

NICKEL AND NICKEL ALLOYS

1. Introduction

The first reported use of nickel [7440-02-0], Ni, was in a nickel–copper–zinc alloy produced in China in the Middle Ages and perhaps earlier. Alloys of nickel may have been used in prehistoric times. The metal was first isolated for analytical study in the mid-1700s by Axel Cronstedt, who named it nickel, which derives from the German word *kupfernickel*, or false copper.

Elemental nickel has a face-centered cubic structure. Nickel is a silver-white metal, harder than iron and capable of taking a brilliant polish, malleable and ductile, and magnetic below 360°C. When compact, nickel is not oxidized on exposure to air at ordinary temperatures.

Stainless steel accounted for more than 60% of primary nickel consumption in the world. In the United States, however, this percentage was only 41% because of the relatively large number of specialty metals industries in the country. Specialty uses include superalloys and related aerospace alloys, high temperature nickel-chromium alloys, electrolytic plating, electroless plating, cupronickel alloys, and naval brasses. Manufacturers of rechargeable batteries have been using increasing amounts of nickel metal foam. This foam is produced in only four countries: Canada; China; Russia; and the United Kingdom.

2. Occurrence

Nickel comprises ca 3% of the earth's composition and is exceeded in abundance by iron (qv), oxygen (qv), silicon (see SILICA, INTRODUCTION), and magnesium (see MAGNESIUM AND MAGNEISUM ALLOYS). However, although nickel comprises ca 7% of the earth's core, it comprises only about 0.009% of the earth's crust, ranking 24th in order of abundance in the crust. Fortunately, ore forms amenable to economic mining exist. The 2003–2004 world production, economic reserve, and reserve base quantities are listed in Table 1.

Australia, Canada, Cuba, and Russia have the largest economic reserves, whereas the United States has less than 0.1% of the world's estimated reserves. In 2002, Australia was the third largest nickel-producing country in the world and was beginning to rival Canada (2).

The world economic (proven) nickel reserves are estimated at 47.0×10^6 t. At the 1992 world rate of mine production (ca 894×10^3 t), these reserves would be expected to last at least until the year 2050. If, however, annual mine production increases at a rate that reflects a predicted increase in the world primary nickel consumption of 2% annually, these reserves would be depleted before 2030 (3–5).

In addition to the reported economic reserves, there are substantial nickel resources which could be amenable to mining and refining once appropriate technology becomes available. The single largest such resource is seabed nodules which contain ca 1% nickel and which could represent up to 800×10^6 t of nickel (see OCEAN RAW MATERIALS).

2.1. Nickel Ores. The two types of nickel ore which can be mined economically are classified as sulfide and lateritic (6). The most common nickel sulfide is pentlandite [53809-86-2], $(\text{Ni,Fe})_9\text{S}_{16}$, which is almost always found in association with chalcopyrite [1308-56-1], CuFeS_2 , and large amounts of pyrrhotite [12063-67-1], Fe_7S_8 . Other, much rarer nickel sulfides include millerite [1314-04-1], NiS , heazlewoodite [12035-71-1], Ni_3S_2 , and the sulfides of the linnaeite series, $(\text{Fe,Co,Ni})_3\text{S}_4$. The nickel sulfides were formed thousands of meters below the surface of the earth by the reaction of sulfur with nickel-bearing rocks. These sulfides generally are found in northern regions where glacial action has planed away much of the overlying weathered surface rock. Important sulfide deposits are found in Canada, Russia, and Finland.

In contrast to the sulfide ores, the lateritic ores were formed over long periods of time as a result of weathering of exposed nickel-containing rocks. The lateritic weathering process resulted in nickel solutions that were redeposited elsewhere in the form of oxides or silicates. One type of laterite is nickeliferous limonitic iron laterite $(\text{Fe, Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$ which consists primarily of hydrated iron oxide in which the nickel is dispersed in solid solution. The other type of laterite is nickel silicate in which nickel is contained in solid solution in hydrated magnesium-iron minerals, eg, garnierite [12178-41-5], $(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$. Lateritic ores occur primarily in tropical regions, eg, New Caledonia, or in regions which were once at least subtropical for extended periods, eg, Oregon. These deposits are distributed widely and constitute the largest nickel reserves.

3. Properties

Nickel occurs in the first transition row in Group 10 (VIII B) of the Periodic Table. Some physical properties are given in Table 2 (7–10). Nickel is a high melting point element having a ductile crystal structure. Its chemical properties allow it to be combined with other elements to form many alloys.

4. Extraction and Refining

The treatments used to recover nickel from its sulfide and lateritic ores differ considerably because of the differing physical characteristics of the two ore types. The sulfide ores, in which the nickel, iron, and copper occur in a physical mixture as distinct minerals, are amenable to initial concentration by mechanical methods, eg, floatation (qv) and magnetic separation (see SEPARATION, MAGNETIC SEPARATION). The lateritic ores are not susceptible to these physical processes of beneficiation, and chemical means must be used to extract the nickel. The nickel concentration processes that have been developed are not as effective for the lateritic ores as for the sulfide ores (see also EXTRACTIVE METALLURGY, MINERALS RECOVERY AND PROCESSING).

4.1. Sulfide Ores. Pyrometallurgical Processes. Sulfide ores first undergo crushing and milling operations to reduce the material to the necessary degree of fineness for separation. Froth floatation or magnetic separation processes separate the sulfides from the gangue. Most sulfide ores then undergo a

series of pyrometallurgical processes consisting of roasting, smelting, and converting. Roasting, in which much of the iron is oxidized and a large portion of the sulfur is removed as sulfur dioxide, is carried out in multihearth furnaces, fluidized-bed roasters, or rotary kilns. The material then is smelted in reverberatory furnaces or blast furnaces or by flash smelting or arc-furnace smelting. During smelting, a siliceous slag containing iron oxide and other oxide compounds is removed and the sulfur content is further reduced, yielding an impure copper–nickel–iron–sulfur matte. In the converting or Bessemerizing stage, the matte is charged into a horizontal-type converter and the molten matte with silica added is blown with air. This procedure removes virtually all the remaining iron in a slag as well as more of the sulfur as sulfur dioxide, yielding a sulfur-deficient copper–nickel matte.

The matte can be treated in different ways, depending on the copper content and on the desired product. In some cases, the copper content of the Bessemer matte is low enough to allow the material to be cast directly into sulfide anodes for electrolytic refining. Usually it is necessary first to separate the nickel and copper sulfides. The copper–nickel matte is cooled slowly for ca 4 d to facilitate grain growth of mineral crystals of copper sulfide, nickel–sulfide, and a nickel–copper alloy. This matte is pulverized, the nickel and copper sulfides isolated by flotation, and the alloy extracted magnetically and refined electrolytically. The nickel sulfide is cast into anodes for electrolysis or, more commonly, is roasted to nickel oxide and further reduced to metal for refining by electrolysis or by the carbonyl method. Alternatively, the nickel sulfide may be roasted to provide a nickel oxide sinter that is suitable for direct use by the steel industry.

