

# Powder Metallurgy Nickel and Nickel Alloys

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A LARGE PORTION OF PURE NICKEL POWDERS is used in production of alloys, primarily low alloy steels, produced by powder metallurgy processing, pressing, and sintering. Nickel improves mechanical properties, such as tensile strength and ductility. These alloys are typically used in very competitive markets and applications, and therefore the nickel powders need to be produced by manufacturing methods that can provide a high value product at competitive pricing.

High performance nickel-base powder metallurgy superalloys are used almost exclusively for manufacturing jet engine components or electric turbines for power generations. The PM processing offers numerous advantages for these high performance applications where the unique microstructural and property characteristics of powder metallurgy superalloys are being utilized. To attain these characteristics, high quality and microcleanliness of the alloy is necessary, which can be only attained by vacuum melting and gas atomization, and consolidation by hot isostatic pressing (HIP), followed frequently by hot working operations. More recently, the use of lower end nickel-base superalloys has gained acceptance in other demanding applications where corrosion resistance, high strength, and good toughness at a broad temperature range provides design and performance advantages. Additionally, using powder alloys provides an opportunity to use near net shape technology, which results in cost saving, design flexibility, and shortened delivery times.

## Nickel and Nickel Alloy Powders

Nickel is added to iron powder metal blends to improve the mechanical properties of sintered PM parts, such as ultimate tensile strength and ductility. Tensile strength increases with increasing nickel content, particularly in the heat-treated condition. The nickel may be added either in pre-alloyed form, where nickel is melted prior to atomization, or preferably, to avoid hardening of the base iron powder, as pure nickel powder

mixed in with the iron powder. Mixing nickel and iron powders can be achieved by admixing or by bonding to the iron powder through chemical or diffusion-bonding processes. When added in powder form, nickel-rich phases stabilize austenite and improve toughness and fatigue properties of sintered steels. Admixed or bonded nickel powder also promotes shrinkage of the sintered part. Shrinkage increases part density, which, in turn, strongly affects mechanical properties. Nickel powder is often added with copper powder to achieve better dimensional control, as copper tends to cause volume expansion in PM steels. Among PM nickel steels, high purity carbonyl nickel powder, with its fine discrete particles, is the form of nickel almost exclusively used (Ref 1).

## Production of Nickel Powders

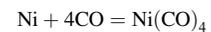
There are several processes being used for production of nickel powders. The most common process, which provides high purity nickel powders, is the carbonyl refining process. Depending on the raw material used, other processes may provide processing and cost benefits.

### The Carbonyl Process

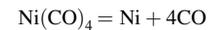
Dr. Carl Langer and Dr. Ludwig Mond discovered the nickel carbonyl process in 1889 and, in 1902, built the first refinery at Clydach, South Wales, to produce high-purity nickel pellets. The International Nickel Company (Inco) acquired the plant in the 1920s, and in 1943, commercial powder production began. In 1973, Inco opened a second carbonyl plant in Sudbury, Canada, the site of its major nickel mining operations. The plants have been continually modernized and continue to operate under the ownership of Vale. 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 with little residue, and the fact that

there are no polluting waste products as virtually all the carbon monoxide gas is continuously recycled.

The carbonyl refining process harnesses the ability of nickel in an impure form to be extracted into a nickel carbonyl gas at ordinary temperatures and then to be 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 (446 °F) to produce an impure nickel in granular form. In the second stage, the volatilization kiln, the nickel reacts with carbon monoxide at close to atmospheric pressure to form nickel carbonyl gas:



The nickel carbonyl gas is then piped to an adjacent plant for thermal decomposition into pure nickel pellet or powder. To produce powder, the nickel carbonyl gas is injected at a metered rate into the top of decomposer towers. The walls of the towers are heated to 300 to 500 °C (572 to 932 °F). The gas decomposes instantly to form nickel powder which settles at the bottom of the unit:

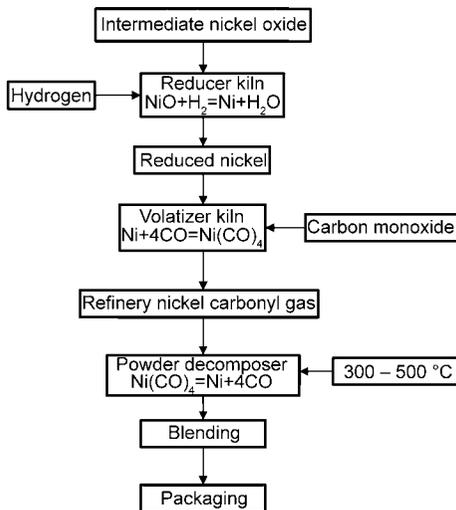


The powder is collected, blended for uniformity, screened, and packaged (Ref 2).

**Carbonyl Production Plants.** This process is used at several refineries across the globe, described here.

*Vale Clydach Refinery.* The production begins with a nickel oxide feedstock received from mines in Sudbury, 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 meters in height by two meters in diameter. The schematic of the process is shown in Fig. 1.

By adjusting feed rates and temperatures, the morphology can be adjusted. Two separate primary shapes are produced by different decomposition conditions, a spiky discrete particle



**Fig. 1** Vale Clydach refinery flow diagram

and a filamentary (three-dimensional chain of fine particles fused together) particle; see Fig. 2 and 3. Combined nickel pellet and powder production capacity is estimated at 45,000 tons per year (Ref 3).

*Vale Sudbury Refinery.* There are three main facilities at the refinery: the Nickel Refinery Converter Plant (NRC), the Pressure Carbonyl Plant, and the Electrowinning building. Unlike the Clydach refinery where the feedstock is relatively high purity nickel oxide, here a variety of smelter crude ores and other nickel bearing intermediates are charged into top blown rotary converters and melted using natural gas-oxygen lance burners. Once converter temperature reaches  $\sim 1600$  °C (2912 °F), petroleum coke is added to reduce the oxygen content of the charge material. High-pressure oxygen is occasionally blown into the charge to desulfurize it if the sulfur content is too high. The melted product is transferred to a teeming ladle and poured through high velocity water jets (called granulation). The resultant granules (containing 65–75% Ni, 15–20% Cu, 2–3% Fe, and 3% S present as sulfides) are dewatered, dried in a gas-fired kiln and transferred to the Pressure Carbonyl Plant.

