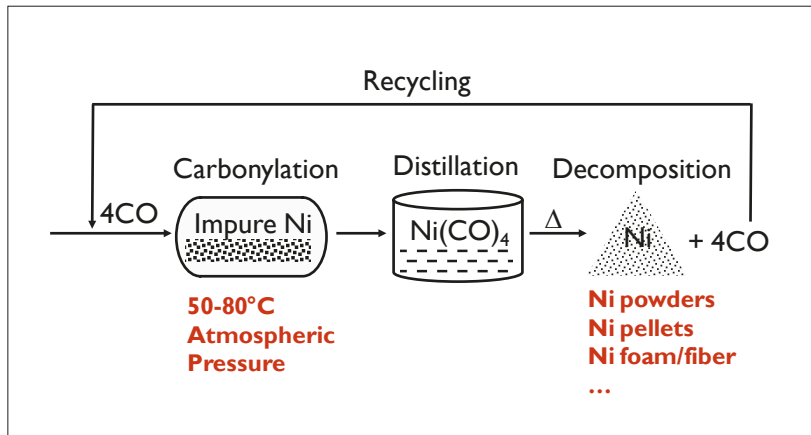


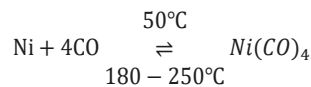
Fig. 2 Schematic diagram of carbonyl nickel extractive metallurgy

production was an invention of the German company BASF in the late 1920s with nickel matte feedstock acquired from the Mond Nickel Company [4].

The International Nickel Company (Inco) acquired the Mond Nickel plant in the 1920s and, in 1943, commercial nickel powder production began. In 1973, Inco opened a second carbonyl plant in Sudbury, Canada, the site of its major nickel mining operations [5]. These plants have been continually modernised and now operate under the ownership of the Brazilian mining giant Vale SA. This mature process is acknowledged as the best available technology for refining pure nickel. The three main reasons for this are the ability to produce a very high purity product, the low energy levels consumed in the process and the fact that, although the process uses highly toxic process intermediates, there are no polluting waste products, as virtually all the carbon monoxide gas is recycled and emissions of toxic carbonyls are controlled in the parts-per-billion concentration range.

The original carbonyl process, still used at Vale's Wales refinery, harnesses the ability of nickel in an impure form to be extracted into a nickel carbonyl gas (boiling point 43°C) at ordinary temperatures and then restored to a pure metallic state by gentle heating. Production begins with a nickel oxide feedstock. The nickel oxide is continuously

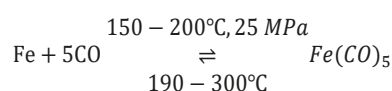
fed into a reduction kiln, where it is tumbled in a stream of pure hydrogen at ~230°C to produce impure nickel in granular form. In the second stage, the volatilisation kiln, the nickel reacts with carbon monoxide at close to atmospheric pressure to form nickel carbonyl gas, or nickel tetracarbonyl Ni(CO)₄:



$$K_{\text{eq}} (50^\circ\text{C}) = 3.78 \times 10^4 \quad (1)$$

The nickel carbonyl gas is then piped to an adjacent plant for thermal decomposition into pure nickel pellets or powders. To produce powder, the nickel carbonyl gas is injected at a metered rate into the top of the decomposer towers. The walls of the towers are heated to 300-500°C. The gas decomposes instantly to form nickel powder which settles at the bottom of the unit. The powder is collected, blended for uniformity, screened and packaged. A schematic of the carbonyl nickel extractive metallurgy is shown in Fig. 2.

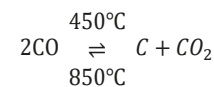
When an iron component is present in the feedstock, iron carbonylation occurs to form iron carbonyl, or iron pentacarbonyl Fe(CO)₅:



$$K_{\text{eq}} (50^\circ\text{C}) = 5.67 \times 10^{-2} \quad (2)$$

At ambient pressure, as practised at Vale's Wales refinery, the iron carbonyl formation equilibrium is negligible in comparison with nickel carbonyl formation. However, this parallel reaction equilibrium increases with pressure, which occurs at the more modern facilities in Vale Canada, Norilsk and Jinchuan, thus making it necessary to separate nickel carbonyl from iron carbonyl in a high pressure carbonyl process in order to produce pure nickel products. In fact, high pressure is fundamental to carbonyl iron synthesis in order to produce carbonyl iron powders upon thermal decomposition.

With the increase of decomposition temperature, a side reaction of CO disproportionation, or the Boudouard reaction, becomes important, resulting in residual carbon deposition on nickel and/or iron particles in specific refining processes:



$$K_{\text{eq}} (250^\circ\text{C}) = 9.53 \times 10^7 \quad (3)$$

Although the Boudouard reaction is thermodynamically favourable at low temperature, its reaction rate is kinetically low until about 450°C in the atmospheric pressure decomposition process. Increasing pressure shifts the position of equilibrium towards the right-hand side, resulting in more residual carbon formation.

The beauty of carbonyl metal refining (for nickel or iron) is that, following the metal extraction and distillation, gaseous metal carbonyl can be thermally decomposed back to high purity metal and carbon monoxide. Under precisely controlled thermal decomposition conditions such as temperature, feed rate, carbonyl concentration, partial pressure and introduction of additives, carbonyl nickel, iron or ferronickel powders can be produced in different morphologies and particle size distributions ranging from micron size powders to centimetre size pellets.

Carbonyl nickel powder production

Worldwide carbonyl nickel powder production capacity trends since the new millennium are shown in Fig. 3. Driven by booming industrial needs, Chinese carbonyl metal refineries have added nearly 20% carbonyl nickel powder capacity in the last ten years. It should be noted that, although world capacity is in excess of 37,000 metric tons per year, demand for carbonyl nickel powders is in the 25,000 metric tons per year range.