Electrolytic Refining. The electrolytic refining process generally is carried out in a divided cell using anodes which are cast from the crude metal or from nickel sulfides. The electrolyte is pumped continuously through the cell, and impure anolyte, which forms by solution of the anode, is pumped out of the electrolyzing tank and through a purification train to remove soluble impurities. The impure anolyte is prevented from coming into direct contact with the cathode by the use of a porous diaphragm. The nickel cathode starting sheets are made by deposition onto stainless steel blanks from which the nickel sheets are stripped after 2 d and then the cathode is built up in ca 10 d. The final nickel metal that is obtained has a purity exceeding 99.9 wt%. The electrorefining process also facilitates the recovery of precious metals and other metals of value, eg, cobalt, that remain in the insoluble anode residues which are collected during the nickel refining process.

Carbonyl Process. Crude nickel also can be refined to very pure nickel by the carbonyl process. The crude nickel and carbon monoxide (qv) react at ca 100°C to form nickel carbonyl [13463-309-3], $\text{Ni}(\text{CO})_4$, which upon further heating to ca 200–300°C, decomposes to nickel metal and carbon monoxide. The process is highly selective because, under the operating conditions of temperature and atmospheric pressure, carbonyls of other elements that are present, eg, iron and cobalt, are not readily formed.

In the carbonyl process, the liquid is purified, vaporized, and rapidly heated to ca 300°C which results in the decomposition of the vapor to carbon monoxide and a fine high purity nickel powder of particle sizes $<10\text{ }\mu\text{m}$. This product is useful for powder metallurgical applications (see POWDER METALLURGY). Nickel

carbonyl can also be decomposed in the presence of nickel powder, upon which the nickel is deposited. This process yields nickel pellets, typically about 0.8 cm dia and of >99.9 wt% purity.

Hydrometallurgical Processes. Hydrometallurgical refining also is used to extract nickel from sulfide ores. Sulfide concentrates can be leached with ammonia (qv) to dissolve the nickel, copper, and cobalt sulfides as amines. The solution is heated to precipitate copper, and the nickel and cobalt solution is oxidized to sulfate and reduced, using hydrogen at a high temperature and pressure to precipitate the nickel and cobalt. The nickel is deposited as a 99 wt % pure powder.

4.2. Lateritic Ores. Pyrometallurgical Processes. Nickel oxide ores are processed by pyrometallurgical or hydrometallurgical methods. In the former, oxide ores are smelted with a sulfiding material, eg, gypsum, to produce an iron–nickel matte that can be treated similarly to the matte obtained from sulfide ores. The iron–nickel matte may be processed in a converter to eliminate iron. The nickel matte then can be cast into anodes and refined electrolytically.

A different type of nickel product is obtained by roasting the nickel matte to the oxide, grinding and compacting the oxide, and reducing the oxide to metal using charcoal in a muffle furnace. The metal sinters to form rondelles that contain ca 99.3 wt% nickel. Alternatively, the nickel oxide ore may be smelted without a sulfiding agent and reduced using coke in an electric furnace to produce ferronickel. Ferronickel generally contains 20–30 wt% nickel, but the nickel content may be higher.

Hydrometallurgical Processes. The hydrometallurgical treatments of oxide ores involve leaching with ammonia or with sulfuric acid. In the ammoniacal leaching process, the nickel oxide component of the ore first is reduced selectively. Then the ore is leached with ammonia which removes the nickel into solution, from which it is precipitated as nickel carbonate by heating. A nickel oxide product used in making steel is produced by roasting the carbonate.

In the acid-leaching process, the oxide ore is leached with sulfuric acid at elevated temperature and pressure, which causes nickel, but not iron, to enter into solution. The leach solution is purified, followed by reaction with hydrogen sulfide and subsequent precipitation of nickel and cobalt sulfides. The nickel sulfide is refined by conversion to a sulfate solution and reduction with hydrogen to produce a high purity nickel powder.

5. Commercial Forms of Nickel

Nickel is available in many commercial forms. The main forms marketed are those listed in Table 3. The very pure unwrought nickels, primarily the electrolytic cathodes and carbonyl pellets and, to a lesser degree, the briquettes and rondelles, are used for production of alloys in which contamination by undesired elements must be minimized in order to obtain desired properties, eg, in nickel-base superalloys and magnetic materials. Pure nickel powder is utilized in the production of porous plates for batteries, introduction (qv) and in the production of powder metallurgy parts. A large amount of nickel is available as nickel oxide

sinter and ferronickel, which is widely used in the steel and foundry industries as an economical nickel source.

6. Economic Aspects

The United States did not have any active nickel mines in 2004. Limited amounts of by-product nickel were recovered from copper and palladium-platinum ores mined in the Western States. Table 4 gives United States economic statistics (1).

Stainless steel accounts for two-thirds of the primary nickel used in the world. U.S. production of austenitic stainless steel reached a record high of 1.56×10^6 t in 2004. This was 13% higher than the record of 1.37×10^6 t set in 2003. U.S. stainless steel producers continued to struggle against significant imports, but demand for specialty steel began to recover in North America during the second half of 2004. World nickel mine production was at an all time high in 2004. Since 1950, stainless steel production in the Western World has been growing at an average rate of 6%. Demand for stainless steel in China has been very strong since 2000 and is now equal to that of Japan (1).

7. Health and Safety Factors

Nickel is a confirmed carcinogen with experimental carcinogenic, neoplastigenic, and tumorigenic data. It is poisonous by most routes. Ingestion of soluble salts causes nausea, vomiting, and diarrhea. Mutation data has been reported. Hypersensitivity to nickel is common and can cause allergic contact dermatitis, pulmonary asthma, conjunctivitis, and inflammatory reactions around nickel-containing implants and prosthesis (11).

The OSHA PEL TWA soluble compounds in 0.1 mg (Ni)/m^3 and 1 mg (Ni)/m^3 . The ACGIH TLV TWA is 0.1 mg (Ni)/m^3 .

Powders can ignite spontaneously. Raney nickel catalysts may initiate hazardous reactions. Nickel catalysts have caused many industrial accidents.

