

The Nickel Industry: Occurrence, Recovery, and Consumption

NICKEL is one of the most versatile and important of the major industrial metals. It is a vital alloying element in cast irons, steels (most notably austenitic stainless steels containing 8 to 35% Ni), and nonferrous alloys. Nickel-base alloys are used in demanding corrosion-resistant and heat-resistant applications. Nickel-iron alloys have been developed for applications requiring controlled thermal expansion or soft magnetic characteristics. Nickel coatings and nickel articles made by electroforming are also technologically important. Nickel and/or nickel compounds are also used in coinage, batteries, catalysts, ceramics, and magnetic superconductors.

Elemental Nickel

Although nickel can be produced commercially to a purity of 99.99%, most of the data reported in the literature concern nickel (plus cobalt) of 99.95% purity. This degree of purity is satisfactory for the determination of many properties, but certain properties, for example, electrical resistivity, are very sensitive to impurities in solid solution.

Most of the data given below are taken from Volume 2 of the *ASM Handbook* (see page 1143). More detailed information about the physical, mechanical, and chemical properties of pure nickel can be found in Ref 1 and 2.

Physical Properties

General. Nickel (symbol Ni) is number 28 in the periodic table of the elements. The three metals—iron, nickel, and cobalt—constitute the transition group in the fourth series in the periodic table. The atomic weight of nickel is 58.6934, representing a composite of five stable isotopes.

Crystal Structure. The normal structure of nickel throughout the entire range of temperatures up to the melting point is face-centered cubic (fcc). The lattice constant of the fcc form is 0.35167 nm at 20 °C (68 °F).

Density. The density of nickel at 25 °C (77 °F) is 8.902 g/cm³. The density of liquid nickel at its melting point is 7.9 g/cm³ and, with increas-

ing temperature, falls approximately linearly to 7.0 g/cm³ at 2500 K (~2227 °C, or 4040 °F).

Thermal Properties. The melting and boiling points of nickel are 1453 °C (2647 °F) and approximately 2730 °C (4946 °C), respectively. Other important thermal properties include the following:

- *Coefficient of linear thermal expansion:* 13.3 μm/m · K at 0 to 100 °C (32 to 212 °F)
- *Specific heat:* 0.471 kJ/kg · K at 100 °C (212 °F)
- *Recrystallization temperature:* 370 °C (698 °F)
- *Thermal conductivity:* 82.9 W/m · K at 100 °C (212 °F)

Electrical Properties. The electrical resistivity of pure nickel is negligible at extremely low temperatures but increases with increasing temperature and increasing amounts of impurities. The resistivity of nickel at 20 °C (68 °F) is 68.44 nΩ · m, and the electrical conductivity is 25.2% IACS.

Magnetic Properties. Nickel is one of the three elements (iron and cobalt being the others) that are strongly ferromagnetic at ambient temperature. Typical normal induction curves of annealed samples of the elements iron, nickel, and cobalt are shown in Fig. 1. Pure nickel is seldom used itself as a magnetic material except for certain special purposes, such as magnetostriction applications. Many types of nickel-containing alloys, however, exploit the ferromagnetic properties of nickel. Examples include materials ranging from high-permeability, soft magnetic alloys to high-coercivity, permanent magnet alloys. Although these alloys are generally iron-base, they frequently contain 10 to 20% Ni or more. Such alloys are described in the article “Special-Purpose Nickel Alloys” in this Handbook. Examples of magnetic properties of nickel are given below:

- *Magnetic permeability:* $\mu_{\max} = 1240$ at $B = 1900$ G
- *Coercive force:* 167 A · m⁻¹ from $H = 4$ kA · m⁻¹
- *Saturation magnetization:* 0.616 T at 20 °C (68 °F)
- *Residual induction:* 0.300 T

- *Hysteresis loss:* 685 J/m³ at $B = 0.6$ T
- *Curie temperature:* 358 °C (676 °F)

The Curie temperature, in the same manner as other structure-sensitive properties, is dependent on purity and on the prior history of the sample but in general lies between 350 and 360 °C (660 and 680 °F) for high-purity nickel (the 358 °C, or 676 °F, previously given value is from Volume 2 of the *ASM Handbook*).