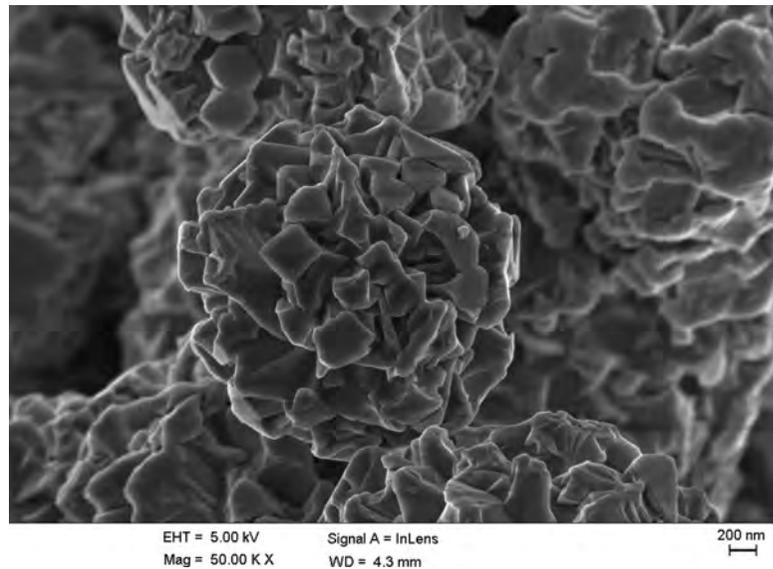
At the Pressure Carbonyl Plant, the granules are batch reacted with carbon monoxide at temperatures up to 180 °C (356 °F) and pressures up to 1000 psi in three 150-ton rotating reactors. Nickel and a small amount of iron are extracted as carbonyl vapors, while copper, cobalt, precious metals, and other impurities are retained in the residue. The residue is milled and pumped to the Electrowinning plant. The nickel and iron carbonyl vapor is liquefied in a vertical distillation column; nickel carbonyl separate and rises to the top of the column while iron carbonyl settles at the bottom of the column. Fractionating the crude carbonyl is easily achieved because the boiling points of nickel and iron carbonyls are 43 °C and 102.8 °C (109 °F and 216 °F), respectively. The nickel carbonyl gas is transferred to

the pellet or powder decomposer towers (10 m, or 33 ft, high by 2 m, or 6.5 ft, diameter), which are similar to the ones at the Clydach refinery. Pure nickel carbonyl vapor is introduced at slightly above atmospheric temperature into the top of the decomposer chamber, whose walls are preset at a temperature between 300 and 500 °C (572 and 932 °F). The thermal shock decomposes nickel carbonyl into very pure nickel powder, with the release of carbon monoxide,  $\text{Ni}(\text{CO})_4 = \text{Ni} + 4\text{CO}$ . Final powder processing consists of removing toxic gases, stabilizing with a very thin oxide coating, blending for uniformity, screening, and packaging. The iron carbonyl at the bottom of the distillation column, mentioned above, is transferred, along with

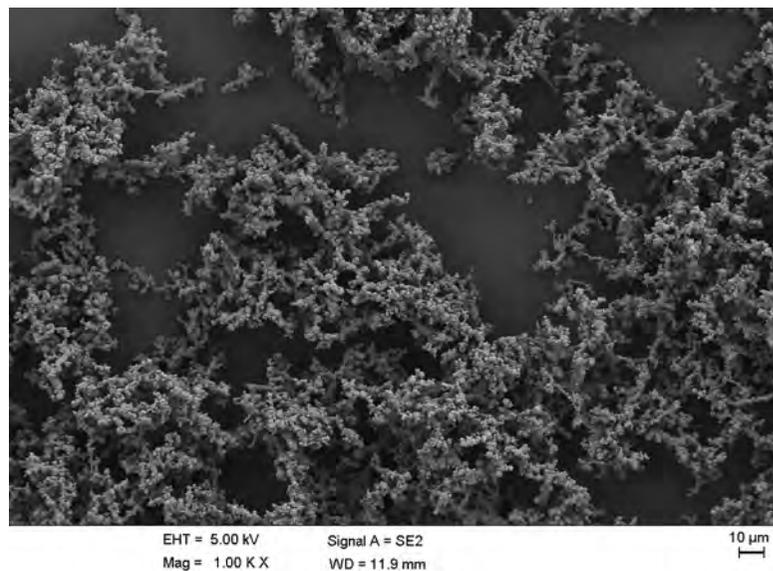
some nickel carbonyl to a recirculating pellet making reactor where 70Fe-30Ni pellets are produced. Combined nickel pellet and powder capacity is estimated at 65,000 tons per year. See flow diagram (Fig. 4) for Copper Cliff Nickel Refinery complex.

At the Electrowinning plant, the residues are treated in an oxidative acid leach circuit to remove nickel, cobalt, iron, and other minor elements. A second leach circuit is used to dissolve copper, selenium, and tellurium.

Unlike other carbonyl plants, which are small add-ons to other refining processes, the Vale plants are the only dedicated carbonyl refineries, thus enjoying significant economies of scale. Another process benefit is that virtually



**Fig. 2** Morphology of discrete T123 nickel powder. Courtesy of Loughborough University



**Fig. 3** Morphology of discrete T255 nickel powder. Courtesy of Loughborough University

all CO is recycled, resulting in an environmentally benign, closed-loop circuit (Ref 4).

**Norilsk Monchegorsk Refinery, Russia.** Since the late 1940s, Norilsk Nickel, the largest nickel producer in the world, has operated a carbonyl refinery at its smelter/refinery complex at Mochegorsk on the Kola Peninsula in northwestern Russia. The plant produces both nickel pellets and nickel powder in 1 meter diameter decomposers. Combined pellet and powder capacity is approximately 5000 tons annually.

**Jilin Jien Nickel, China.** Jilin Jien, a major producer of nickel chemicals, began production of carbonyl nickel powder in 2004 at its complex in Panshi City, northeast China. The original technology was purchased from a Canadian company, CVMR. Jilin Jien Nickel, together with the Chinese Academy of Science and China Iron & Steel Institute, jointly established a research laboratory to further study the nickel and iron carbonyl processes. Following laboratory trials, Jilin Jien Nickel built a commercial nickel and iron carbonyl plant.

Their feedstock is a nickel hydroxide intermediate. The nickel hydroxide is heat treated to nickel oxide, and the nickel oxide is further reduced under hydrogen to pure nickel. The nickel is then reacted with carbon monoxide at atmospheric pressure to produce nickel carbonyl gas. The carbonyl gas is thermally decomposed into nickel powder in reactors similar to those of Vale. Both discrete and filamentary particles are produced for the local Chinese PM steel and diamond tool industries. Estimated powder capacity is about 2000 tons per year of nickel powder and iron powder respectively.

**Jinchuan Group, China.** Jinchuan is China's largest nickel producer at its complex in Gansu province in northwest China. Jinchuan built

a carbonyl nickel powder pilot plant in 2003. A commercial carbonyl plant was commissioned in 2013 with announced annual capacity of 5500 tons of nickel pellet, 4500 tons of nickel powder, and 10,000 tons of iron powder. Feedstock is tailings and other waste material from Jinchuan's other nickel refining operations. The process follows standard carbonyl processing; that is upgrading the feedstock, reacting with carbon monoxide, distillation, decomposition, blending, and packaging. Two particle shapes are produced, a filamentary particle for the rechargeable battery market and a discrete powder for powder metallurgy.

**Production Capacity for Carbonyl Nickel Powders.** Estimated total worldwide production of carbonyl nickel powders is in excess of 30,000 tons, well above annual sales, which are in the 20,000 tons range. Vale, at its two plants, produces over 80% of the powder sold. The estimated production capacities of carbonyl refineries are given Table 1.