Carbonyl refining requires strict process safety measures, throughout the entire refinery operation, due to the extremely toxic nature of nickel carbonyl. For many decades, carbonyl nickel refining was the exclusive domain of the mining companies Inco Limited in Canada and Wales (acquired by Vale in 2006) and Norilsk Nickel in Russia. In 2015, a third mining company, Jinchuan in China, also commercialised carbonyl refining of nickel pellets and powders [6]. Below is a brief description of existing carbonyl nickel refining operations, with a comparison of characteristic operating parameters listed in Table 1.

United Kingdom: Vale Clydach Refinery

The first ever carbonyl refinery still uses the atmospheric pressure carbonyl refining process. Production begins with a nickel oxide feedstock received from mines in Sudbury,

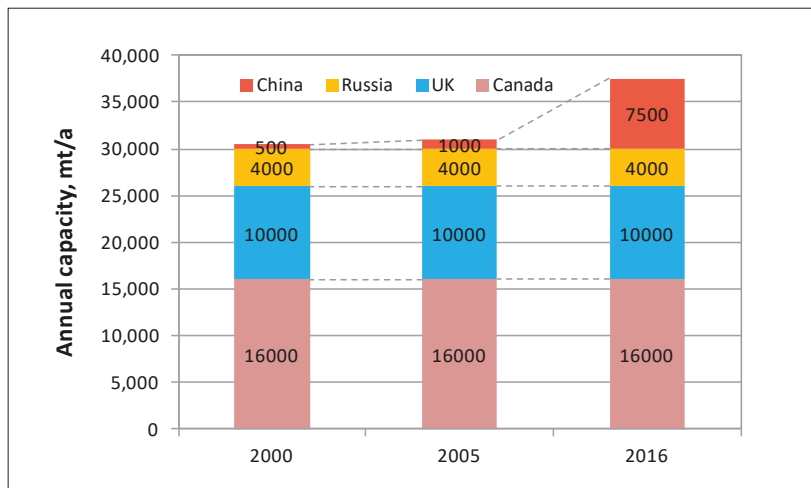


Fig. 3 Worldwide carbonyl nickel powder production capacity

Canada. Powder is produced in the final stage of the process by injecting nickel carbonyl gas at a metered rate into the top of one of eight decomposer towers, each ten metres in height by two metres in diameter [7]. By adjusting feed rates and temperatures, the powder particle morphology can be adjusted.

Two separate primary shapes are produced by different decomposition conditions; a spiky discrete powder and a filamentary powder. Combined nickel pellet and powder production capacity at Clydach is estimated at 45,000 metric tons per year, of which 10,000 metric tons are produced in powder form.

Canada: Vale Sudbury Refinery

This refinery was commissioned in 1973 using an intermediate pressure carbonyl refining process to increase

the nickel extraction yield. In intermediate pressure nickel carbonyl refining, nickel containing metallics are batch-charged into a rotating carbonylation reactor and allowed to react with carbon monoxide at ~7.0 MPa and 170°C [7, 8]. Nickel carbonyl and a fraction of iron carbonyl are condensed for storage, followed by distillation to separate nickel carbonyl and iron carbonyl based on their different boiling temperatures. Pure nickel carbonyl from the top of the distillation column is the feed for production of carbonyl nickel powders and pellets. Powder is produced in ten decomposer towers, each ten metres in height by two metres in diameter [7]. The mixture of nickel carbonyl and iron carbonyl from the bottom of the distillation column is the feed for production of FeNi pellets.

Refinery	Vale Clydach Nickel Refinery	Vale Sudbury Nickel Refinery	Norilsk Nickel Kola MMC	Jinchuan Carbonyl Refinery
Feed	Impure Ni oxide	Impure Ni metallics	Ni metallics, Off-spec Ni	Ni metallics, Off-spec Ni
Pressure (MPa)	Atmospheric	7.0	22.5	7.0-9.0
Temperature (°C)	50-60	170	150-250	150-220
Annual capacity (mt/a)	45,000 (10,000 powder)	60,000 (16,000 powder)	5,000 (4,000 powder)	10,000 (5,000 powder)
Ni extraction (%)	90	97-98	97-98	97-98
Commissioning year	1902	1973	Early 1960s	2015
Typical products	Ni powders, Ni pellets	Ni powders, Ni pellets FeNi pellets	Ni powders, Ni pellets	Ni powders, FeNi powders, Fe powders, Ni pellets