Mechanical Properties

Tensile Properties. Tensile properties for annealed high-purity nickel have been reported as follows:

- *Tensile strength:* 317 MPa (46 ksi)
- *0.2% offset yield strength:* 59 MPa (8.6 ksi)
- *Elongation in 50 mm (2 in.):* 30%

Suitable choice of hot rolling, annealing, and cold drawing or cold rolling can yield tensile strengths ranging from 448 to 793 MPa (65 to 115 ksi) in rods and bars, as high as 896 MPa (130 ksi) in strip, and 1103 MPa (160 ksi) in wire.

Hardness. Values as low as 64 HV (35 HRB) have been reported for annealed high-purity nickel. Cold work and the presence of impurities increase the hardness.

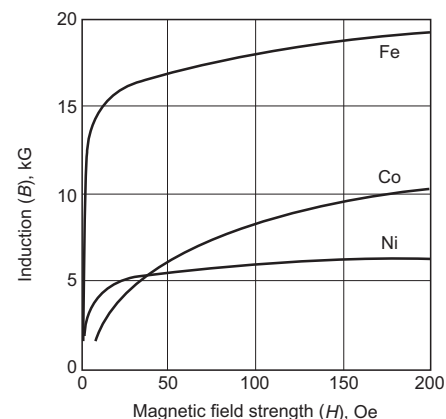


Fig. 1 Typical normal induction curves of annealed samples of iron, nickel, and cobalt. Source: Ref 1

Elastic Properties. Average values of Young's modulus of elasticity are 207 GPa (30×10^6 psi) for 99.95% Ni. The modulus of shear is 76 GPa (11×10^6 psi). Poisson's ratio, that is, the ratio of transverse contraction to longitudinal extension under tensile stress, is 0.31 for nickel.

Chemical Properties

Nickel is not an active element chemically and does not readily evolve hydrogen from acid solutions; the presence of an oxidizing agent is usually required for significant corrosion to occur. Generally, reducing conditions retard corrosion, whereas oxidizing conditions accelerate corrosion of nickel in chemical solutions. However, nickel may also form a protective corrosion-resistant, or passive, oxide film on exposure to some oxidizing conditions. Additional information is available in the article "Corrosion Behavior of Nickel Alloys in Specific Environments" in this Handbook.

Occurrence and Supply

A large number of nickel-bearing minerals have been identified, but relatively few are abundant enough to be industrially significant. Nickel materials that are or have been important are classified as sulfides, laterites (which include oxides and silicates), and arsenides. Of these, the most important present-day ores are sulfides and laterites.

Sulfide Ores. In the sulfide ores, nickel occurs chiefly as the mineral pentlandite, $(\text{Ni,Fe})_9\text{S}_8$, in association with large amounts of pyrrhotite, Fe_7S_8 , and usually with a significant amount of chalcopyrite, CuFeS_2 . In addition to nickel, iron, and copper, these ores contain varying amounts of cobalt and precious metals: the platinum group metals, gold, and silver. Their chemical composition falls in the general range of 0.4 to 3% Ni, 0.2 to 3% Cu, 10 to 35% Fe, and 5 to 25% S, with the balance being substantially SiO_2 , Al_2O_3 , MgO , and CaO .

Sulfide ores are generally found in areas where glacial action has removed much of the overburden of weathered rock. Important known deposits are in Sudbury, Ontario, Canada; in the Voisey's Bay deposit in northeastern Labrador, Canada; in the Thompson-Moak Lake area of northern Manitoba, Canada; in Russia at Norilsk in Siberia; in the Kola Peninsula bordering Finland; in western Australia; and in South Africa.

Laterites. The oxide resources of nickel (commonly known as laterite ores) are generally found in tropical regions, with the largest deposits being in Cuba, New Caledonia, Indonesia, the Philippines, and Central and South America. These ores formed through weathering processes that resulted in nickel being leached from surface rock layers and precipitated at lower levels.

Two general types of oxide ore can be distinguished: silicate-type ore, in which nickel is contained in the lattice of hydrated magnesium-iron-silicates, of which garnierite $(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ is the most common; and limonitic-type ore, predominantly the hydrated mineral goethite, $(\text{Ni,Fe})_2\text{O}_3 \cdot \text{H}_2\text{O}$, in which nickel is dispersed. The chemical composition of oxide ores varies widely and, in addition to 1 to 3% Ni, may comprise significant amounts of cobalt and chromium. Silicate-type ore in New Caledonia analyzes about 2 to 3% Ni, 0.1% Co, 2% Cr_2O_3 , and 10 to 25% MgO . Cuban ore, primarily of the limonitic type, analyzes in the range of about 1.2 to 1.4% Ni, 0.1 to 0.2% Co, 3% Cr_2O_3 , and 35 to 50% Fe.