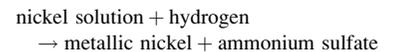
**Types of Carbonyl Nickel Powders.** Two distinct types of carbonyl nickel powders are commercially available: (1) a discrete spherical-like particle with a spiky morphology and average particle size (laser methodology) of 8 to 10 microns (Fig. 2) and (2) a filamentary three-dimensional chainlike particle with a high aspect ratio and average particle size (laser methods) of 15 to 20 microns (Fig. 3). Both are used in PM applications with the discrete particle (Vale T123 and Norilsk UT3) favored for most applications. Filamentary powders such as Vale T255 tend to be used in hard metal applications where intensive mixing tends to break up the chains, resulting in a uniform distribution of very fine particles throughout the matrix.

The chemistry of carbonyl powders is extremely pure, especially with respect to other metallic elements, with the only significant impurities being carbon and oxygen at ~0.1% (Table 2). Physical properties vary with the structure, the discrete particles having a higher apparent density than the filamentary particles, Table 3. A note of caution: Producers tend to use Fisher size in their specifications to define the powder particle size. Fisher size is a one-point, average size, measured by air-permeability through a compressed tablet of powder that can cause confusion about the true particle size distribution of carbonyl powders. For example, in the filamentary particles, the Fisher size measures the diameter of the individual particles making up the chain and reports particle size in the 2–3 microns range. When using laser measurement methods, the chainlike powders are immersed in a liquid, which passes the spinning particles in front of a laser beam that measures the full length of the particle in the 20 micron range. When measuring a smooth-surfaced true spherical particle, both the Fisher and laser methods will report similar results (Ref 5).

**The Hydrometallurgical Process**

This process, developed by Sherritt Gordon mines in 1954, is now used by several mining companies (Impala, BHP, Norilsk) to refine both sulfide and laterite nickel containing ores. The first stage involves a leaching process where the nickel-containing feedstock is blended with ammonium sulfate. This is a continuous process carried out at 90–95 °C (194–203 °F) and 758–827 kPa (110–120 psi). Before the nickel is reduced from the leach solution, cobalt, copper and other impurities are removed.

To produce nickel powder, nickel is precipitated from solution through a process known as hydrogen reduction. In this method, nickel is reduced onto core particles in reduction autoclaves following the reaction:



The hydrogen reduction process is carried out in mechanically agitated horizontal autoclaves at elevated temperatures and pressures. This is a batch process consisting of two distinct stages, initial nucleation, and subsequent densification. In the initial nucleation stage, fine seed powder

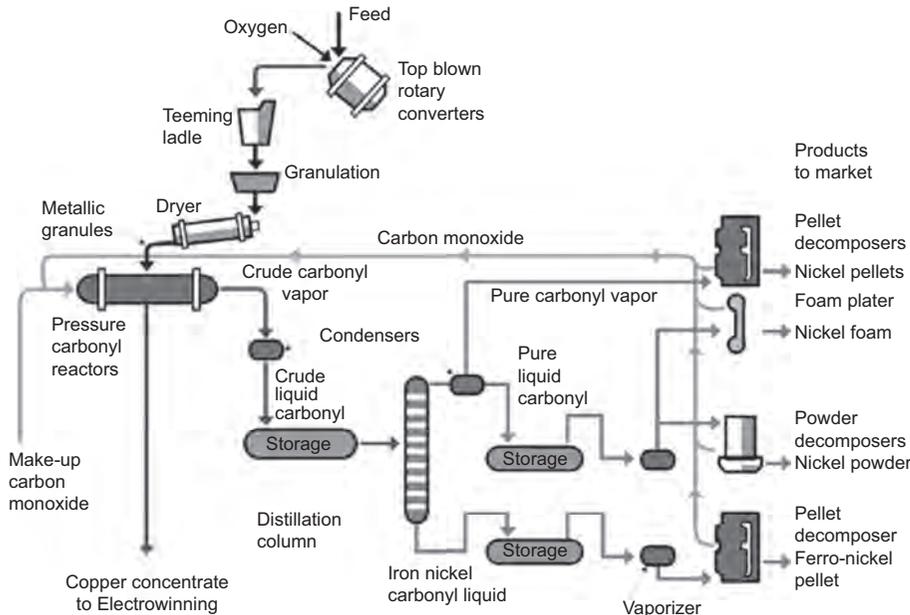


Fig. 4 Flow diagram of Copper Cliff Nickel Refinery

Table 1 Carbonyl nickel powder, capacity estimate

Source	Capacity, ton
Vale, Wales	10,000
Vale, Sudbury	16,000
Norilsk, Monchegorsk	4,000
Jilin Jien, China	2,000
Jinchuan Group, China	2,000
<b>Total</b>	<b>34,000</b>

**Table 2** Typical chemical analysis of commercially available carbonyl nickel powders

Producer	Ni%	C%	O%	Fe%	S%
Vale T123	>99.8	<0.0750	<0.0800	<0.0010	<0.0001
Vale T255	>99.7	<0.2000	<0.0750	<0.0030	<0.0002
Norilsk UT3	99.8	0.0650	Not reported	0.0008	0.0005
Jinchuan N06	>99.6	<0.1500	<0.1500	>0.0150	>0.0010
Jinchuan N24	>99.6	<0.2000	<0.1500	>0.0150	>0.0010
Jilin JCN1-5	>99.5	<0.2500	<0.1500	<0.0100	<0.0100
Jilin JCN1-2	>99.5	<0.2500	<0.1500	<0.0100	<0.0100

**Table 3** Typical physical properties of commercially available carbonyl nickel powders

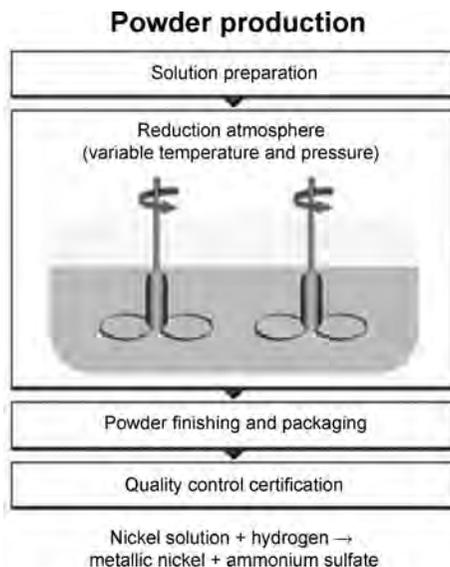
Producer	Average particle size Fisher, $\mu\text{m}$	Bulk density, $\text{g}/\text{cm}^3$
Vale T123	3.5–4.0	1.9–2.3
Vale T255	2.2–2.6	0.50–0.58
Norilsk UT3	3.0–6.0	1.9–2.6
Jinchuan N06	2.2–2.8	0.50–0.60
Jinchuan N24	3.5–5.0	1.8–2.5
Jilin JCN1-5	3.0–7.0	1.6–2.6
Jilin JCN1-2	1.5–3.0	0.5–0.7

is formed in the autoclave. The densification occurs as nickel from solution is reduced onto the seed powder, which then grows in size. Once reduction is complete, the agitation is stopped, and the nickel powder is allowed to settle. The spent solution is then pumped out, and the autoclave is filled with a fresh nickel solution. The agitators are restarted, and hydrogen pressure is applied. This batch reduction process is repeated 50–60 times to build up consecutive coatings of nickel on the powder particles. The overall process is stopped when the powder has reached the desired size. The hydrometallurgy method (reduction reaction) can also be used to produce composite particle powder or nickel briquettes.