Table 1 Comparison of commercial carbonyl nickel refining processes

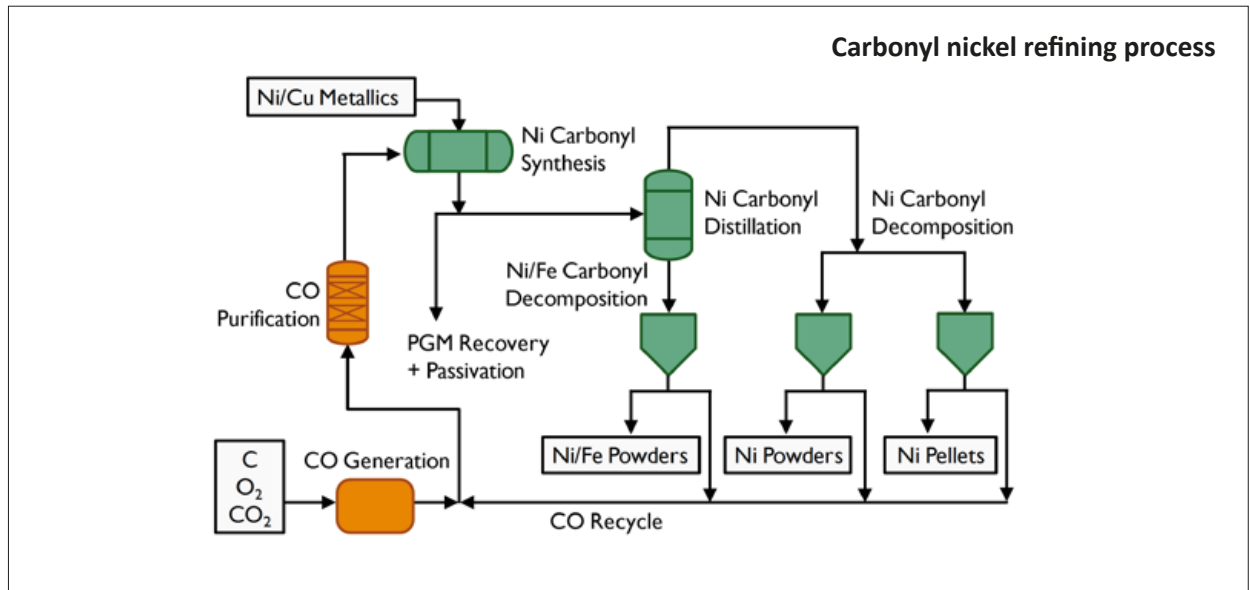


Fig. 4 Jinchuan nickel carbonyl refining process flow-sheet

It should be mentioned that, in the original design of the Vale Sudbury refinery, this stream was used to produce FeNi powder [9]. Carbon monoxide from the decomposers is compressed and cycled back to the carbonylation reactor. Estimated annual capacity in Sudbury is around 60,000 metric tons, of which 16,000 metric tons is in powder form. Powder capacity is higher here than at Clydach due to higher carbonyl gas strength (~40% versus ~14% [7]) generated by intermediate pressure refining.

Russia: Norilsk Monchegorsk Refinery

Carbonyl nickel refining in Russia can be traced back to the initial German activities at I G Farben before World War II. Two small carbonyl plants were developed by I G Farben in Germany in the late 1920s for the production of carbonyl iron and carbonyl nickel powders. As an extension of its original iron carbonylation technology, I G Farben conducted nickel carbonylation at a high pressure of ~20.0 MPa and 200°C. Carbonyl nickel powder production promoted the development of nickel-cadmium batteries suitable for tanks and military aircraft during the 1930s [4]. After the end of World War II, Russia is said to have

dismantled and moved one of the I G Farben carbonyl plants, located in the Soviet Occupation Zone, to Monchegorsk on the Kola Peninsula (now Norilsk Nickel) in north-western Russia and constructed a commercial plant for production of carbonyl nickel powders in the early 1960s [10].

Norilsk Nickel practises high pressure carbonylation at around 22.5 MPa and 150-250°C. Off-spec electrolytic nickel cuts and/or granular nickel metallics are batch charged in a fixed carbonylation tower to react with a continuous carbon monoxide feed, followed by fractional distillation of nickel and iron carbonyls. Subsequent decomposition of nickel carbonyl in one-metre diameter decomposer towers yields nickel powder and nickel pellets [10]. Estimated capacity at Norilsk is around 5,000 metric tons per annum, of which 4,000 metric tons is in powder form.

China: Jiangyou Hebao Nanomaterials Co Ltd

The Chinese carbonyl nickel industry debuted in the early 1960s with the development of the nuclear industry. The former state-owned 857 Factory was built in the mountainous region of Jiangyou, Sichuan Province for the production of carbonyl nickel

powders under the sponsorship of the Chinese Ministry of Nuclear Industry. This plant developed a high pressure carbonylation process at about 150-180°C and 15.0-20.0 MPa, with scrap nickel as the feedstock. Annual production capacity of carbonyl nickel powders was up to a few hundred metric tons for China's nuclear industry use [11,12]. With technological advancement in the nuclear industry and the increased availability of imported carbonyl nickel powders into China, the former state-owned 857 Factory was gradually phased out at the beginning of the new millennium. Its core carbonyl technology business was then restructured as Jiangyou Hebao Nanomaterials Co., Ltd., for the production of small volumes of carbonyl nickel powders and carbonyl iron powders for niche markets.

China: Jinchuan Carbonyl Refinery

Development of carbonyl nickel refining technology at Jinchuan Group started in the late 1990s following the Chinese economic boom. A pilot plant with a designed carbonyl nickel capacity of 500 metric tons was built in the early 2000s in order to establish the engineering basis for a commercial plant. Various technical issues were solved, ranging from carbonylation to subsequent

carbonyl decomposition into high purity nickel products, as reflected by over 70 Chinese patent applications. In 2015, Jinchuan Group commissioned a new carbonyl refinery with a design capacity of 10,000 metric tons of carbonyl nickel products, of which half are in powder form. Fig. 4 shows the basic flow-sheet of Jinchuan carbonyl nickel refining.

Jinchuan's nickel resource is sulphide ores, similar to Vale and Norilsk. Their carbonyl refining unit operations are based on similar principles. Process deviations are mainly driven by availabilities of feedstocks at Jinchuan Group. In the Jinchuan carbonyl refining process, the starting raw materials include Ni/Cu metallics from smelting, nickel shot and electrolytic nickel scrap. Carbon monoxide is generated from coal burning and purification. Initially, the pilot plant adopted the high pressure carbonylation route [11]. Through extensive assessment and improvement of the technology, the operating pressure was decreased to the intermediate pressure range (refer to Table 1) and applied to the commercial refining process [12]. Due to the simultaneous carbonylation of iron impurities, distillation is necessary to separate nickel carbonyl from iron carbonyl before the final thermal decomposition into carbonyl nickel products such as nickel powders and nickel pellets. Precise control of nickel powder particle size distribution and morphology is readily achieved through sophisticated modern process control systems.