8. Uses

In the United States, 41 % of the primary nickel consumed went into the production of nonferrous alloy and superalloy production, 41 % went into stainless and alloy steel production, 16 % went into electroplating, and 2 % into other uses. Ultimate end uses were as follows, transportation, 32 %; chemical industry, 14 %; electrical equipment, 11 %; construction, 9 %; fabricated metal products, 8 %; household appliances, 7 %; machinery, 6 %; petroleum industry, 6 %; and other, 7 % (1).

At least four automobile manufacturers were using nickel-metal hydride batteries to power their gasoline-hybrid vehicles for the 2006 and 2007 model years. Demand for the gasoline-hybrid cars has gone up in the United States since their introduction in 1999, and has accelerated with rising gasoline prices.

New nickel-hydride battery modules are being produced for a variety of applications including stationary backup or uninterruptible power supply systems for telecommunications (1).

9. Alloys

9.1. Properties. Selected chemistries and properties of commercially available nickel and typical cast and wrought nickel alloys are given in Tables 5 and 6 (4, 5, 7–9, 12–33). Nickel-base alloys provide excellent mechanical properties from cryogenic temperatures through temperatures in excess of 1000°C. The development paths of typical wrought nickel alloys is depicted in Figure 1 (6). Nickel alloys are strengthened by solid solution hardening, carbide strengthening, and precipitation hardening.

9.2. Nickel. Nickel metal is available in many wrought forms and usually is designated as Nickel 200 or Nickel 201 [39369-16-9] and according to the Unified Numbering System (UNS) as UNS N02201, 205 (UNS N02205), and 270 [128355-61-3] (UNS N02270). Nickel 200 is the general-purpose nickel used in ambient-temperature applications in food processing (qv) equipment, chemical containers, caustic-handling equipment and plumbing, electromagnetic parts, and aerospace and missile components. Nickel 201 has a much lower trace carbon content than the 200 and is thus more suitable for elevated temperature applications. The lower carbon content prevents elevated temperature stress-corrosion cracking. Nickel 205 is low in carbon but contains trace amounts of magnesium; Nickel 270 is one of the purest, ie, 99.98 wt%, commercial nickels. DURANICKEL alloy 301 (UNS N03301), which contains about 4.5 wt% aluminum and 0.5 wt% titanium, can be aged to form very fine [12003-81-5] precipitates. This type of alloy combines high strength and hardness with the excellent corrosion resistance that is characteristic of Nickel 200. Various of these nickel metals also are used as (qv) electrodes for joining ferritic or austenitic steels to high nickel-containing alloys and for welding the clad side of nickel-clad steels.

Nickel has excellent corrosion-resistance properties. Nickel and nickel alloys are useful in reducing environments and under some oxidizing conditions in which a passive oxide film is developed. In general, nickel is very resistant to corrosion in marine and industrial atmospheres, in distilled and natural waters, and in flowing seawater. Nickel has excellent resistance to corrosion by caustic soda and other alkalies. In nonoxidizing acids, nickel does not readily discharge hydrogen. Hence, nickel has fairly good resistance to sulfuric acid, hydrochloric acid, organic acids, and other acids, but has poor resistance to strongly oxidizing acids such as nitric acid. Nickel has excellent resistance to neutral and alkaline salt solutions. Nonoxidizing acid salts are moderately corrosive, and oxidizing acid salts and oxidizing alkaline salts generally are corrosive to nickel. Nickel also is resistant to corrosion by chlorine, hydrogen chloride, fluorine, and molten salts.

Wrought and cast nickel anodes and sulfur-activated electrodeposited rounds are used widely for nickel electrodeposition onto many base metals. Nickel also can be plated by an electroless process (see ELECTROLESS DEPOSITION).

Nickel plating provides resistance to corrosion for many commonly used articles, eg, pins, paper clips, scissors, keys, fasteners, etc, as well as for materials used in food processing (qv), the paper (qv) and pulp (qv) industries, and the chemical industry, each of which is often characterized by severely corrosive environments. Nickel plating is used in conjunction with chromium plating to provide decorative finishes and corrosion resistance to numerous articles. Nickel plating is used to salvage worn, corroded, or incorrectly machined parts. Nickel electroforming, in which nickel is electrodeposited onto a mold which subsequently is separated from the deposit, is used to form complex shapes, eg, printing plates, tubing, nozzles, screens, and grids.

Porous nickel electrodes made from nickel powder are used in storage batteries, introduction (qv) and fuel cells (qv). Nickel–cadmium batteries have attractive properties including long operating and storage lives, high rate discharge capability, high rate charge acceptance, and high and low temperature capability.

Nickel also is an important industrial catalyst. The most extensive use of nickel as a catalyst is in the food industry in connection with the hydrogenation or dehydrogenation of organic compounds to produce edible fats and oils (see FATS AND FATTY OILS).

Nickel foam can be used as a pin connector for inert anodes (34).

9.3. Nickel Alloying. Nickel is alloyed into low alloy steels, ferritic alloy steels, and austenitic stainless steels through the conventional steelmaking processes, eg, open hearth, basic oxygen conversion, and the argon–oxygen decarburization (AOD) processes. The AOD process is used to produce a substantial quantity of the stainless steels in the world. It is a highly productive process that yields cleaner products at lower operating and materials costs as compared to the older conventional electric-arc-furnace (EAF) steelmaking practice. EAF or AOD melting and air-induction melting (AIM) are used for some nickel-base alloys. Electroslag remelt (ESR) processing also is used to further refine these steels and nickel alloys.

Nickel alloys that are heavily alloyed with other elements including the nickel-base and iron-base superalloys, also are produced by vacuum-induction melting (VIM). In the VIM process, the melting, alloying, melt treatments, and ingot casting are carried out under vacuum. Industrial VIM furnaces generally can process up to 20-t batches. For further alloy refinement, VIM castings are used as electrodes and are ESR- or vacuum-arc remelted (VAR). Investment castings of the chemically complex nickel-base alloys, especially those containing the reactive elements aluminum and titanium, also are carried out under vacuum. More recently, directional solidification techniques, in which the heat is extracted directionally through a controlled solidification rate and temperature gradient, are used to produce either monocrystalline nickel-base superalloys or polycrystalline structures having long columnar grains. Gas powder-atomizing techniques, which involve VIM master melts, also are used routinely to produce fine nickel-base powders for subsequent powder metallurgical consolidation of near-net-shape components. Melting technologies involving electron-beam and plasma melting are also being used to melt nickel alloys (see PLASMA TECHNOLOGY).