The slurry of nickel powder and reduction end solution is discharged from the autoclave and collected in settling tanks where the nickel powder is drawn off as a ~90% solids slurry and filtered. From the filter, the wet powder (~5% moisture) is fed into a gas-fired rotary dryer. The dried powder is either packaged as powder or briquetted (Fig. 5) (Ref 6).

### Hydrogen Reduction Process

Shenzen GEM High-Tech Company, (GEM), Hubrei China, has developed a process to produce fine nickel and cobalt powders from recycled rechargeable batteries and other electronic waste. The process consists of a leaching line where most impurities are removed to produce a nickel chloride intermediate, an extraction line that combines the nickel chloride with ammonium oxalate to produce a nickel oxalate that is crushed powder. A hydrogen reduction line further reduces the nickel oxalate to a semi-spherical smooth surfaced nickel powder (Fig. 6). These powders have physical and chemical properties similar to carbonyl powder and are suitable for PM applications (Table 4). Production capacity is about 1500 tons per year.

**Fig. 5** Flow diagram of nickel powder production in the hydrometallurgical process

### Atomization Process

Nickel powder can be produced by inert gas atomization. However, this process is rarely used, as production costs are significantly higher than other production methods. A more detailed description of the gas atomization process is available in the article “Powder Metallurgy Superalloys” in this Volume.

### Production of Nickel Alloy Powders

Nickel-base alloys are used in a variety of applications including hot isostatic pressing (HIP), press and sinter, thermal spray, metal injection molding (MIM), laser welding, additive manufacturing (AM), as well as magnetic and electronic applications; see Table 5. These powders are generally produced by three methods: water atomization, high-pressure water atomization, and gas atomization.

### Water Atomization

Water atomization is the preferred production process for low cost, high volume metal powder and alloys. Most iron, copper, and stainless steel

powders used in conventional (press and sinter) PM are made by this method. Other applications include hardfacing and filter element production. The process begins with the raw material melted in an induction furnace. After the raw materials are molten and homogeneous, the melt is transferred to a tundish, which is a reservoir used to supply a constant, controlled flow of liquid metal into the atomizing assembly atop the atomization chamber. As the molten metal stream exits the tundish, high velocity streams of water strike the molten metal. The molten metal stream is disrupted and disperses into irregular-shaped droplets that solidify almost instantaneously. The powder particles are collected at the bottom of the tank and through cyclonic separation and subsequently dried; see Fig. 7. The resulting powder is irregularly shaped in a range of 5 to 500 microns. Screening or air classification is utilized to provide the appropriate particle size distribution (PSD) depending on application; see Fig. 8.

### High-Pressure Water Atomization

High-pressure water atomization (see Fig. 9) is the preferred methodology to produce very fine,  $d_{50}$  10 micron average, low oxygen, spherical powders. MIM is a typical application for these very fine spherical powders; see Fig. 10. Production is similar to conventional water atomization in that the melted alloy is poured into a tundish and through a nozzle into a sealed collection vessel where water, under very high pressure, is sprayed into the metal stream as it leaves the nozzle. A bed of water at the bottom of the collection vessel cools and collects the fine powder. The powder is separated from the water by filtration, dried, and air-classified. The particle size can be closely controlled by adjusting the atmosphere in the collection vessel, pressure of the atomization water, and the angle and configuration of the water jets.

### Gas Atomization

The arrangement of the equipment for gas atomization is similar to that of water atomization, with the main difference being a gas (usually nitrogen or argon) is used to disrupt and cool the molten stream. In gas atomization, the charge material is melted in an induction furnace, transferred to a tundish and poured into the chamber, and poured through the atomization assembly atop the chamber. The induction furnace can be housed in a vacuum chamber, in an inert chamber, or in open air. The high-pressure gas stream breaks the molten metal stream into fine particles resulting in rapid solidification of the metal powder, which causes rapid solidification of the metal. The powder is separated from the gas stream via gravity and water-cooled cyclones and is dry collected in a vessel. The spherical powder is in the 2–1000 micron range as determined by the gas pressure, flow rate of the gas, and metal and nozzle design.