China: Jien Nickel

It should be mentioned that carbonyl nickel refining has also been practised at Jilin Jien Nickel Industry Co., Ltd., in the north eastern Chinese Province of Jilin since 2004, utilising the consulting services of the Canadian CVMR Corporation [13]. An atmospheric pressure carbonylation process was adopted in this refinery, using imported nickel oxide as feedstock. The design capacity of carbonyl nickel powders at Jien Nickel was 2,000 metric tons per year. Due to limitations in

feed material supplies, Jien Nickel later tested a nickel hydroxide feed derived from a lateritic ore leaching process [14, 15]. While Jien is still optimising the atmospheric pressure carbonylation process, their production activity remains minor on the global carbonyl nickel powder supply market.

Characteristics of carbonyl nickel powder

In general, carbonyl nickel powders with an apparent density lower than 1.0 g/cm^3 are referred to as light nickel powders, often in the form of filamentary morphology (three-dimensional chain of fine particles fused together), while carbonyl nickel powders with an apparent density over 1.0 g/cm^3 are referred to as heavy nickel powders, often in the form of discrete particle shapes. Fig. 5 shows typical microscopic images of filamentary and discrete carbonyl nickel powders produced by the Jinchuan Group. Their

N series carbonyl nickel grades are named in relation to their apparent density (bulk density), e.g., N24™ is for nickel powder with an average apparent density of 2.4 g/cm^3 , and N06™ with an average apparent density of 0.6 g/cm^3 . Jinchuan filamentary carbonyl nickel powder N06™ is equivalent to Vale Type 255™ nickel powder, and their discrete nickel powder N24™ is equivalent to Vale Type 123™ nickel powder [16] and Norilsk UT3™ nickel powders.

Table 2 gives a comparison of typical physical and chemical properties of commercially available carbonyl nickel powders [6, 17, 18]. For general descriptions of carbonyl nickel powder properties, refer to reference [6]. Due to their high purity and well-defined microstructures, carbonyl nickel powders have found growing industrial applications. A list of primary applications for filamentary and discrete carbonyl nickel powders is as follows:

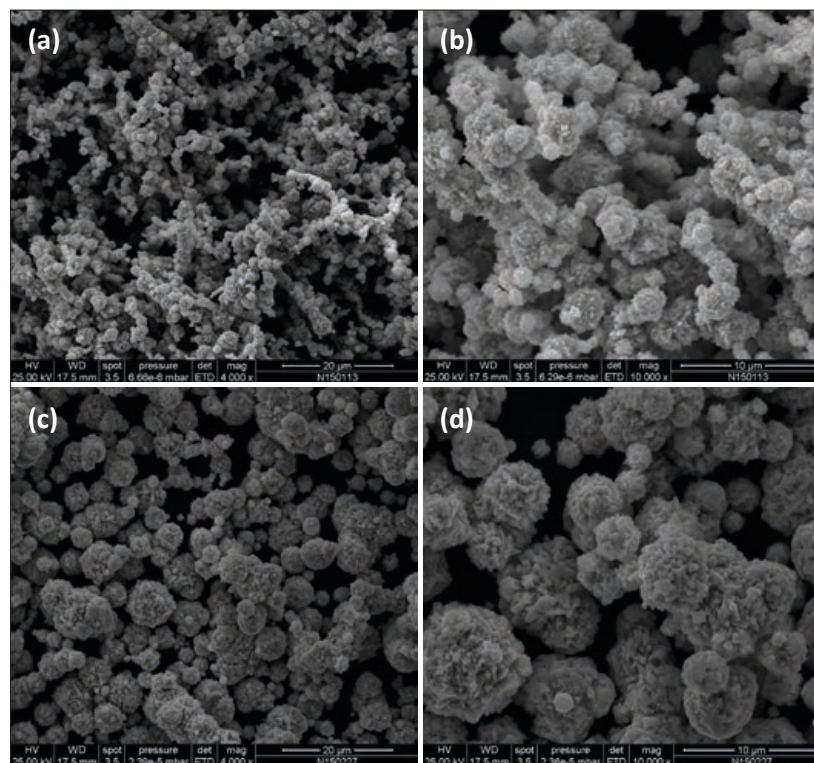


Fig. 5 Typical SEM images of carbonyl nickel powders produced by the Jinchuan Group (a) N06™ filamentary powder, 4,000x (b) N06™ filamentary powder, 10,000x (c) N24™ discrete powder, 4,000x (d) N24™ discrete powder, 10,000x

Powder type	A.D. g/cm ³	FSSS* μm	Ni wt%	Fe wt%	C wt%	O wt%	S wt%
Jinchuan N06™	0.50-0.65	2.0-2.8	>99.8	<0.0015	<0.150	<0.1500	<0.0010
Vale T255™	0.50-0.58	2.2-2.6	>99.7	<0.0030	<0.2000	<0.0750	<0.0002
Jinchuan N24™	1.8-3.0	2.3-4.0	>99.8	<0.0015	<0.100	<0.1000	<0.0010
Vale T123™	1.9-2.3	3.5-4.0	>99.8	<0.0010	<0.075	<0.0800	<0.0001
Norilsk UT3™	1.9-2.5	3.0-6.0	>99.8	<0.0015	<0.090	N/A	0.0007

*FSSS – Fisher Sub-Sieve Sizer, refer to ASTM Standard B330

Table 2 Comparison of typical properties of commercial carbonyl nickel powders

Filamentary carbonyl nickel powders (light nickel powders):

- Sintered electrodes for batteries and fuel cells
- Hard metal binders
- Powder Metallurgy
- Sintered filters
- Conducting additives for electronic applications

Discrete carbonyl nickel powders (heavy nickel powders):

- Powder Metallurgy
- Hard metal binders
- Welding rods
- High purity nickel strips
- Industrial diamond synthesis
- Anti-seize lubricant
- Electronic materials
- Chemicals and catalysts