9.4. Nickel–Copper. In the solid state, nickel and copper form a continuous solid solution. The nickel-rich, nickel–copper alloys are characterized by a

good compromise of strength and ductility and are resistant to corrosion and stress corrosion in many environments, in particular water and seawater, nonoxidizing acids, neutral and alkaline salts, and alkalies. These alloys are weldable and are characterized by elevated and high temperature mechanical properties for certain applications. The copper content in these alloys also ensure improved thermal conductivity for heat exchange. MONEL alloy 400 is a typical nickel-rich, nickel-copper alloy in which the nickel content is ca 66 wt%. MONEL alloy K-500 is essentially alloy 400 with small additions of aluminum and titanium. Aging of alloy K-500 results in very fine γ' -precipitates and increased strength (see also COPPER ALLOYS, WROUGHT).

Typical applications for the nickel-copper alloys are in industrial plumbing and valves, marine equipment, petrochemical equipment, and feedwater heat exchangers (see PIPING SYSTEMS). The age-hardened alloys are used as pump shafts and impellers, valves, drill parts, and fasteners (see PUMPS). Nickel-copper alloys also are used as coated electrodes or filler alloys for welding purposes. Coinage is typically an alloy of 75 wt% Cu and 25 wt% Ni.

Copper and nickel can be alloyed with zinc to form nickel silvers. Nickel silvers are ductile, easily formed and machined, have good corrosion resistance, can be worked to provide a range of mechanical properties, and have an attractive white color. These alloys are used for ornamental purposes, as silverplated and uncoated tableware and flatware; in the electrical industry as contacts, connections, and springs; and as many formed and machined parts (see ELECTRICAL CONNECTORS).

9.5. Nickel-Chromium. Nickel and chromium form a solid solution up to 30 wt% chromium. Chromium is added to nickel to enhance strength, corrosion resistance, oxidation, hot corrosion resistance, and electrical resistivity. In combination, these properties result in the nichrome-type alloys used as electrical furnace heating elements. The same alloys also provide the base for alloys and castings which can withstand hot corrosion in sulfur and oxidative environments, including those containing vanadium pentoxides which are by-products of petroleum combustion in fossil-fuel electric power plants and in aircraft jet engines. Alloy additions to nickel-chrome usually are ca 4 wt% aluminum and ca ≤ 1 wt% yttrium. Without these additions, the nichrome-type alloys provide hot oxidation or hot corrosion resistance through the formation of surface nickel-chromium oxides. Aluminum provides for surface Al_2O_3 formation and the yttrium or other rare-earth additions improve the adherence of the protective oxide scales to the nickel-chromium-aluminum substrates.

9.6. Nickel-Iron. A large amount of nickel is used in alloy and stainless steels and in cast irons. Nickel is added to ferritic alloy steels to increase the hardenability and to modify ferrite and cementite properties and morphologies, and thus to improve the strength, toughness, and ductility of the steel. In austenitic stainless steels, the nickel content is 7–35 wt%. Its primary roles are to stabilize the ductile austenite structure and to provide, in conjunction with chromium, good corrosion resistance. Nickel is added to cast irons to improve strength and toughness.

Many nickel-iron alloys have useful magnetic characteristics and are used in a wide range of devices in the electronics and telecommunication fields. Some nickel-iron alloys are magnetically soft and have attractive properties

of high initial permeability, high maximum magnetization and low residual magnetization, low coercive force, and low hysteresis and eddy-current losses. These properties are sensitive to alloying and to precipitate and grain morphologies. Important soft magnetic alloys are based on compositions of 78 wt% Ni–22 wt% Fe, 65 wt% Ni–35 wt% Fe, and 50 wt% Ni–50 wt% Fe, which often include a few weight percent of molybdenum, copper, or chromium.

The majority of permanent magnets are made from magnetically hard alloys of nickel and iron that are characterized by high values of residual magnetization and coercive force. The many Alnico alloys, consisting of (14–28) wt% Ni–(5–35) wt% Co–(6–12) wt% Al–(0–6) wt% Cu–(0–8) wt% Ti–balance iron, are precipitation-strengthened, hard, brittle alloys in which the magnetic properties are sensitive to heat treatments which determine precipitate and grain morphologies.

Some nickel–iron alloys have anomalously low thermal-expansion coefficients within certain temperature ranges. This behavior results from a balance between the normal thermal expansion and a contraction caused by magnetostriiction. These alloys, eg, nickel–iron alloys having 36 wt%, 42 wt%, or 50 wt% nickel, and a 29 wt% Ni–17 wt% Co–54 wt% Fe alloy, are used as glass-to-metal joints and in metrology equipment, thermostats and thermometers, cryogenic structures and devices (see CRYOGENIC TECHNOLOGY), and many other electrical and engineering applications.

Demands for improved efficiency in aircraft gas turbines led to the use of a family of age hardenable, controlled expansion superalloys for engine seals and casings. INCOLOY alloys 903 [61107-16-2] (UNS N19903), 907 [107652-23-3] (UNS N19907), and 909 evolved from a continuing effort to improve the environmental resistance of this Cr-free, Fe–Ni–Co based system.

Another anomalous property of some nickel–iron alloys, which are called constant-modulus alloys, is a positive thermoelastic coefficient which occurs in alloys having 27–43 wt% nickel. The elastic moduli in these alloys increase with temperature. Usually, and with additions of chromium, molybdenum, titanium, or aluminum, the constant-modulus alloys are used in precision weighing machines, measuring devices, and oscillating mechanisms (see WEIGHING AND PROPORTIONING).

9.7. Nickel–Molybdenum. Molybdenum in solid solution with nickel strengthens the latter metal and improves its corrosion resistance, eg, in the HASTELLOY alloys. HASTELLOY alloy B-2 is noted for its superior resistance to corrosion by hydrochloric acid at all concentrations up to the boiling point; by other nonoxidizing acids, such as sulfuric and phosphoric; and by hot hydrogen chloride gas. Other nickel–molybdenum alloys contain chromium, which improves the resistance to corrosion and, especially, to oxidation. The Ni–Cr–Mo HASTELLOY alloy C-22, which also contains cobalt and tungsten, is resistant to a wide range of chemical process environments, including strong oxidizing acids, organic and inorganic media, chlorine, and brine. HASTELLOY alloy C-276 also has excellent resistance to corrosion by oxidizing environments, oxidizing acids, chloride solutions, and other acids and salts.

Another set of nickel alloys, which have a high chromium content, a moderate molybdenum content, and some copper, are the ILLIUM alloys. These cast

alloys are wear and erosion resistant and highly resistant to corrosion by acids and alkalies under both oxidizing and reducing conditions.