Procedure of using waste resources to reproduce cobalt and nickel materials

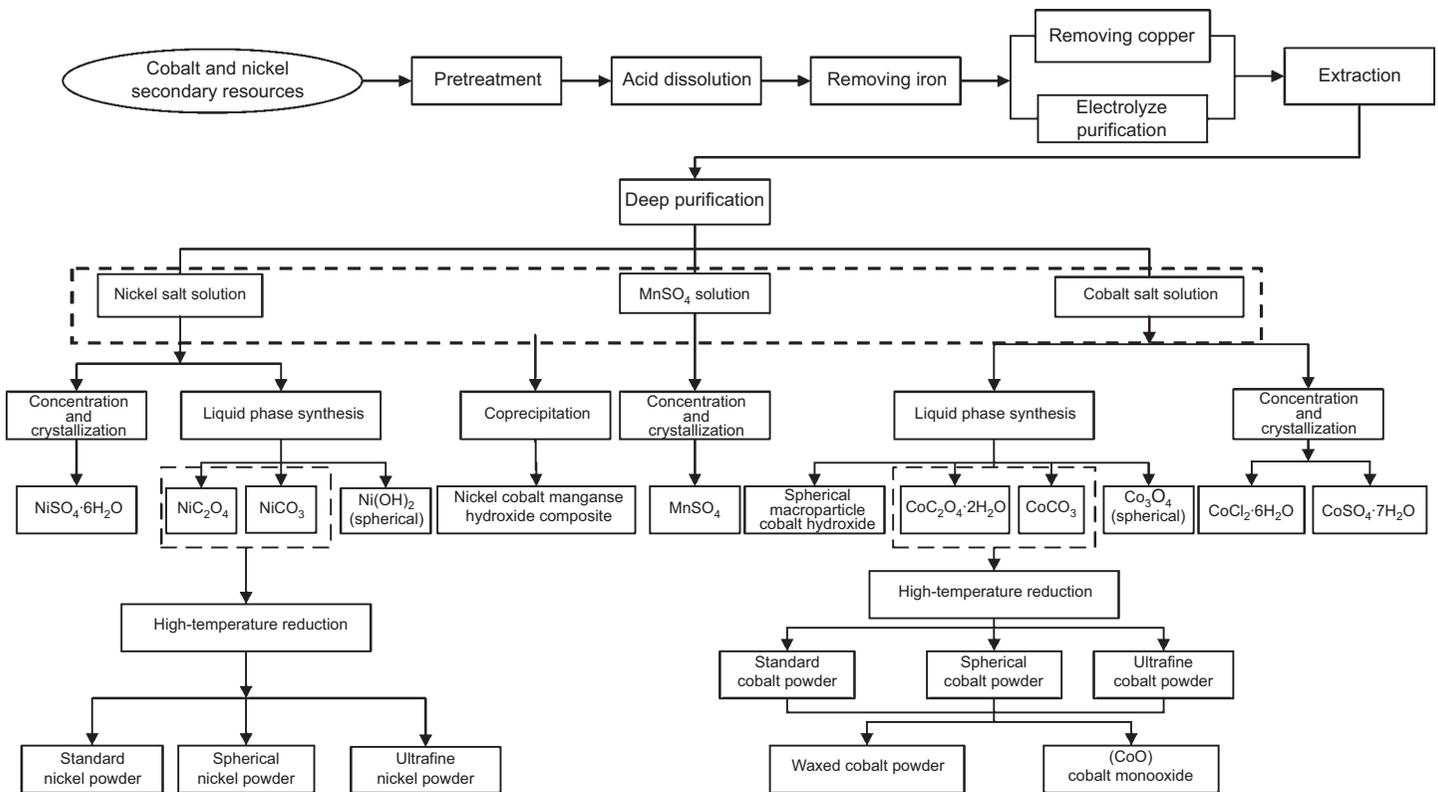


Fig. 6 Flow diagram of the hydrogen reduction process for nickel powders

Table 4 Properties of hydrogen reduced nickel powders

Grade	Nickel powder														
	Ni%	FSSS (μm)	D50 (μm)	Apparent density (g/cm <sup>3</sup> )							O%	C%			
FNiH-1a	99.9%	1.00~1.50	≤8.00	0.50~0.90							≤0.50	≤0.03			
FNiH-1b															
FNiH-2a		1.51~3.00	≤10.00	0.60~1.20							≤0.40	≤0.03			
FNiH-2b															
FNiH-3a		3.01~5.00	≤15.00	1.10~1.90							≤0.30	≤0.02			
FNiH-3b															
Impurities ≤ ppm	Co	Cu	Fe	Ca	Mg	Pb	Zn	Cd	Mn	Na	Al	Li	Cr	Si	S
a	20	20	50	50	30	30	20	20	20	50	20	10	20	10	50
b	50	50	80	80	80	50	50	50	50	80	50	30	50	30	80

Note: 1) The content of Ni is calculated by the subtraction method, the subtraction elements are other metals, C and S. 2) Grade a: Maximum content of impurities ≤0.05%; The single impurity of each element ≤0.005%; Grade b Maximum content of impurities ≤0.08%; The single impurity of each element ≤0.008%

Table 5 Common atomized high-nickel alloys

Alloy	Composition, typical	Application
NiChrome	80Ni, 20Cr	Thermal spray
Inconel 600	15Cr, 8Fe, bal Ni	Thermal spray
Permalloy	80Ni, 5Mo, 0.5Si, bal Fe	Magnetics
Fe-50Ni	50Fe, 50Ni	Magnetics
Inconel 625	22Cr, 9Mo, 4Nb, bal Ni	Oil and gas
ATI 720	16Cr, 14Co, 5Ti, 3Mo, 2.5Al, bal Ni	Aerospace
B-60	14.5Cr, 4.3Si, 4.3Fe, 3.2B, 0.8C, bal Ni	Hardfacing
NiAl	97Ni, 3Al	Electronics
AMEBRAZE 102	7Cr, 3.1B, 4.5Si, 3Fe, bal Ni	Brazing
PHAX	22Cr, 19Fe, 9Mo, 2Co, 0.5W, 0.1C, bal Ni	Filter element

## Applications of Nickel Powders

### Applications for Carbonyl Nickel Powders

Current demand for carbonyl nickel powders is in the 20,000 ton per annum range; see Table 6. Over 60% of consumption is by the chemical industry to produce high purity nickel salts (nickel sulfate, chloride, sulfamate, hydroxide) and in nickel catalyst applications ranging from nylon production to automotive catalytic

converters. During the 1990s when nickel cadmium (NiCd) rechargeable batteries gained popularity, over 5,000 tons per year of filamentary (T255) powder was consumed in the production of high porosity nickel electrodes. When higher capacity nickel metal hydride and lithium ion batteries replaced many NiCd applications, demand for filamentary carbonyl powder declined. However, some of this decline was offset by the increased use of discrete carbonyl nickel, primarily T123 and UT3, in powder metallurgy applications.

**Powder metallurgy applications** include the following.

**PM Steels.** Carbonyl nickel powder, usually Vale T123 or Norilsk UT3, is added to iron powder in the range of 1.5 to 4% to improve the mechanical properties of sintered PM parts, such as ultimate tensile strength and ductility. The metallurgical structures obtained by adding nickel powder are usually nonuniform. This non-uniformity can be advantageous depending on the performance requirements of the PM part.