Extraction and Refining (Ref 3)

Recovery from Sulfide Ores. Figure 2 illustrates the major processes for the extraction and recovery of nickel from sulfide ores. These ores are first crushed and ground to liberate the mineral values and then subjected to froth flotation to concentrate the valuable constituents and reject the gangue or rock fraction. Depending on the copper and pyrrhotite (iron) contents of the ore, it is sometimes appropriate to produce a separate copper concentrate and a separate pyrrhotite concentrate.

Selective flotation and magnetic separation may be employed to divide the bulk concentrate into nickel, copper, and iron-rich fractions for separate treatment (see process A in Fig. 2). A high-grade iron ore, nickel oxide, and sulfuric acid are recovered from the iron concentrate. The nickel concentrate is treated by pyrometallurgical processes. The major portion undergoes partial roasting in multihearth or fluidized-bed furnaces to eliminate about half of the sulfur and to oxidize the associated iron. The hot calcine, plus flux, is smelted in natural gas or coal-fired reverberatory furnaces operating at about 1200 °C (2200 °F) to produce a furnace matte that is enriched in nickel and a slag for discard. The furnace matte is transferred to Pierce-Smith converters and blown with air in the presence of more flux to oxidize the remaining iron and associated sulfur, yielding Bessemer matte containing nickel, copper, cobalt, small amounts of precious metals, and approximately 22% sulfur. The slag that is generated in the converting operation is returned to the smelting furnace to recover its metal values.

The molten Bessemer matte is cast into 25 ton molds in which it undergoes controlled slow cooling to promote formation of relatively large, discrete crystals of copper sulfide, nickel sulfide, and a small quantity of a metallic phase, a nickel-copper alloy that collects most of the precious metals. After crushing and grinding, the metallics are removed magnetically and treated in a refining complex for recovery of metal values, and the main sulfide

fraction is separated into copper sulfide and nickel sulfide concentrates by froth flotation.

The nickel sulfide is converted to granular nickel oxide sinter in fluidized-bed reactors. A portion of this product is marketed directly for alloy steel production. Another part of the granular oxide is treated by chlorination at high temperature (1200 °C, or 2200 °F) to lower its copper content to approximately 0.5%, and then reduced by hydrogen at about 500 °C (930 °F) to yield a highly metallized product (95% Ni) for market.

Two processes are employed to convert the remaining oxide to pure metal for market. One involves reduction smelting to metal anodes and is followed by electrolytic refining, using a sulfate-chloride electrolyte with divided cells and continuous electrolyte purification. The product of this operation is electrolytic nickel cathodes, and the by-products are cobalt and precious metals.

The other process is the atmospheric-pressure carbonyl process, which is used in Clydach, Wales, United Kingdom, and in Copper Cliff, a subdivision of Sudbury, Ontario, Canada. The nickel oxide sinter is reduced with hydrogen and treated with carbon monoxide at approximately 50 °C (120 °F) to volatilize nickel as gaseous nickel carbonyl. This compound is decomposed at approximately 200 °C (390 °F) to yield high-purity nickel in pellet form. Copper and cobalt salts and precious metals are recovered from the residue. Nickel powder is also produced at this plant in a pressure carbonyl system.

The nickel-copper alloy from the matte separation step, containing significant platinum-group metal values, is melted in a top-blown rotary converter, and its sulfur content is adjusted by blowing with oxygen at temperatures up to 1600 °C (2900 °F). The metal product is granulated with water, and the dried metal granules are treated in high-pressure (6.7 MPa, or 970 psi) reactors with carbon monoxide at 150 °C (300 °F) to form nickel carbonyl and some iron carbonyl. The mixed carbonyls are separated by fractionation, and the pure nickel carbonyl is decomposed at approximately 200 °C (390 °F) to yield high-purity nickel pellets and nickel powder for market.

