NBS MONOGRAPH 106

Nickel and Its Alloys

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

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UNITED STATES DEPARTMENT OF COMMERCE • C. R. Smith, *Secretary*

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Nickel and Its Alloys

Samuel J. Rosenberg

Institute for Materials Research
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Foreword

Publications by the National Bureau of Standards include a series of Monographs (previously designated as Circulars), each of which represents a compilation and critical review of available information on a particular subject. Metallurgical Circulars, each dealing with a particular metal and its alloys, have been prominent in this series.

Circular 100, entitled "Nickel and its Alloys," authored by P. D. Merica, was published in 1921 when expansion and growth of the nickel industry were becoming noticeable. A second edition (revised by E. C. Groesbeck) was issued in 1924. At the close of World War II the subject was again reviewed and Circular 485, written by M. R. Meyerson, was published in 1950. However, much information about the strategic element, nickel, had been developed during World War II but was not yet available for publication in Circular 485. The phenomenal expansion of the North American nickel industry since 1950, the release of some of the previously restricted information, the development of new theories of alloying and heat treatment, and the development of new alloys to meet industrial requirements of ever-increasing severity made it desirable again to revise the Nickel Circular. That revision, Circular 592, was written by J. G. Thompson and published in 1958.

During the relatively few years since the publication of the last nickel circular, development of nickel alloys and steels has continued so that considerable information needed to be incorporated in a revised edition, and much old data needed to be updated. This task was assigned to S. J. Rosenberg, formerly Chief of the Engineering Metallurgy Section, Metallurgy Division, Institute for Materials Research, of the National Bureau of Standards.

The current revision, like the previous one, was sponsored by The International Nickel Company, Incorporated, and was written at the National Bureau of Standards under the Bureau's Research Associate plan. This revision represents a review of the literature through 1965 and includes some 1966 references.

A. V. ASTIN, *Director*

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WASPALLOY	Pratt and Whitney Aircraft
WELCON	Japanese Steel Works, Ltd.
WEL-TEN	Yawata Iron & Steel Company, Ltd.
YOLOY	Youngstown Sheet & Tube Company

Contents

Nickel and Its Alloys

Samuel J. Rosenberg*

This monograph reviews available information on the production, properties, and uses of high-purity and commercial forms of nickel, and on the properties and applications of its important alloys, both ferrous and nonferrous. It is a revision of National Bureau of Standards Circular 592, issued in 1958.

Key Words: Alloys, corrosion-resisting alloys, copper-nickel alloys, electroplating, electrical resistance alloys, heat resisting alloys, magnetic alloys, maraging steels, nickel, stainless steels, steels.

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* Research Associate from The International Nickel Company, Inc., at the National Bureau of Standards, Washington, D.C. 20234, 1965–1967.

1. Introduction

1.1. History

Alloys of nickel had been known and used for thousands of years before its identification as a metallic element was established. There is reliable evidence that prehistoric man made use of iron-nickel alloys of meteoric origin [1].[1] The earliest authenticated artifact from such a source is what is believed to be a portion of a dagger found at Ur of the Chaldees (c. 3100 B.C.); analysis has shown it to contain 10.9 percent Ni [2].

The first manmade alloy containing nickel, believed to date back to 3500–3100 B.C., is a bronze reamer containing 2.73 percent nickel found in the plain of Antioch in Syria [3]. The earliest copper-nickel alloy objects which are known to have survived to the present day are coins minted in Bactria, an ancient kingdom situated north of present-day Afghanistan [4]. Coins (c. 200–190 B.C.) issued during the reign of the Greek sub-king Euthydemus II analyzed 20.038 percent nickel and 77.585 percent copper [5]. It is interesting to note that this composition is very near that of the 75/25 Cu/Ni alloy used for minting the U. S. five-cent coin.

Nickel was first identified as an element by Cronstedt in 1751 [6], although he did not name it until 1754 [7]. Its identity was confirmed by Bergman in 1755 [8]. According to Fourcroy [9], the nickel prepared by Bergman was much purer than Cronstedt's. Richter [10] apparently was the first to obtain pure nickel. His description of its characteristics is interesting:

"Its color is half-way between that of silver and pure tin.

"It is not affected by air or atmospheric water, that is, it does not rust.

"It is perfectly ductile; rods can be made from nickel when it has been heated and one can beat them into very thin plates when cold. Because of this property, nickel cannot be considered a semi-metal and takes its place amongst '*perfect*' metals.

"Its specific weight or density is 8.279 for molten nickel and 8.666 for wrought nickel.

"Its strength is considerable.