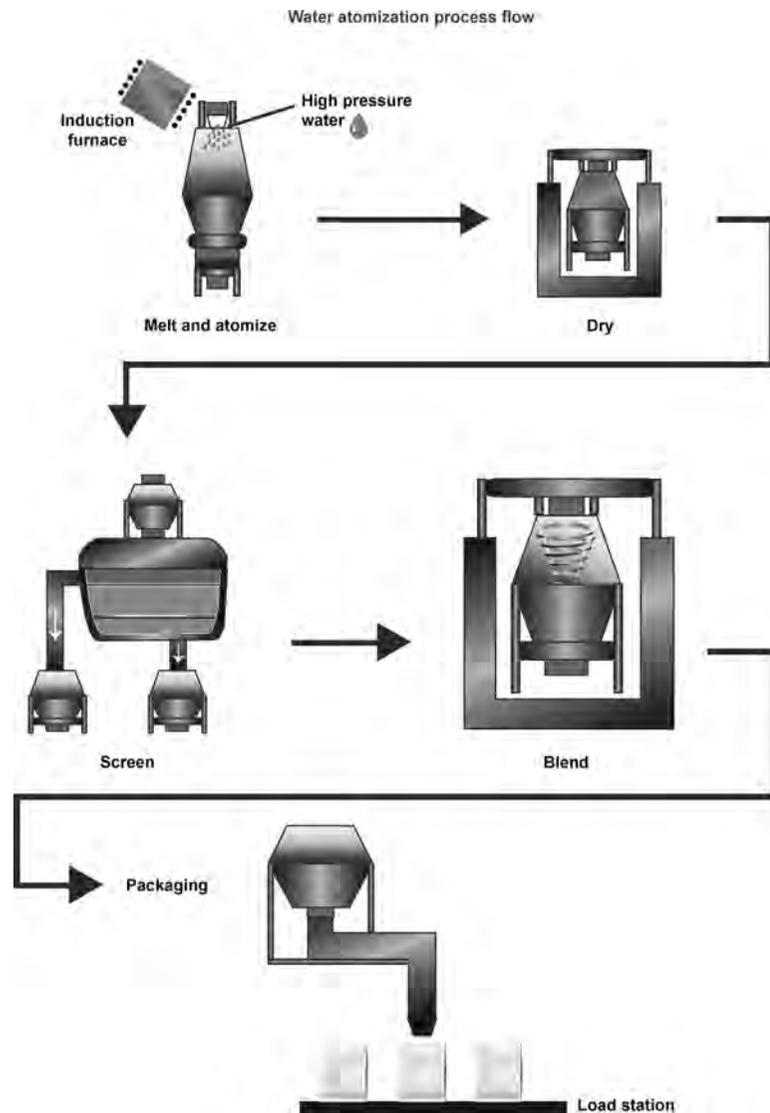


Fig. 7 Flow diagram of water atomization process

Nickel does not fully diffuse during conventional sintering cycles (1120 °C, or 2048 °F, 20 to 30 minutes), and nickel-rich phases develop in the steel microstructure. Nickel stabilizes a high temperature phase of steel called austenite; this austenitic phase is relatively ductile and is thought to be responsible for an increase in ductility and toughness observed for sintered nickel steels. The inhomogeneous microstructure of sintered nickel steels achieved with nickel powder additions also significantly improves fatigue properties by arresting the propagation of cracks and by absorbing energy through austenitic phase transformations (Ref 1).

Nickel may also be added in prealloyed form, where nickel is melted with iron prior to atomization. However, there is a limit as to how much nickel can be prealloyed before the compressibility and green strength of the iron powder compact are significantly affected. In practice, prealloyed nickel content tends to be on the order

of 0.5%, but may be as high as 1.75% for low alloy steels.

**Hard Metals.** Fine cobalt powder is the most widely used binder in tungsten carbide (WC) base hard metals due to its outstanding wetting and adhesion characteristics. About 90% of WC hard metals use cobalt binders. Carbonyl nickel can be substituted for the usual cobalt powder binders in tungsten carbides when corrosion resistance in aqueous environments or increased toughness to improve hot cracking resistance (mill rolls) is important. Increased ductility and toughness of cemented carbides with nickel containing binders comes at the expense of lower apparent hardness and bend strength compared to cobalt tungsten carbide materials. The processing of nickel containing tungsten carbide materials requires slightly higher temperature for the same weight percent binder content and care needs to be taken due to the higher solubility of carbon in nickel versus cobalt in order to avoid

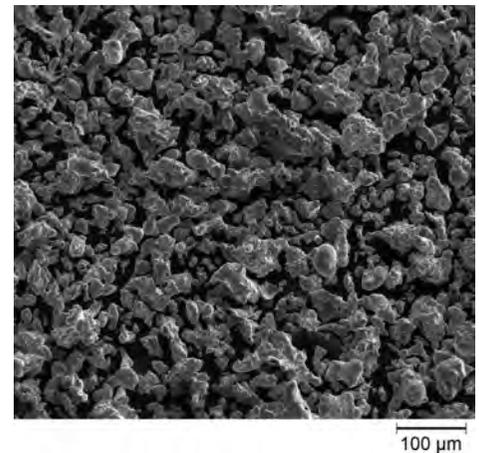


Fig. 8 Morphology of water atomized powder

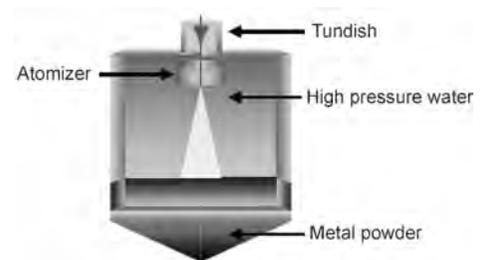


Fig. 9 Schematic of high pressure water atomization

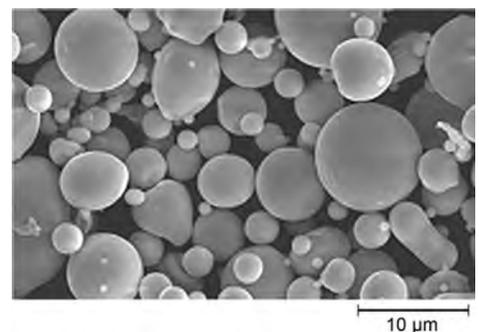


Fig. 10 Morphology of high pressure water atomized powder

Table 6 Estimated demand for carbonyl nickel powders (by application)

Application	Demand, tons
Energy	2,000–3,000
Powder metallurgy	4,000–5,000
Salts, catalysts, other	12,000–13,000
<b>Total</b>	<b>20,000</b>

the formation of brittle phases. Nickel is preferred for some other hard metals such as TiCN, for which nickel wets the surface unlike cobalt or carbonyl iron.

**Diamond Tools.** Diamond impregnated cutting tools consist of a metallic binder with a dispersion of fine diamond particles. The metallic binders most commonly employed are cobalt, nickel or iron base alloys, and bronze. Due to the high price of fine cobalt powder, combinations of carbonyl nickel and carbonyl iron are substituted for a portion of the cobalt to reduce cost while retaining acceptable properties. Nickel is a lower cost substitute for fine cobalt powder and increases the toughness of Co-Fe binders at the expense of lower hardness and bend strength. In bronze-base diamond binder segments, nickel increases hardness and yield strength (Ref 7).

**Tungsten Heavy Alloys.** The solubility of tungsten in nickel is relatively high, and for this reason, carbonyl nickel powder is a common binder in tungsten heavy alloys. To avoid the formation of brittle phases, carbonyl iron powder is typically added at a ratio of 7 parts nickel to 3 parts iron.

**Metal Injection Molding (MIM).** Discrete carbonyl nickel powders (T123 or UT3) are combined with carbonyl iron powders to produce MIM FeNi alloys ranging in nickel content from 2 to 50%. The carbonyl iron powders used in MIM are smooth spheres in the 5 micron, by laser, range. Before blending, the nickel powders are usually screened –400 mesh (37 microns) or air-classified even finer to remove larger particles and promote more uniform distribution.

**Nickel Strip.** Carbonyl nickel powder can be roll compacted under heat and pressure to form thin nickel strip. Strip formed from powder has lower electrical resistivity than strip formed from bar stock, thus making it the material of choice in rechargeable batteries and electronic applications.

**Other carbonyl nickel powder applications** include the following.

**Salts and Chemicals.** Carbonyl nickel powder reacted with sulfuric acid produces very high purity nickel sulfate for plating applications. Nickel sulfate can be further processed into high purity nickel hydroxide,  $\text{Ni}(\text{OH})_2$ , used in the positive electrode in nickel metal hydride batteries for hybrid electric vehicles, such as the Toyota Prius. A new market is emerging for  $\text{Ni}(\text{OH})_2$  combined with cobalt sulfate and manganese sulfate for lithium ion batteries used in pure electric vehicles.  $\text{Ni}(\text{OH})_2$  can be calcined to very high purity nickel oxide. Nickel powder can be heat treated directly into green nickel oxide. Carbonyl nickel powder in combination with sulfamic acid produces a very high purity nickel sulfamate for electroless nickel plating. Nickel powder is used to produce adiponitrile (ADN) and hexamethylenediamine (HMDA) salts, which are used in the production of nylon 66. Other salts produced from carbonyl nickel powder include nickel acetate, chloride, and phosphate.