Carbonyl iron powder production

As mentioned earlier, I G Farben pioneered the production of both carbonyl nickel powders and carbonyl iron powders nearly 90 years ago [19]. The iron carbonylation (reaction 2) was not favourable at atmospheric pressure, due to a lower equilibrium reaction constant versus nickel carbonylation (reaction 1). Therefore, carbonyl iron synthesis was done under high pressure, a process that in the 1920s I G Farben had experience of through various high pressure chemical process operations. In its iron carbonyl synthesis, hydrogen reduced iron granules (or sponge iron) are used to react with carbon

monoxide under a pressure of ~25.0 MPa and 150-200°C, resulting in an iron extraction of ~65% from a batch operation of about 120 hours. The pale-yellow liquid carbonyl released from the carbonylation reactor has a boiling point of 103°C and is then purified through distillation. Upon evaporation and dilution with CO, iron carbonyl is introduced to the top of a cylindrical decomposer to produce ultrafine carbonyl iron powder at a temperature ranging from 250-300°C, together with adding ammonia (NH₃) as an inhibitor to minimise the CO disproportionation rate (reaction 3). The carbonyl iron powder is removed from the decomposer bottom, with the released CO recycled back for further iron extraction.

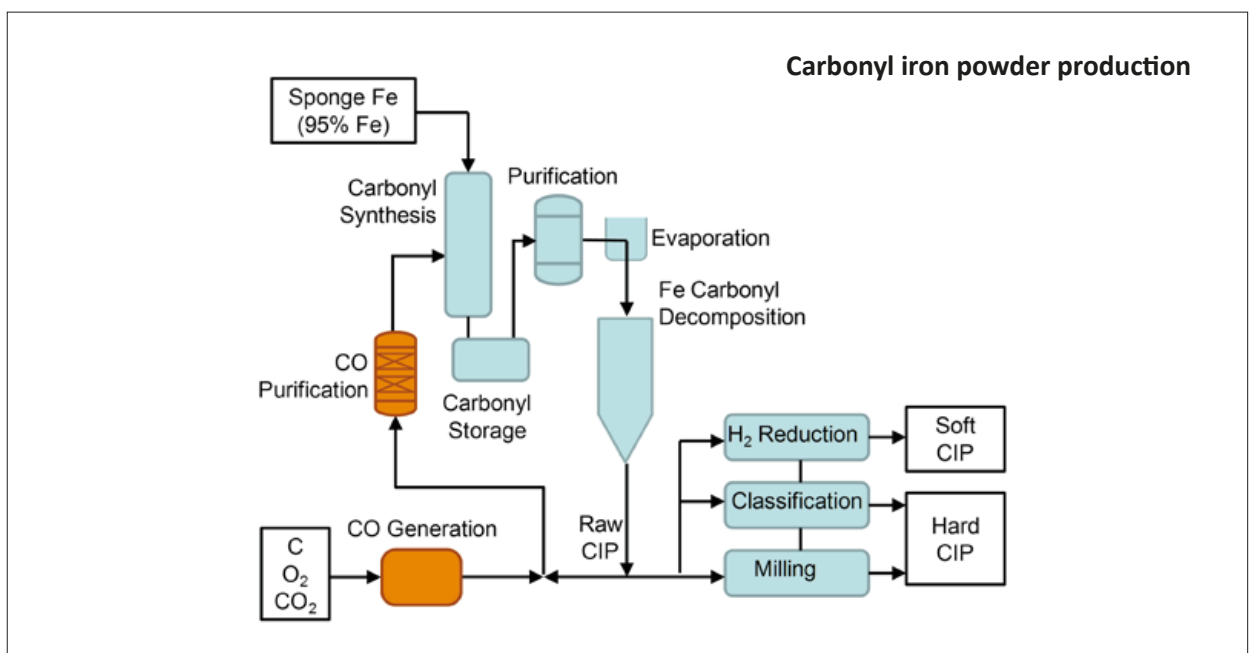


Fig. 6 A typical carbonyl iron powder production process flow-sheet

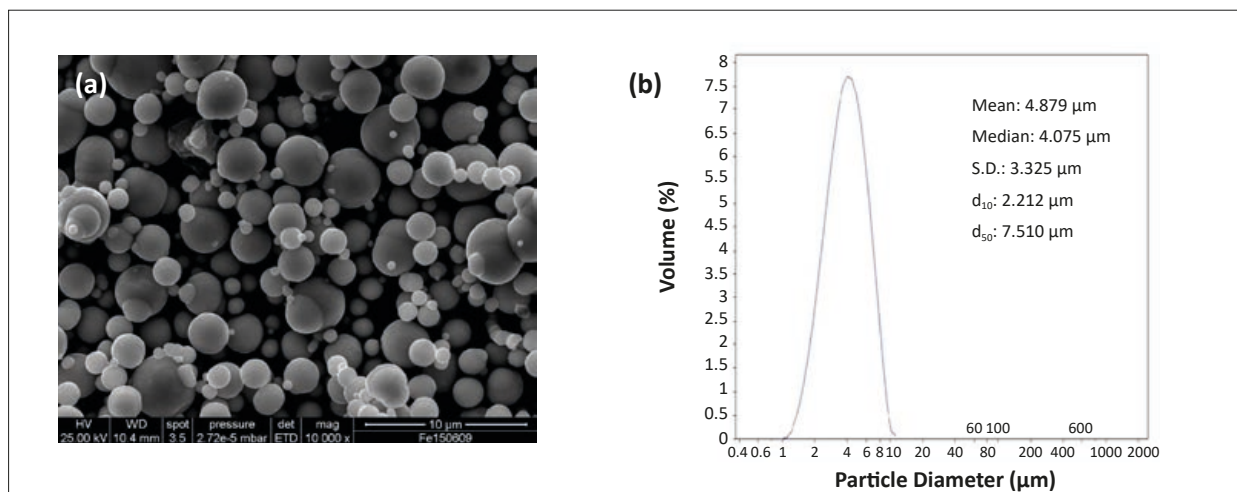


Fig. 7 Typical SEM image and particle size distribution of carbonyl iron powders from Jinchuan Group (a) Hard CIP (b) CIP particle size distribution