9.8. Nickel–Iron–Chromium. A large number of industrially important materials are derived from nickel–iron–chromium alloys. These alloys are within the broad austenitic, gamma-phase field of the ternary Ni–Fe–Cr phase diagram and are noted for good resistance to corrosion and oxidation and good elevated temperature strength (see HIGH TEMPERATURE ALLOYS). Examples are the INCONEL alloys, which are based on the INCONEL alloy 600 composition. Alloy 600 is a solid solution alloy with good strength and toughness from cryogenic to elevated temperatures and good oxidation and corrosion resistance in many media. In addition, the alloy is easily fabricated and joined. Many modifications of alloy 600 have been made to produce other alloys with different characteristics. For example, INCONEL alloy 601 [12631-43-5] (UNS N06601) contains aluminum for improved high temperature oxidation resistance, INCONEL alloy 625 contains molybdenum and niobium in solid solution for better strength, and INCONEL alloy 690 [54385-90-9] (UNS N06690) with further additions of chromium was developed for use in the nuclear industry and is particularly noted for its resistance to corrosion by high purity water (see NUCLEAR REACTORS, WASTE MANAGEMENT, INTRODUCTION).

Other alloys have been developed for use in particular corrosive environments at high temperatures. Several of these are age-hardenable alloys which contain additions of aluminum and titanium. For example, INCONEL alloys 718 and X-750 [11145-80-5] (UNS N07750) have higher strength and better creep and stress rupture properties than alloy 600 and maintain the same good corrosion and oxidation resistance. Alloy 718 exhibits excellent stress rupture properties up to 705°C as well as good oxidation resistance up to 980°C and is widely used in gas turbines and other aerospace applications, and for pumps, nuclear reactor parts, and tooling.

The INCOLOY alloys exemplify another class of nickel–iron–chromium alloys. INCOLOY alloy 800 is resistant to hot corrosion, oxidation, and carburization and has good elevated-temperature strength. Modifications of alloy 800 impart different strength or corrosion-resistance characteristics. For example, INCOLOY alloy 801 [12605-97-9] (UNS N08801) contains more titanium, which, with appropriate heat treatments, can age-harden the alloy and provide increased resistance to intergranular corrosion; INCOLOY alloy 802 [51836-04-5] (UNS N08802) contains more carbon which provides improved high temperature strength through carbide strengthening. INCOLOY alloy 825 [12766-43-7] (UNS N08825) and HASTELLOY alloy G-3 contain molybdenum, copper, and other additions and are exceptionally resistant to attack by aggressive corrosive environments.

The corrosion- and heat-resistant alloys, eg, alloys 600 and 800, are used extensively in heat-treating equipment, nuclear and fossil-fuel steam generators, heater-element sheathing and thermocouple tubes, and in chemical and food-processing equipment. Alloys 625 and 825 are used in chemical processing, pollution control, marine and pickling equipment, ash-pit seals, aircraft turbines and thrust reversers, and radiation waste-handling systems. The age-hardened INCONEL and INCOLOY alloys are used in gas turbines, high temperature springs and bolts, Nuclear Reactors, Waste Management, Introduction, rocket

motors, spacecraft, and hot-forming tools. There are also nickel–iron–chromium alloys used as welding electrode and filler metals.

9.9. Nickel-Base Superalloys. Superalloys, which are critical to gas-turbine engines because of their high temperature strength and superior creep and stress rupture-resistance, basically are nickel–chromium alloyed with a host of other elements. The alloying elements include the refractory metals tungsten, molybdenum, or niobium for additional solid-solution strengthening, especially at higher temperatures and aluminum in appropriate amounts for the precipitation of γ' for coherent particle strengthening (see REFRACTORIES). Titanium is added to provide stronger γ' , and niobium reacts with nickel in the solid state to precipitate the γ'' -phase; γ'' is the main strengthening precipitate in the 718-type alloys. Cobalt, generally present in many superalloys in large (≥ 10 wt%) amounts, enhances strength, oxidation, and hot-corrosion resistance which is also provided by the chromium in the alloy. Small excess amounts of carbon usually are present in superalloys for intentional carbide precipitation at grain-boundaries which, as discrete and equiaxed particles, can provide obstacles for grain-boundary sliding and motion, thus suppressing creep at high temperatures. Small or trace amounts of elements, eg, zirconium, boron, and hafnium, may be present and these enhance grain-boundary strength and improve ductility. The strength and elevated-temperature properties of a superalloy are dependent on the volume fraction of the fine γ' -precipitates, which can be increased to ca 60 wt%, depending on the aluminum and titanium content. Besides precipitation control at the grain boundaries, improved heat resistance can result from either the elimination of grain boundaries or through the growth of aligned grains with minimum grain boundaries perpendicular to the principal applied stress direction, eg, in turbine-blade applications.

Because of constitutional complexity, the exact chemistries of nickel-base superalloys must be controlled carefully in order to avoid the precipitation of deleterious topologically close-packed (TCP) phases and extraneous carbides after long-term high temperature exposure. Heat-treatment schedules and thermomechanical treatments in the case of wrought alloys also are important to provide optimum strength and performance.

9.10. Oxide-Dispersion-Strengthened Alloys. Through mechanical alloying and other powder-metallurgical techniques, highly hot-oxidation and corrosion-resistant nickel–chromium matrices are strengthened by very fine dispersions of somewhat chemically inert oxide particles to produce alloys such as INCONEL alloy MA754. These oxide dispersions replace γ' as the main strengthening agent and provide strength benefits close to the melting temperature. Gamma-prime precipitation strengthening usually begins to decline above 800°C. The oxide-dispersion-strengthened (ODS) nickel-, iron-, and cobalt-base alloys are used mainly in bar and sheet forms in gas turbine vanes in combustion chambers and as exhaust hardware in very high temperature applications.

9.11. Nickel Aluminide Intermetallics. Cast and wrought nickel aluminides are being developed for high temperature applications. Using additions of 0.1% Zr to β -NiAl, and alloys containing $\geq 40\%$ Al, an adherent, protective oxide is that improves cyclic oxidation performance. Additions of B, Cr, Co, and titanium diboride, TiB_2 , reportedly enhance ductility and the strength of nickel aluminides. Bars, wires, and continuously cast strip have been produced

that have excellent strength and oxidation resistance (35) (see also GLASSY METALS).

9.12. Nickel-Matrix Composites. Nickel and nickel–titanium compositions are used as powder binders for carbide cutting tools (see CARBIDES, SURVEY; TOOL MATERIALS). Gas turbine engine engineers have begun development of ceramic-filled honeycomb structures using nickel-base oxide dispersion-strengthened alloys. Additional studies are underway to develop nickel-base superalloy composites using tungsten, molybdenum, silicon carbide, and sapphire fibers (36) (see also ABLATIVE MATERIALS; METAL-MATRIX COMPOSITES).