**Catalysts.** Combining carbonyl nickel powder with carbonyl iron, carbon, and seed diamonds under heat and pressure produces most of the world's industrial diamonds. Nickel powder is used in a variety of petrochemical catalysts. Controlled surface area nickel oxide produced from

nickel powder is added to 3-way auto catalytic converters to act as a sulfur getter.

**Electric Batteries.** Nickel cadmium (NiCd) and nickel metal hydride (NiMH) batteries use porous nickel electrodes formed by the “slurry-sinter” continuous process which (a) mixes filamentary nickel powder with a methylcellulose binder to form a slurry, (b) coats both sides of a nickel plated perforated foil, (c) converts to a “green” state by drying, and (d) sinters in a high temperature furnace to achieve porosity >80%.

Filamentary nickel powder is used in the positive electrode of sodium nickel chloride batteries. Filamentary nickel powder is also loose sintered to form the porous structure of the positive electrode in molten carbonate fuel cells that convert natural gas to electric power.

**Other.** High purity nickel niobium alloys are produced by combining nickel powder, niobium oxide, and aluminum powder in a crucible where the aluminum powder promotes an exothermic reaction. The niobium and nickel alloy with aluminum forms as dross on the top.

Both filamentary and discrete nickel powders can be ball milled into nickel flake for electronic applications.

### Properties and Applications of Hydrometallurgical Nickel Powders

Hydrometallurgical nickel powders are significantly larger than carbonyl nickel powders, typically ranging from 40 to 325 mesh (44 to 420 microns). A typical chemical composition is given in Table 7. They have a spherical shape with a “cauliflower” surface (Fig. 11). Generally, these powders are further screened into more usable fractions. PM applications for these powders include welding electrodes and nickel strip for coinage. Hydrometallurgical powder is also used to produce nickel salts and catalysts. However, the vast majority of these powders are compacted into briquettes for melting applications in the production of nickel steels or alloys.

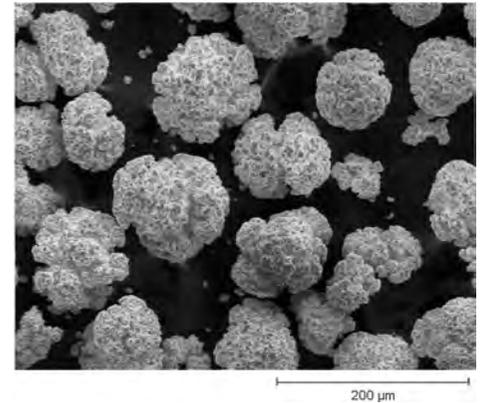
## Nickel Alloy Powder Metal HIP in Oil and Gas

Paal Bratland, OneSubsea

Nickel alloys have a long history of use in oil and gas applications, dating back more than 30 years (Ref 8). Nickel alloys are selected for particular components that must withstand an aggressive environment, high loading, high temperatures, or a combination of these factors. Most of the nickel alloys used in oil and gas applications are produced by traditional methods such as forging. Use of PM HIP has been

**Table 7 Chemical composition of hydrometallurgical nickel powders**

Element	Typical composition, %	Apparent density, g/cm <sup>3</sup>
Nickel	99.9	3.2 to 4.5
Carbon	0.0560	
Cobalt	0.0030	
Copper	<0.0010	
Iron	0.0300	
Phosphorus	<0.0002	
Sulfur	0.0280	
Zinc	<0.0001	



**Fig. 11** Morphology of powder produced by hydrometallurgical process. 250 $\times$

gaining market share particularly for duplex stainless steels (DSS) due to favorable properties of PM HIP DSS, with respect to hydrogen induced stress cracking, as described in DNV RP-F112 (Ref 10). The use of powder metal HIP for nickel alloys in oil and gas have been rather limited; this is to a certain extent unexpected as many of the advantages of PM HIP may be beneficial for a number of components in typical oil and gas applications. Of particular interest are the isotropic physical and mechanical properties, uniform microstructure, and the ability to produce very good through thickness properties on heavy wall sections. Solid body nickel alloys should be of particular interest for components featuring numerous seal surfaces, complex shapes, or narrow bore pressure tapping.

Some oil and gas applications of PM HIP nickel alloy do however exist, and HIP UNS N07626 is listed in NACE MR-0175 (Ref 11). For valve bodies and other wellhead components, HIP clad has been used. In such applications, all process flow exposed features of the component are covered by a nickel alloy layer. The substrate is usually a low alloy steel component; a can is welded to the low alloy steel part and filled with nickel alloy powder. Using this method, thick clad layers and features that are not easily accessible for weld cladding can be realized. The Engineering Equipment and Materials Users' Association (EEMUA) publication No. 194 (Ref 9) identifies forging and PM HIP as the two preferred manufacturing

options for subsea manifold fittings and equipment. Solid body CRA tees and valve bodies are given as examples of components where PM HIP should be considered.

## PM HIP Nickel Alloy Applications in Oil and Gas

Given the recent success of PM HIP for duplex stainless steels in subsea oil and gas combined with the good material properties achievable, nickel alloy PM HIP should be a manufacturing method with great potential for oil and gas applications. For more expensive alloys, the cost difference of the PM HIP process compared to ingot metal based methods are more favorable for PM HIP than what is the case for a less expensive alloy e.g. duplex stainless steel. This is due to the base material cost being a higher fraction of the total cost, resulting in good economical return on the reduced need for excess material in near net shape PM HIP. PM HIP nickel alloys are likely to be particularly interesting for subsea high pressure and high temperature applications, where integrity and life time are the two main concerns. For high temperature applications, the potential for crevice corrosion on the seawater side of duplex stainless steel component raises some concern (Ref 9). This may result in alternative material selection being pursued for components so far typically manufactured from forged or PM HIP duplex stainless steel. The outlook in the subsea oil and gas market is development towards higher design pressures, higher design temperatures, and water depths beyond 305 m (10,000 ft). The current industry status as of 2014 is that 103 MPa (15 ksi) design pressure subsea equipment are being installed and operated, with initial qualification for 138 MPa (20 ksi) equipment being started up. Temperature wise, qualification of 204 °C (400 °F) subsea equipment is underway. The higher pressures result in the need for higher strength materials, and the higher temperature combined with very high chloride content in the produced water and presence of H<sub>2</sub>S in the process gives rise to challenging conditions for the subsea process containing components. The life time target for these subsea installations are typically 20 to 30 years; maintenance and inspection through the service life is very expensive and not desirable. In this context, the percentage of nickel alloy components can be expected to rise. As mentioned previously, solid body nickel alloy makes a particularly good case for complex components with multiple seal surfaces minimizing the risk for seal failures due to crevice corrosion. This can typically be subsea instruments, subsea sampling systems, and subsea manifold fittings (Ref 9). EEMUA publication No. 194 indicates that due to increasing water depths with resulting complexity in interventions, the current trend is for “fit and forget,” selecting more robust materials to reduce the need for inspection and monitoring of the equipment installed subsea. PM HIP

nickel alloy is a promising candidate to address this requirement.