As-decomposed carbonyl iron powders are mostly spherical, with a particle size distribution in the range of 1–10 microns. They contain approximately 97% iron, with non-metallic elements of residual carbon (≤ 1.0 wt.%), nitrogen species (≤ 1.0 wt.%, mostly in the form of iron nitride [20] and a small amount of chemisorbed ammonia), and oxide (≤ 0.5 wt.%) from the passivation step. The residual carbon is enriched in an onion-skin layered structure due to the endothermic nature of iron carbonyl decomposition and the formation of carbon species on fresh iron particles, being mechanically hard (as in hard powder) due to tension between onion-skin layers.

Jet milling is often practised in order to produce agglomerate-free primary particles, followed by classification in a protective nitrogen atmosphere to cut carbonyl iron powders into fractions with the required particle size range as per customer needs and specific applications. To reduce residual carbon content, as-decomposed carbonyl iron powder may be subject to hydrogen reduction to yield a new carbonyl iron powder category of soft grades. This can be done in H_2 at 400–600°C for 1–4 hours to make soft grades with Fe content >99.5 wt.%, and low contents of C, N, O [21]. The new soft grade carbonyl iron powder is mechani-

cally soft (as in soft powder) with excellent compaction properties. Fig. 6 is a schematic flow chart showing various carbonyl iron powder production steps.

Production in Europe and North America

In the last century, BASF was the dominant manufacturer of carbonyl iron powders (CIP) with an annual capacity of around 12,000 mt. Two other players were International Specialty Products (ISP), since acquired by Ashland Inc., in the USA and Sintez-CIP in Russia [22, 23], each with around 1500 mt CIP capacity per year based on their website claims. Ashland carbonyl iron powder production can be traced back to the iron carbonyl plant established by GAF Corporation in the US with patents and know-how acquired from I G Farben [24]. Despite several ownership transfers in the past, carbonyl iron powder production continues in the US [25].

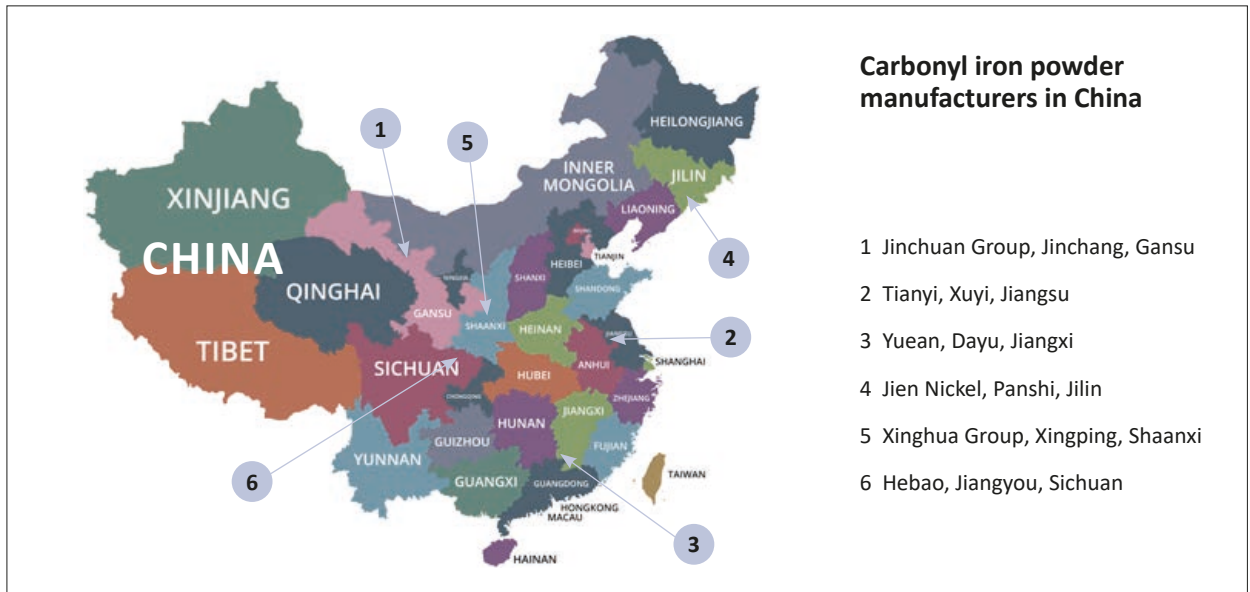
Growth in Chinese production

China has had limited activities in carbonyl iron powder production since the early 1960s, with the former state-owned 857 Factory and another small chemical company (now known as Shaanxi Xinghua Group) producing carbonyl iron products for military uses. Following the restructuring of the 857 Factory in the new millennium, its knowledge accumulated

from the early iron carbonyl synthesis promoted the development of several carbonyl iron powder projects in such newly formed companies as Tianyi Ultrafine Metal Powder Co., Ltd. [26] and Yuean Superfine Metal Co., Ltd. [27].

In 2001, Tianyi Ultrafine Metal Powder Co., Ltd. was founded in the Province of Jiangsu to test a pilot scale carbonyl iron powder plant. This start-up company survived the proverbial “valley of death” in its first two years and gradually ramped up the carbonyl iron powder production to a new level of around 3,000 mt per year in 2009, subject to further expansion. Iron carbonylation in the Tianyi process is done at a pressure below 20.0 MPa and at 140–160°C.