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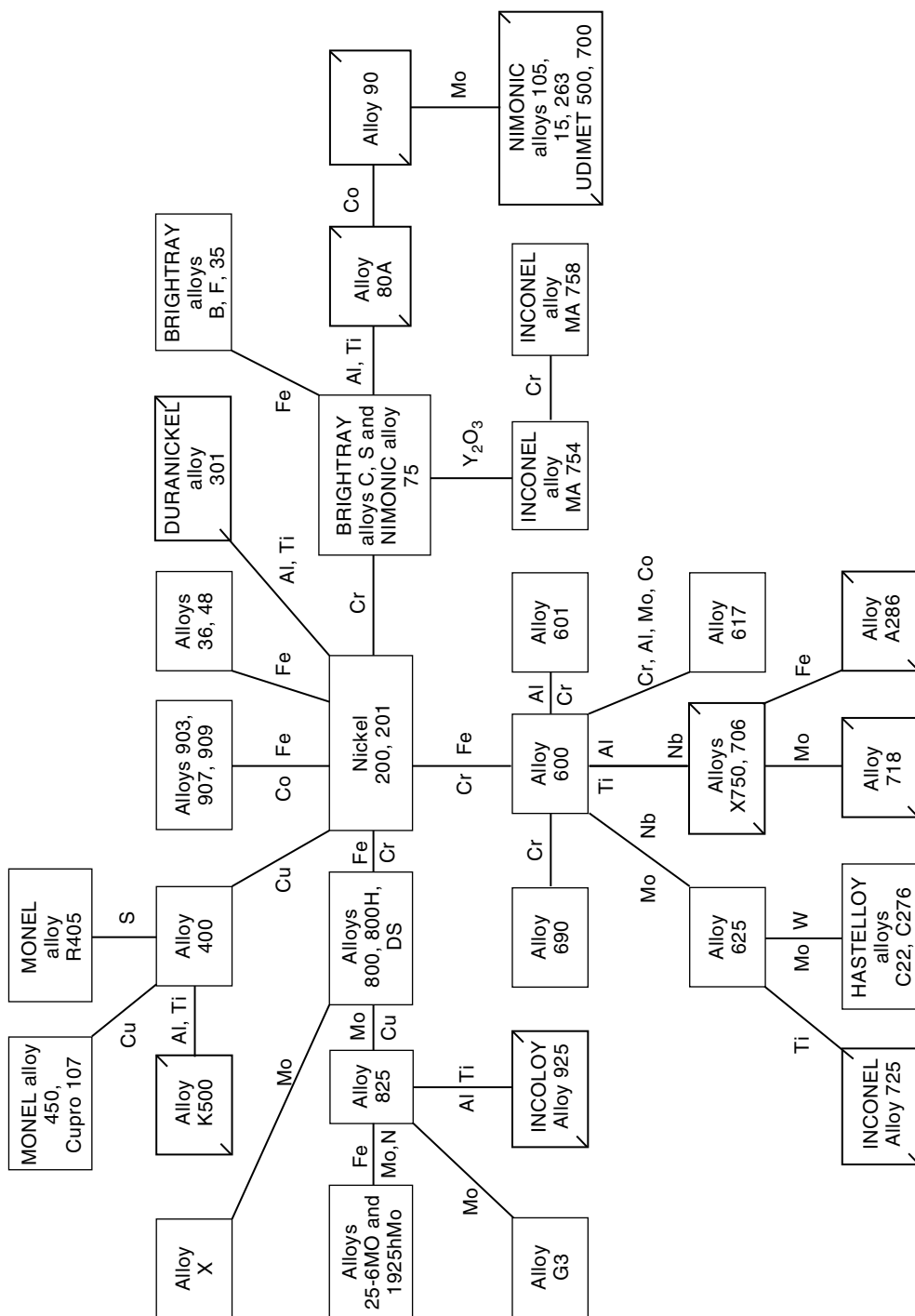


Table 1. World Nickel Mine Production, Reserves, and Reserve Base, $\times 10^3$ t^a

| Country | Mine production | | Reserves ⁵ | Reserve base ⁵ |
|-----------------------|-----------------|-------------------|-----------------------|---------------------------|
| | 2003 | 2004 ^b | | |
| United States | — | — | — | — |
| Australia | 210 | 210 | 22,000 | 27,000 |
| Botswana | 32.74 | 37 | 490 | 920 |
| Brazil | 45 | 45 | 4,500 | 8,300 |
| Canada | 162.776 | 180 | 4,800 | 15,000 |
| China | 60 | 62 | 1,100 | 7,600 |
| Colombia | 70.8 | 72.5 | 830 | 1,100 |
| Cuba | 74 | 75 | 5,600 | 23,000 |
| Dominican Republic | 45.4 | 47 | 720 | 1,000 |
| Greece | 21.4 | 22.1 | 490 | 900 |
| Indonesia | 143 | 144 | 3,200 | 13,000 |
| New Caledonia | 111.9 | 122 | 4,400 | 12,000 |
| Philippines | 21.2 | 20 | 940 | 5,200 |
| Russia | 315 | 315 | 6,600 | 9,200 |
| South Africa | 40.8 | 40.7 | 3,700 | 12,000 |
| Venezuela | 20.7 | 22 | 560 | 630 |
| Zimbabwe | 9.5 | 9.3 | 15 | 260 |
| Other countries | 14 | 14 | 1,300 | 5,100 |
| World total (rounded) | 1,400 | 1,400 | 62,000 | 140,000 |

^aRef. 1.^bEstimated.

Table 2. Physical Constants of Nickel^a

| Property | Value |
|--|--------------------------|
| atomic weight | 58.71 |
| crystal structure | fcc |
| lattice constant 25°C, nm | 0.35238 |
| melting point, °C | 1453 |
| boiling point (by extrapolation), °C | 2732 |
| density at 20°C, g/cm ³ | 8.908 |
| specific heat at 20°C, kJ/(kg·K) ^b | 0.44 |
| avg. coefficient of thermal expansion × 10 ⁻⁶ , °C ⁻¹ | |
| at 20–100°C | 13.3 |
| 20–300°C | 14.4 |
| 20–500°C | 15.2 |
| thermal conductivity, W/(n·K) | |
| at 100°C | 82.8 |
| 300°C | 63.6 |
| 500°C | 61.9 |
| electrical resistivity at 20°C, μΩ·cm | 6.97 |
| temperature coefficient of resistivity at 0–100°C, (μΩ·cm)/°C | 0.0071 |
| Curie temperature, °C | 353 |
| saturation magnetization, T ^c | 0.617 |
| residual magnetization, T ^c | 0.300 |
| coercive force, A/m ^d | 239 |
| initial permeability, mH/m ^e | 0.251 |
| max permeability, mH/m ^e | 2.51–3.77 |
| modulus of elasticity × 10 ³ , MPa ^f | |
| tension | 206.0 |
| shear | 73.6 |
| Poisson's ratio | 0.30 |
| reflectivity, % | |
| at 0.30 μm | 41 |
| 0.55 μm | 64 |
| 3.0 μm | 87 |
| total emissivity, μW/m ^{2g} | |
| at 20°C | 45 |
| 100°C | 600 |
| 500°C | 120 |
| 1000°C | 190 |
| thermal neutron cross section, neutron velocity of 2000 m/s, m ^{2h} | |
| absorption | 4.5 × 10 ⁻²⁸ |
| reaction cross section | 17.5 × 10 ⁻²⁸ |