There is a simpler procedure that can be used to process nickel sulfide ores with lower copper contents. As shown by process B in Fig. 2, selective flotation is employed to produce a nickel concentrate low in copper and a small amount of copper concentrate for treatment elsewhere. The dewatered nickel concentrate is fluid-bed-roasted for partial elimination of sulfur, and the calcine plus flux is smelted in arc-type electric furnaces. Waste furnace slag is granulated for disposal while the molten matte is transferred to Pierce-Smith converters for further upgrading to Bessemer matte. The conventional procedure of flux addition and blowing with air removes all but traces of iron from the matte, and the slag produced is returned to the electric furnace for recovery of metal values. The converter matte, essentially nickel sulfide (Ni_3S_2), is cast into anodes and electro-

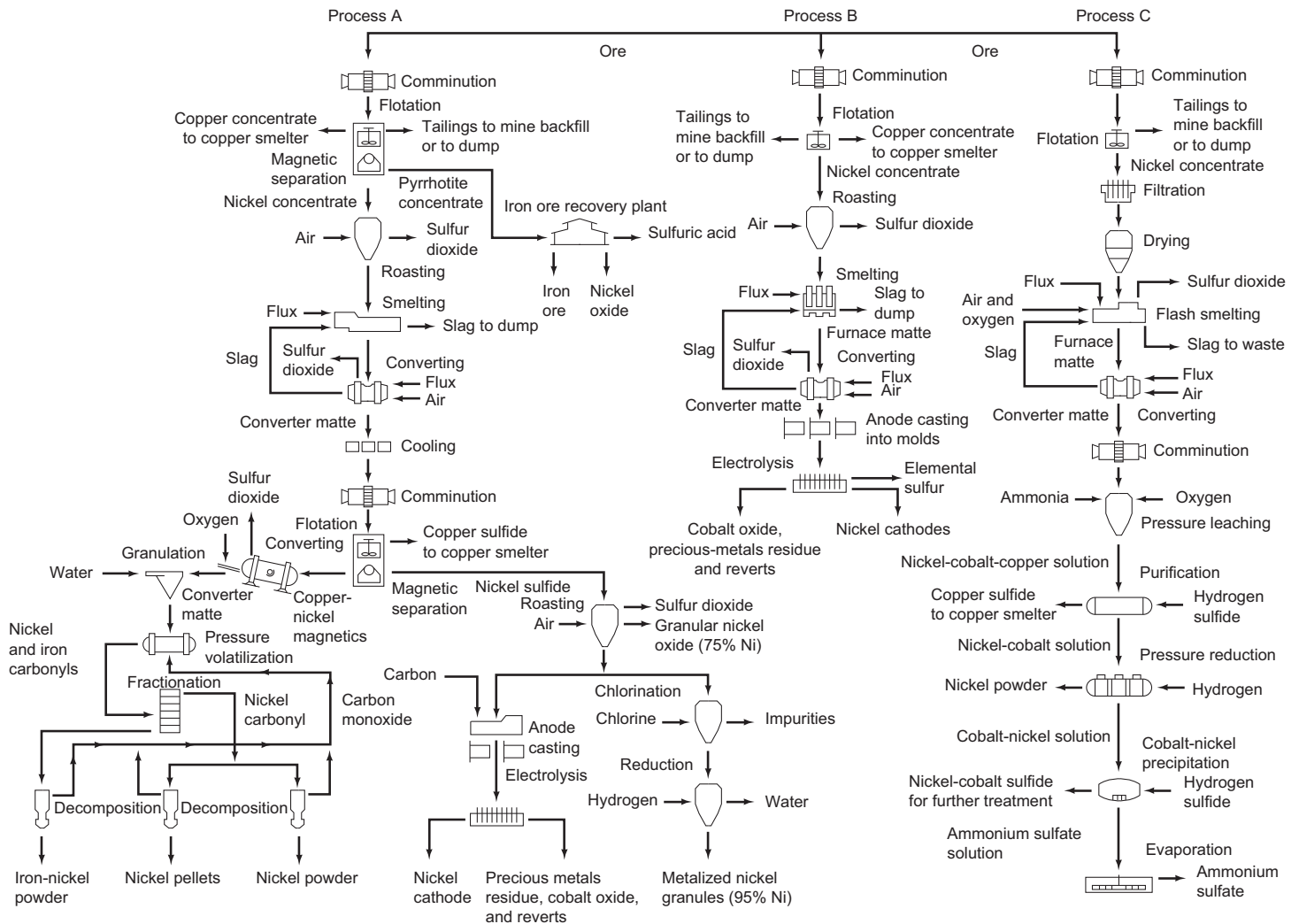


Fig. 2 Flow sheets for three methods of nickel recovery from sulfide ores. See text for processing details. Source: Ref 3

lyzed to yield elemental sulfur at the anode and pure nickel at the cathode. The refining operation also produces cobalt oxide and precious-metal residues.