Yuean Superfine Metal Co., Ltd. in the Province of Jiangxi is a joint venture by Yuelong Superfine Metal Co., Ltd. and other investors. The holding company, Yuelong, was founded in 2003 for the new carbonyl iron powder business development. They achieved a successful iron carbonylation process under a pressure of 15.0–18.0 MPa and temperature ranging from 100–200°C in a three day batch operation [28]. In 2005, a new joint venture (Yuean) was set up to further expand carbonyl iron powder production capacity to ~2,000 mt and this now stands at 3,000 mt per year. Their carbonyl iron powder products are marketed under the trademark of Yuelong Powder [29].



Carbonyl iron powder manufacturers in China

- 1 Jinchuan Group, Jinchang, Gansu
- 2 Tianyi, Xuyi, Jiangsu
- 3 Yuean, Dayu, Jiangxi
- 4 Jien Nickel, Panshi, Jilin
- 5 Xinghua Group, Xingping, Shaanxi
- 6 Hebao, Jianguo, Sichuan

Fig. 8 Locations of Chinese carbonyl iron powder manufacturers

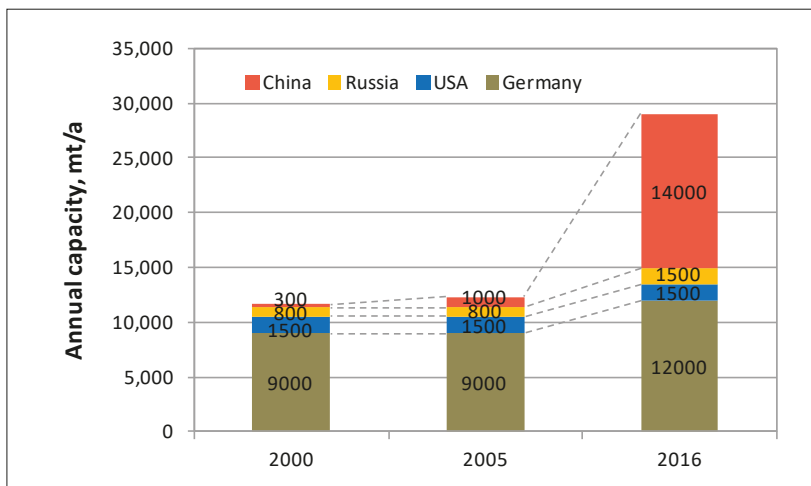


Fig. 9 Worldwide carbonyl iron powder production capacity

claim - nearly half of worldwide total production. Real production figures of Chinese carbonyl iron powder might be lower and fluctuating depending on the market digestion of the newly added CIP capacities. A global landscape of current carbonyl iron powder production is shown in Fig. 9.

A comparison of major iron carbonyl synthesis processes in the world as of 2017 is shown in Table 3. Technologically, there are common features in the production of carbonyl iron powders and carbonyl nickel powders by different suppliers. Business extensions were often seen to produce carbonyl powders along both series of iron and nickel, as practised earlier at Inco and BASF (before 1970).

Characteristics of carbonyl iron powder

In comparison with the original BASF high pressure iron carbonyl process (over 20.0 MPa), a majority of Chinese iron carbonylation processes operate in the lower pressure range (8.0–20.0 MPa). The pressure decrease in iron carbonylation not only lowers the operation cost, but brings in higher iron extraction (75% in Chinese processes versus 65% in the BASF process). It is now understood that, during iron carbonylation at over 200°C and at

While developing nickel carbonyl refining technology, Jinchuan Group also developed its own carbonyl iron synthesis technology. Starting from a sponge iron feedstock, the iron carbonyl synthesis is done in a batch operation (~3 days) at a pressure between 16.0–20.0 MPa and temperature ranging from 200–250°C [30]. Jinchuan’s carbonyl iron powder production capacity is about 5,000 mt per year, being the largest in China. A typical SEM image of Jinchuan carbonyl iron powder is shown in Fig. 7, with a particle size distribution curve shown on the right-hand side.

Another Chinese nickel company, Jien Nickel, also commissioned a carbonyl iron powder plant with

the help of the Lanzhou Branch of The Chinese Academy of Science. Under an intermediate pressure of 3.0–8.5 MPa and a temperature in the range of 120–250°C, iron extraction reached ~75% after 60 hours batch carbonylation [31].

Small carbonyl iron powder manufacturers also include the Shaanxi Xinghua Group and the spin-off company from the former state-owned 857 Factory (several hundred metric tons each). Fig. 8 shows the geological locations of the above Chinese carbonyl iron powder manufacturers. As of today, the combined total production capacity of carbonyl iron powders from China is ca. 14,000 mt/year as per each manufacturer’s

Producer, Country	BASF, Germany	Ashland, USA	Sintez, Russia	Jinchuan, China	Tianyi, China	Yuean (Yuelong), China	Jien, China
Pressure (MPa)	~25.0	13-18	20	16-20	13-20	15-18	3.0-8.5
Temperature (°C)	150-200	170-200	180-200	200-250		100-200	120-250
Annual capacity (mt/a)	12,000	1,500	1,500	5,000	3,000	3,000	2,000
Batch hrs/Fe extraction, %	120h/~65%			72h/		72h/	60h/~75%
Commissioning year	1925	1942	1953	2012	2005-2008	2005-2009	2009
Typical products	Hard/soft CIP, coated CIP	Hard/soft CIP	Hard/soft CIP	Hard/soft CIP	Hard/soft/coated CIP other metal carbonyls	Hard/soft CIP, liquid iron carbonyl	Hard/soft CIP

Table 3 Comparison of iron carbonyl synthesis at major carbonyl iron powder manufacturers

high pressure, CO disproportionation could be promoted on the fresh iron surface, resulting in carbon deposition on iron, which gradually decelerates the carbonylation reaction rate and inhibits further iron extraction. In comparison with nickel carbonylation, the effect of CO disproportionation under high pressure is particularly pronounced in iron carbonylation, as iron is a more active catalyst towards CO disproportionation. This can be easily understood by the fact that residual carbon content in as-decomposed carbonyl iron powders (<1.0%) is several times higher than that in as-decomposed carbonyl nickel powders (<0.2%).