^aRefs. 7–10.^bTo convert J to cal, divide by 4.184.^cTo convert T to G, multiply by 1.0 × 10⁴.^dTo convert, A/m to Oe, divide by 79.58.^eTo convert mH/m to G/Oe, multiply by 795.8.^fTo convert MPa to psi, multiply by 145.^hTo convert μW/m² to erg/(s·cm²), multiply by 10⁻³.^gTo convert m² to barn, divide by 1.0 × 10⁻²⁸.

Table 3. Commercial Forms of Nickel

| Type | Nickel content, wt% ^a | Uses |
|---------------------------|----------------------------------|------------------------------------|
| electrolytic (cathode) | >99.9 | alloy production, electroplating |
| electrolytic rounds | >99.9 | electroplating |
| carbonyl pellets | >99.7 | alloy production, electroplating |
| briquettes | 99.9 | alloy production |
| rondelles | 99.3 | alloy production |
| powder | 99.74 | sintered parts, battery electrodes |
| nickel oxide sinter | 76.0 | steel and ferrous alloy production |
| ferronickel ^b | 20–50 | steel and ferrous alloy production |
| nickel salts ^c | | electroplating, catalysts |
| nickel chloride | 24.70 | |
| nickel nitrate | 20.19 | |
| nickel sulfate | 20.90 | |

^aValues are approximate.^bDifferent grades of ferronickel are produced, and the nickel content denoted includes 1–2 wt% Co.^cNickel content is theoretical.

Table 4. **United States Economic Statistics**^{a,b}

| Statistics | 2000 | 2001 | 2002 | 2003 | 2004 ^{b,c} |
|--------------------------|----------------|----------------|----------------|----------------|---------------------|
| production, mine | | | | | |
| shipments of | 123,000 | 141,000 | 137,000 | 129,000 | 129,000 |
| purchased scrap | | | | | |
| imports: primary | 156,000 | 136,000 | 121,000 | 125,000 | 133,000 |
| secondary | 10,700 | 8,760 | 9,110 | 11,500 | 19,300 |
| exports: primary | 8,150 | 8,450 | 6,520 | 6,330 | 7,910 |
| secondary | 49,900 | 48,600 | 39,400 | 47,300 | 48,000 |
| consumption: reported, | 115,000 | 98,800 | 87,400 | 86,400 | 92,300 |
| primary | | | | | |
| reported, | 84,000 | 102,000 | 106,000 | 93,400 | 100,000 |
| secondary | | | | | |
| apparent, | 147,000 | 129,000 | 121,000 | 118,000 | 126,000 |
| primary | | | | | |
| <i>Total</i> | <i>231,000</i> | <i>230,000</i> | <i>227,000</i> | <i>211,000</i> | <i>226,000</i> |
| price, average annual, | | | | | |
| London Metal | | | | | |
| Exchange: | | | | | |
| cash, dollars per metric | 8,638 | 5,945 | 6,772 | 9,629 | 13,843 |
| ton | | | | | |
| cash, dollars per pound | 3.918 | 2.696 | 3.072 | 4.368 | 6.279 |
| stocks: consumer, year | 14,400 | 14,300 | 13,700 | 8,890 | 8,500 |
| end | | | | | |
| producer year end | 12,300 | 12,600 | 6,150 | 7,250 | 7,100 |
| employment, year end, | 1 | — | — | — | — |
| number, mine | | | | | |
| net import reliance as a | 56 | 46 | 46 | 48 | 49 |
| percentage of apparent | | | | | |
| consumption ^d | | | | | |

^aRef. 1.^bData in metric tons of nickel content unless otherwise noted.^cEstimated.^dDefined as imports–exports + adjustment for government and industry stock changes.

Table 5. **Nominal Chemical Composition of Nickel Alloys^a, wt %**

| Alloy | CAS Registry number | Ni | Fe | Cr | Mo | Mn | Si | C | Al | Ti | Other |
|-----------------------|---------------------|------|------|------|------|------|------|------|-----|-----|--|
| Nickel 200 | [12671-92-0] | 99.5 | 0.1 | | | 0.25 | 0.05 | 0.06 | | | 0.05 Cu |
| MONEL alloy 400 | [11105-19-4] | 65.5 | 1.5 | | | 1.0 | 0.25 | 0.15 | | | 31.5 Cu |
| MONEL alloy K-500 | [11105-28-5] | 65.0 | 1.0 | | | 0.5 | 0.15 | 0.15 | 3.0 | 0.5 | 29.5 Cu |
| NIMONIC alloy 75 | [11068-69-2] | 76.0 | 2.5 | 20.0 | | 0.5 | 0.5 | 0.1 | | 0.5 | |
| INCONEL alloy 600 | [12606-02-9] | 75.5 | 8.0 | 15.5 | | 0.5 | 0.2 | 0.08 | | | |
| INCONEL alloy 625 | [12682-01-8] | 62.0 | 2.5 | 22.0 | 9.0 | 0.2 | 0.2 | 0.05 | 0.2 | 0.2 | 3.5 Nb |
| INCOLOY alloy 800 | [11121-96-3] | 31.0 | 46.0 | 21.0 | | 0.8 | 0.5 | 0.05 | 0.4 | 0.4 | |
| HASTELLOY alloy B-2 | [61608-60-4] | 65.5 | 2.0 | 1.0 | 28.0 | 1.0 | 0.1 | 0.02 | | | 2.5 Co |
| HASTELLOY alloy C-22 | [98686-65-8] | 54.5 | 4.0 | 21.5 | 13.5 | 0.5 | 0.05 | 0.01 | | | 2.5 Co, 3.0 W, 0.3 V |
| HASTELLOY alloy C-276 | [12604-59-0] | 55.5 | 5.0 | 16.0 | 16.0 | 1.0 | 0.05 | 0.02 | | | 2.5 Co, 4.0 W |
| HASTELLOY alloy G-3 | [77644-65-6] | 40.5 | 19.5 | 22.0 | 7.0 | 1.0 | 1.0 | 0.01 | | | 5.0 Co, 0.5 (Cb + Ta), 1.5 W, 2.0 Cu |
| INCONEL alloy 718 | [12606-10-9] | 52.5 | 18.5 | 19.0 | 3.0 | 0.2 | 0.2 | 0.04 | 0.5 | 0.9 | 5.0 Nb |
| INCOLOY alloy 909 | [95569-75-8] | 38.0 | 42.0 | | | | 0.4 | 0.01 | 0.1 | 1.5 | 13.0 Co, 4.7 Nb |
| B-1900 | [12773-54-5] | 64.5 | | 8.0 | 6.0 | | | 0.1 | 6.0 | 1.0 | 10.0 Co, 4.0 Ta, 0.015 B, 0.1 Zr |
| MAR-M247 | [97265-31-1] | 59.5 | | 8.5 | 0.5 | | | 0.15 | 5.5 | 1.0 | 10.0 Co, 10.0 W, 0.015 B, 0.1 Zr, 1.5 Hf, 3 Ta |
| RENÉ 80 | [12612-07-6] | 60.0 | | 14.0 | 4.0 | | | 0.17 | 3.0 | 5.0 | 9.5 Co, 4.0 W, 0.015 B, 0.03 Zr |
| WASPALOY | [11068-93-2] | 58.0 | 19.5 | 19.5 | 4.5 | | | 0.08 | 1.3 | 3.0 | 13.5 Co, 0.006 B, 0.06 Zr |