In the all-hydrometallurgical Sherritt process (see process C in Fig. 2), the nickel ore is concentrated by conventional froth flotation, and the dried nickel concentrate is flash-smelted with oxygen-enriched air and flux to produce furnace matte and waste slag. The furnace matte is cooled, crushed, and finely ground as feed for the hydrometallurgical plant, where it is leached under pressure with a strong ammonia solution and air to solubilize the base metal values, with the simultaneous production of ammonium sulfate. The pregnant leach liquor is treated to remove impurities and then reduced with hydrogen at elevated pressure (3 MPa, or 435 psi) and temperature (190 °C, or 375 °F) to yield a granular nickel powder product. The tail liquor from this operation is treated further to recover ammonium sulfate crystals and a mixed nickel-cobalt sulfide.

Recovery from Laterite Ores. The bulk of the nickel originating from lateritic ores is marketed as ferronickel. The process employed is basically simple and involves drying and preheating the ore, usually under reduction conditions. The hot charge is then further reduced and melted in an electric arc furnace, and the crude metal is refined and cast into ferronickel pigs. A typical operation is shown in Fig. 3 (process A).

A substantial amount of nickel is produced from lateritic ores by the nickel-sulfide matte technique. In this process the ore is mixed with gypsum or other sulfur-containing material such as high-sulfur fuel oil, followed by a reduction and smelting operation to form matte. As in the treatment of sulfide concentrates, the molten furnace matte is upgraded in either conventional or top-blown rotary converters to a high-grade matte, which can be further refined by roasting and reduction to a metallized product. An example of this procedure is shown in Fig. 3 (process B).

Other large-scale operations are based on selective reduction of the ore followed by ammoniacal leaching at atmospheric pressure to dissolve the nickel values. The pregnant liquor is treated to remove impurities and then heated in suitable vessels to drive off ammonia and carbon dioxide and to precipitate a basic nickel carbonate. This material may be sintered under reducing conditions to yield a metallized nickel oxide sinter, or the carbonate may be redissolved in ammoniacal solution and then treated with hydrogen under pressure to yield nickel powder for briquetting. This process is depicted by process C in Fig. 3. Process D in Fig. 3 depicts a process wherein limonitic-type ores are leached with sulfuric acid at elevated temperature and pressure to solubilize nickel and cobalt. The pregnant solution is then treated with hydrogen sulfide to precipitate mixed nickel-cobalt sulfides. This precipitate may be treated by the Sherritt pressure, ammonia-leach process to yield separate nickel and cobalt powders.

6 / Introduction to Nickel and Nickel Alloys

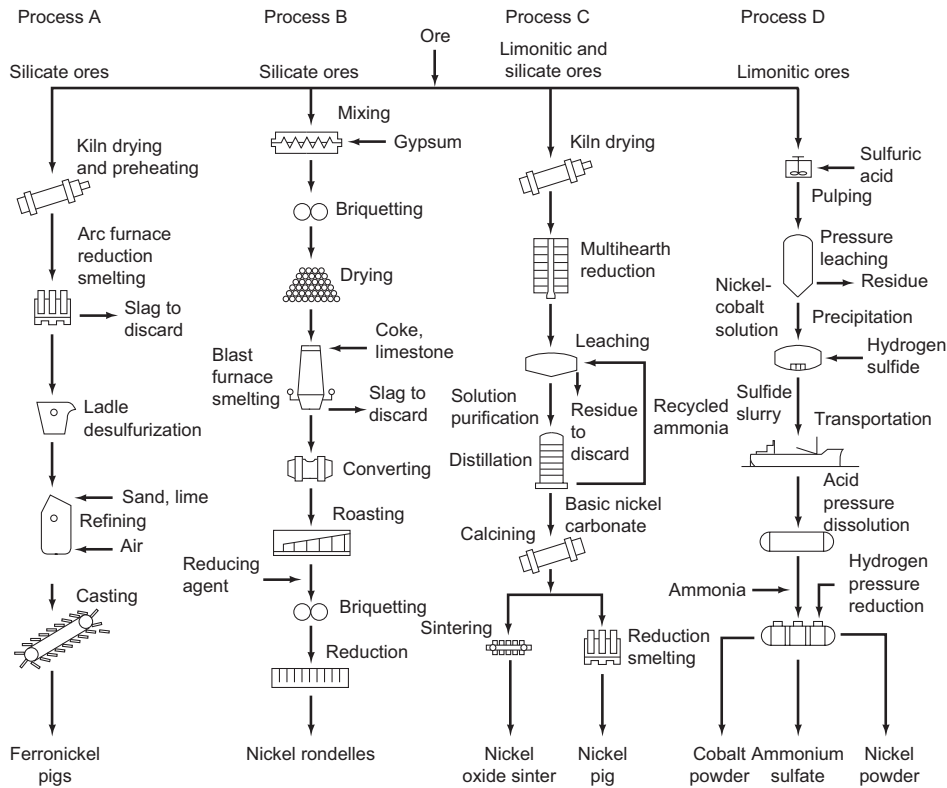


Fig. 3 Flow sheets for four methods of nickel recovery from laterite ores. See text for processing details. Source: Ref 3