### PM HIP UNS N06625 Flowmeter Bodies

For subsea multiphase flowmeter bodies, a number of units in annealed alloy 625 have been manufactured using PM HIP at various HIP manufacturers; the first unit was produced in 2008. An example of a 103 MPa (15 ksi), 204 °C (400 °F) subsea multiphase flowmeter for installation down to 3500 m (3828 yd) of water depth can be seen in Fig. 12. These venturi units have wall thickness of up to 203 mm (8 in.). The properties presented in Table 8 are averages from testing on 34 HIP items, tested at half of the wall thickness.

More detailed data has been extracted from a full size qualification unit, geometry as sketched



Fig. 12 103 MPa (15 ksi), 204 °C (400 °F) subsea multiphase flowmeter with PM HIP alloy 625 body

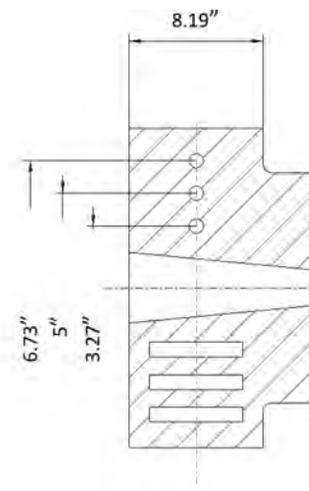
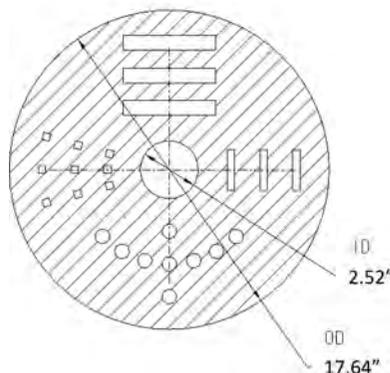


Fig. 13 Test sample locations

in Fig. 13. Test samples for tensile testing, impact toughness testing, elevated tensile testing, and hardness testing have been extracted in three depths through the cross section and in two perpendicular directions per test location.

The values in Table 9 are taken from just one unit, and are included to show the potential for through thickness properties on an actual heavy wall thickness oil and gas component. Most potential oil and gas applications for PM HIP nickel alloy are related to direct process exposure. Typically the temperature range specified will be from maximum +232 °C (+450 °F) down to -46 °C (-50 °F). Some test values in this temperature range for the same locations on the same item as presented in Table 9, are shown in Table 10.

Further oil and gas qualification work is being performed to qualify an age hardened alloy 625 for subsea high pressure, high temperature applications for a subsea flowmeter body. The typically applied design codes for permanent installed subsea oil and gas equipment are API 17D (Ref 12), API 6A (Ref 13), and NACE MR-0175 (Ref 11). The codes and standards are currently in development to address the increasing demands in high temperature, high pressure applications. For materials, the focus is particularly on fatigue and environmental qualification. The API

Table 8 Alloy 625 typical mechanical properties PM HIP 625 in annealed condition

	UTS		$R_{p0.2}$		CVN at	
	MPa	ksi	MPa	ksi	-46 °C (-50 °F)	J ft · lbf
Typical mechanical values	938	136	462	67	75	55
Specified minimum values ASTM B564 >102 mm (4 in.)	758	110	345	50	N/A	N/A
Specified minimum values ASTM B834	827	120	414	60	N/A	N/A

**Table 9 Alloy 625 mechanical properties**

For section shown in Fig. 12. Results from OneSubsea and Kennametal

Direction	Location	UTS		$R_{p0.2}$		El, %	RA, %	CVN $-46^{\circ}\text{C}$ ( $-50^{\circ}\text{F}$ ) ASTM A370, average		CVN $-64^{\circ}\text{C}$ ( $-148^{\circ}\text{F}$ ) ASTM A370, average	
		MPa	ksi	MPa	ksi			J	ft · lbf	J	ft · lbf
Longitudinal	T/4	945	137	503	73	48	51	107	79	98	72
Transverse	T/4	951	138	455	66	49	47	102	75	...	...
Longitudinal	T/2	945	137	496	72	49	47	109	80	103	76
Transverse	T/2	945	137	469	68	49	49	103	76	...	...
Longitudinal	¼ T	945	137	476	69	48	46	106	...	94	69
Transverse	¼ T	945	137	490	71	49	48	105	...	...	...

**Table 10 Alloy 625 elevated temperature properties**

Results from OneSubsea and Kennametal

Location	Temperature		UTS		$R_{p0.2}$		El, %	RA, %
	$^{\circ}\text{C}$	$^{\circ}\text{F}$	MPa	ksi	MPa	ksi		
T/4	100	212	937	136	483	70	46	41
T/2	100	212	931	135	462	67	48	54
¼ T	100	212	931	135	441	64	48	47
T/4	250	482	883	128	427	62	50	52
T/2	250	482	883	128	414	60	48	49
¼ T	250	482	889	129	407	59	47	51

standards (Ref 12 and 13) require flange material to have a yield strength of at least 517 MPa (75 ksi) for applications where design pressure is 103 MPa (15 ksi) or higher. The purpose of the qualification of age hardened PM HIP alloy 625 is to meet this strength requirement as well as retaining suitability for sour service, and maintaining an acceptable level of ductility and impact toughness. In addition to the more standardized mechanical testing presented for the annealed UNS N06625, the HPHT qualification will include fatigue crack growth testing as well as slow strain rate testing at design temperature in simulated environment containing chlorides and H<sub>2</sub>S. This test program is at the time of writing yet to be completed. The age hardening response in Alloy 625 is highly composition dependent, and the ranges defined for alloying elements in UNS N06625 are too wide to ensure that the material will have an aging response. A tighter control of chemistry can be achieved in the powder manufacture, enabling repeatable production of material that does respond to aging heat treatment.

### Future Use

There are certain factors that could facilitate the market penetration of PM HIP nickel alloys in oil

and gas. The most important would be to get the nickel alloy HIP product approved and listed in the most relevant codes and standards, such as NACE MR-0175 (Ref 11), ASME IID (Ref 14), API 6A (Ref 13), and API 17D (Ref 12). Some work is ongoing driven by various users, but it would also be in the interest of the manufacturers to achieve listing in the codes, hence a status as a more conventional material selection. Of particular importance is further test data on fatigue properties under simulated realistic environmental conditions.

PM HIP nickel alloys are limited in size to the capacity of the HIP autoclave so certain very large components will be outside the manufacturing range for PM HIP. Typical oil and gas components, such as pipe fittings, instrument bodies, valve bodies, and flanges, however, should be well within the available envelope.

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