Table. 5 (*Continued*)

| Alloy | CAS Registry number | Ni | Fe | Cr | Mo | Mn | Si | C | Al | Ti | Other |
|---------------------|---------------------|------|------|-----|----|-----|-----|------|-----|-----|-----------------------------------|
| UDIMET 500 | [11068-87-4] | 53.5 | 18.0 | 4.0 | | | | 0.08 | 2.9 | 2.9 | 18.5 Co, 0.006 B, 0.05 Zr |
| UDIMET 700 | [11068-91-0] | 53.0 | 15.0 | 5.0 | | | | 0.08 | 4.5 | 3.5 | 18.5 Co, 0.03 B |
| NIMONIC alloy 80A | [11068-71-6] | 76.0 | 19.5 | | | 0.2 | 0.2 | 0.05 | 1.5 | 2.5 | 0.003 B, 0.06 Zr |
| NIMONIC alloy 115 | [51204-21-8] | 59.0 | 14.5 | 3.5 | | | | 0.15 | 5.0 | 4.0 | 13.5 Co, 0.16 B, 0.04 Zr |
| INCONEL alloy MA754 | [62112-97-4] | 78.5 | 20.0 | | | | | 0.05 | 0.3 | 0.5 | 0.6 Y ₂ O ₃ |

^aMONEL, DURANICKEL, BRIGHTRAY, INCONEL, INCOLOY, and NIMONIC are trademarks of the Inco family of companies; HASTELLOY and C-22 are trademarks of Haynes International; ILLIUM is a trademark of Stainless Foundry and Engineering Co.; UDIMET is a trademark of Special Metals Corp.; MAR-M is a trademark of Martin Marietta Corp.; RENÉ is a trademark of General Electric Co.; and WASPALOY is a trademark of United Technologies Corp.

Table 6. Properties of Nickel Alloys^a

| Alloy | UNS number | Melting range, °C | Yield strength, ^b MPa ^c | | | | 100-h rupture strength, MPa ^c | | | |
|----------------------------------|------------|-------------------|---|------------------|-------|-------|--|------------------|------------------|-------|
| | | | 20°C | 538°C | 760°C | 982°C | 649°C | 812°C | 982°C | 982°C |
| Nickel 200 | N02200 | 1435–1446 | 103–931 | 139 ^d | | | | | | |
| MONEL alloy 400 | N04400 | 1299–1349 | 172–1173 | 179 ^d | | | | | | |
| MONEL alloy K-500 | N05500 | 1316–1349 | 241–1380 | 648 ^d | | | | | | |
| NIMONIC alloy 75 | N06075 | 1340–1380 | 275 | 210 | 172 | 70 | 255 | 39 | 10 | |
| INCONEL alloy 600 | N06600 | 1355–1415 | 285 | 220 | 180 | 41 | 160 | 55 | 19 | |
| INCONEL alloy 625 | N06625 | 1290–1350 | 490 | 415 | 415 | 140 | 440 | 125 | 32 | |
| INCOLOY alloy 800 | N08800 | 1355–1385 | 250 | 180 | 150 | | 240 | 63 | 21 | |
| HASTELLOY alloy B-2 ^e | N10665 | 1320–1350 | 412 | | | | | | | |
| HASTELLOY alloy C-22 | N06022 | 1357–1399 | 373–1391 | 234 | 214 | | | | | |
| HASTELLOY alloy C-276 | N10276 | 1323–1371 | 356 | 233 | | | | | | |
| HASTELLOY alloy G-3 | N06985 | 1260–1343 | 311 | 186 | 165 | 94 | | | | |
| INCONEL alloy 718 | N07718 | 1260–1335 | 1125 | 1020 | 800 | | 725 | | | |
| INCOLOY alloy 909 | N19909 | 1395–1430 | 975 | 850 | 440 | | 510 | | | |
| B-1900 ^f | | 1275–1300 | 825 | 870 | 808 | 415 | | 505 | 170 | |
| MAR-M247 | | 1221–1357 | 958 | 875 | 841 | 380 | | 572 | 193 | |
| RENE 80 | | | | | | | | 350 ^g | 165 | |
| WASPALOY | N07001 | 1330–1355 | 795 | 725 | 675 | 140 | 760 | 275 | 45 | |
| UDIMET 500 | N07500 | 1300–1395 | 840 | 795 | 730 | 230 | 930 | 305 | 83 | |
| UDIMET 700 | | 1205–1400 | 965 | 895 | 830 | 305 | 828 | 400 | 110 | |
| NIMONIC alloy 80A | N07080 | 1360–1390 | 620 | 530 | 505 | 62 | 595 | 195 | 14 | |
| NIMONIC alloy 115 | | 1260–1315 | 865 | 795 | 800 | 240 | | 400 | 110 | |
| INCONEL alloy MA754 | N07754 | 1320–1390 | 662 | 504 | 262 | 166 | | | 131 ^h | |

^aRefs. 4,5,7–9,12–33.^bWhere two numbers appear, the first refers to the annealed or solution heat-treated condition, the second to the condition when maximum strength is achieved by cold-working or aging. Otherwise the number refers to the alloy heat-treated for optimum strength.^cTo convert MPa to psi, multiply by 145.^dValue is at 316°C.^e3.18-mm sheet.^fAs cast.^gValue is at 871°C.^hValue is at 1093°C.