Table 1 Consumption of nickel in the United States by end use

Use	Form/tonnes of contained nickel(a)(b)(c)							Grand total	
	Metal	Ferronickel	Oxide and oxide sinter	Chemicals	Other forms	Total primary	Secondary (scrap)	1997	1996
Cast irons	168	W	...	1	45	214	428	642	563
Chemicals and chemical uses	W	...	W	2,730	...	2,730	...	2,730	5,350
Electric, magnet, expansion alloys	W	W	...	(d)	...	(d)	W	W	W
Electroplating (sales to platers)	15,800	...	W	61	1	15,800	...	15,800	16,300
Nickel-copper and copper-nickel alloys	2,650	W	W	...	W	2,650	3,390	6,040	7,280
Other nickel and nickel alloys	17,000	W	W	...	W	17,000	2,040	19,100	19,300
Steel									
Stainless and heat resistant	26,100	21,000	1,760	...	57	48,900	56,900	106,000	94,100
Alloys (excludes stainless)	5,180	1,090	1,060	(d)	W	7,320	1,330	8,650	6,970
Superalloys	18,200	...	(d)	1	465	18,700	W	18,700	15,600
Other(e)	6,000	410	79	645	1,070	8,210	4,790	13,000	13,300
Total reported	91,000	22,500	2,890	3,440	1,640	122,000	68,800	190,000	179,000
Total all companies, apparent	NA	NA	NA	NA	NA	154,000	38,100	192,000	181,000

(a) Data are rounded to three significant digits and may not add to totals shown. (b) W, withheld to avoid disclosing company proprietary data; included with "Other." (c) NA, not applicable. (d) Less than 1/2 unit. (e) Includes batteries, catalysts, ceramics, coinage, other alloys containing nickel, and data indicated by symbol "W." Source: U.S. Geological Survey

End Uses of Nickel

According to the Nickel Development Institute, worldwide consumption of nickel can be broken into the following market segments:

Use	Nickel consumption, %
Stainless steel	62.7
Nickel-base alloys	11.9
Plating	9.7
Alloy steels	9.0
Foundry products	3.5
Copper-base alloys	1.4
Other	1.8

Consumption statistics in the United States follow similar trends (Table 1), with stainless steels making up about 55% of all nickel consumed. According to the American Iron and Steel Institute, nickel-bearing grades accounted for 63% of the total stainless steel production for 1997. Demand for austenitic stainless steels is expected to continue to drive the world nickel market for at least another 20 years. Demand for nickel-bearing superalloys is also expected to grow. In 1997, U.S. consumption of primary nickel in superalloys increased almost 20% because of growing orders in the aerospace industry (Table 1).

The use of primary nickel by battery manufacturers is another potential growth market for nickel. Rechargeable nickel-cadmium and nickel-metal hydride batteries are used in handheld power tools, cellular telephones, laptop computers, and camcorders. Nickel base batteries, including the more recently developed sodium metal-nickel battery called the ZEBRA (Zero Emission Batterie Research Activity), are also being used in electric vehicles and the rapidly growing electric scooter/bicycle market. Nickel consumption patterns could change significantly due to tightening oil supplies combined with increased oil and gasoline prices. The market for large energy-storage devices for nationwide communications systems and for emergency power supplies would also grow, further encouraging the scale-up of both nickel-metal hydride and sodium metal-nickel batteries.

REFERENCES

1. S.J. Rosenberg, *Nickel and Its Alloys*, National Bureau of Standards Monograph 106, U.S. Department of Commerce, May 1968
2. W. Betteridge, *Nickel and Its Alloys*, Ellis Horwood Ltd., 1984
3. A. Illis, *Nickel Metallurgy*, *McGraw-Hill Encyclopedia of Science and Technology*, Vol 11 (MET-NIC), 7th ed., 1992, p 711-714