Carbonyl iron powder manufacturers can produce various grades of spherical iron powders in the size

range of 1-10 microns from atmospheric decomposition operations. Table 4 lists typical carbonyl iron powder products from a selection of major manufacturers. The fundamental categories are actually hard grades (as-decomposed) and soft grades (H₂ reduced). Further deviations, in such product specifications as particle size distribution and bulk density, are achievable through post processing by milling and classification to meet specific application requirements. Carbonyl iron powders have found wide applications in Metal Injection Moulding (MIM, ca. 30-35%, being the largest among others), magnetic cores for high-frequency coils, hard metal binders, radar absorption materials (RAM), magneto-rheological fluids

(MRF) for shock/vibration damping, clutch and brake systems, precision polishing (for example, to produce the smooth surface finish found on the Jet Black iPhone 7), industrial diamond synthesis and food iron supplements. Excellent literature references with regard to specific applications can be found on BASF's corporate website [32].

It should be mentioned that, similar to carbonyl nickel powder products, the production of light weight filamentary iron powder and nano iron powders is also possible under special decomposition conditions. As an example, Ashland used to offer a filamentary carbonyl iron powder with characteristics of <0.2 µm diameter and average 4 µm in length.

Company	Grade	D ₅₀ µm	A.D. g/cm ³	T.D. g/cm ³	Fe _{min} %	C _{max} %	O _{max} %	N _{max} %
BASF	CIP OM	3.9-5.2			97.8	0.75-0.9	0.15-0.40	0.65-0.90
Jinchuan	F01	1-6	1.0-3.5		97.5	0.8	0.5	1.0
Tianyi	YMIM90	<5.0	<3.0	≥4.0	Bal.	0.76-0.90	0.6	0.9
Yuean	O1S	3.5		4.0-4.1	97.0	0.6-0.9	0.35-0.65	
BASF	CIP CC	3.8-5.3			99.5	0.05	0.18-0.35	0.01
Jinchuan	F02	<5.5	2.5-3.2	3.5-4.5	99.0	0.1	0.3	0.1
Tianyi	RMIM20	<6.0	<3.0	≥4.0	Bal.	0.06-0.15	0.2	0.05
Yuean	HY1	5.5			99.5	0.03	0.3	

Table 4 Comparison of typical commercial carbonyl iron powders for MIM

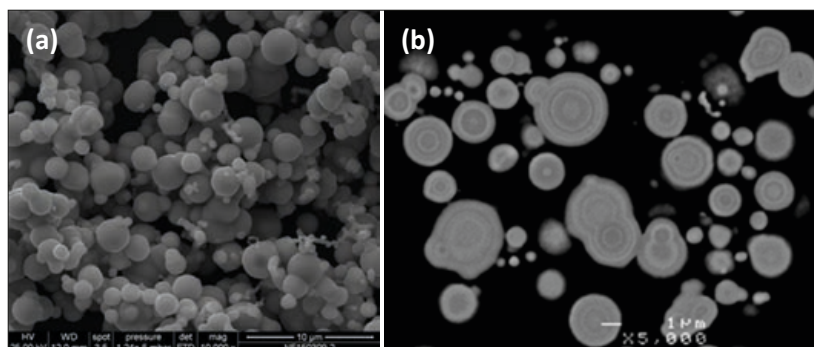


Fig. 10 Typical SEM images of (a) carbonyl ferronickel powder and (b) cross-sectional view of internal onion-skin structure

Carbonyl ferronickel powders

The Chinese Jinchuan Group produces carbonyl ferronickel powders with mixtures starting from liquid iron carbonyl and the bottom fraction of nickel carbonyl distillation columns. The mixture fraction of iron carbonyl and nickel carbonyl is easily adjusted to the required Fe/Ni ratio for production of ferronickel powders. Currently, five ferronickel powder grades are commercially available from Jinchuan Group, being NF19™, NF28™, NF37™, NF46™ and NF55™, containing 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.% and 50 wt.% nickel, respectively.

Typical SEM images of carbonyl ferronickel powder NF37™ are shown in Fig. 10. They are, in general, micron-size spherical particles with an internal onion-skin structure (Fig. 10b). Similar to carbonyl iron powders, the formation of an onion-skin microstructure inside carbonyl ferronickel particles results from the endothermic decomposition of iron carbonyl and the CO disproportionation on the more catalytically active iron surface. The alternate layers appear to be very fine inhomogeneous mixture of elemental iron and elemental nickel, as evidenced by X-ray diffraction. Carbonyl iron is in a body centred cubic (bcc) crystalline structure, whereas carbonyl nickel is in a face centred cubic (fcc) crystalline structure. The interface between the alternate iron and nickel layers might exhibit

interesting ferromagnetic behaviour, which is yet to be investigated. Applications of carbonyl ferronickel powders include Power Metallurgy, magneto-rheological fluids, radar absorbing materials, EMI/RFI shielding, industrial diamond synthesis, etc.

Conclusion

In summary, the availability and varieties of carbonyl metal powder products are expanding, especially following the recent technological progress in the Chinese carbonyl metal refining industry. With continuous carbonyl refining technology development, more carbonyl nickel and ferronickel powders will no doubt become available in the near future.

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Acknowledgment

The authors wish to thank Dr Vladimir Paserin and Dr Dmitri Terekhov for their valuable input in preparing this article.

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