"It has a high melting point and so is extremely difficult to melt, at least as difficult as manganese.

"The metal oxidized very little on being heated until red, when it becomes a little duller than platinum, gold or silver. Thus nickel is not only a *perfect* metal but also a *noble* one.

"The action of magnets on nickel is very great, only slightly less than their action on iron."

The earliest recorded use of nickel in modern times (i.e., the last few hundred years) was in "white copper" or "*pai-thung,*"[2] first mentioned in 1597 [11]. von Engestrom [12] gave its analysis as 40.60 percent copper, 18.75 percent nickel, and 31.25 percent zinc. A basin and ewer made in China of "white copper" was analyzed by Fyfe [13] as containing 40.4 percent copper, 31.6 percent nickel, 25.4 percent

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Variations of this term are *petong, pehtong, paaktong, packtong, pak-fong,* and *packfong.*

zinc, and 2.6 percent iron. These utensils were so attractive that Thomason [14] began the manufacture of an alloy based on the above composition; his alloy was mixed in the following proportions: 40 percent copper, 31 percent nickel, 26 percent zinc, and 3 percent iron.

Although many attempts were made to incorporate nickel in cast iron, wrought iron, and steel, it remained for Riley [15] to be the first to describe the improved mechanical properties of nickel steel in 1889. These nickel steels found their first extensive use in ordnance material in the 1890's and the role of nickel as an alloying element in steel to develop strength and toughness became firmly established. An historical review of nickel steels was written by Yeo and Miller [15a]. The twentieth century witnessed the development and tremendous growth of a large variety of corrosion- and heat-resistant alloys, including stainless steels and superalloys, as well as numerous nonferrous alloys. There are many uses where the importance cannot be evaluated in terms of tonnage involved, for example, in magnetic alloys, in alloys with controlled rates of thermal expansion, and in alloys for monitoring neutron doseage.

1.2. Occurrence, Minerals, Ores

In his classic work, Clarke [16] estimated the average nickel content of the earth's crust to a depth of 10 miles as 0.019 percent. A reestimate by Wells [17] changed this figure slightly, to 0.016 percent, which indicates an abundance greater than the total of copper, zinc, and lead. Sandell and Goldich [18] estimated that nickel constitutes 0.008 percent of the uppermost crust of the earth. Fraser [19] stated that nickel is the 23d element in the order of abundance in the lithosphere and that the average nickel content of all igneous rock is about 0.009 percent. Queneau and Roorda [20] note that nickel ranks 24th in the earth's crust in the order of abundance of the elements. They report that geochemists estimate that the earth's crust averages about 0.01 percent of nickel.

Although nickel is widely distributed over the face of the earth, the igneous rocks in which it occurs are not readily susceptible to concentration of the contained minerals by weathering. Hence there are workable deposits of nickel minerals in relatively few localities, and even in these the concentration of nickel is so low that economic exploitation usually depends upon the recovery of valuable by-products.

The presence of nickel has been identified in the spectrum of the sun [21] and many of the stars, in deep sea silt [22,23], and it has long been known that nickel is an important constituent of metallic meteorites. It is interesting, as a future possibility, to consider that the nickel content of sea water, reported by Ishibashi [24] to be 0.7 to 0.8 microgram per liter, can be expressed as 3 tons of nickel contained in each cubic mile of sea water.

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

In the sulfide ores, nickel occurs chiefly as the mineral pentlandite, $(FeNi)_9S_8$, in association with large amounts of pyrrhotite, $Fe_{n-1}S_n$, commonly 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, gold and silver. Their chemical composition falls in the general range 0.4-3 percent Ni, 0.2-3 percent Cu, 10-35 percent Fe, 5-25 percent S, with the balance being substantially SiO_2, Al_2O_3, MgO, and CaO. The nickel content of pentlandite is normally close to 34 percent, although it has been found to range up to 36 percent, and its cobalt content varies between about 1 percent and 5 percent of the contained nickel. Pyrrhotite, about 57 percent iron, accounts for most of the ore's iron content. This mineral often contains a small portion of nickel, partly as a very fine dispersion of pentlandite, partly as a solid solution, with a combined minimum nickel content varying around 1 percent of the contained iron. Chalcopyrite is usually the only important copper mineral, although cubanite, $CuFe_2S_3$, may also occur.

The chief minerals of nickel are given in table 1. Some other nickel minerals are polydymite, Ni_3S_4; ullmanite, NiSbS; parkerite, $Ni_3Bi_2S_2$; and trevorite, $NiO \cdot Fe_2O_3$.

TABLE 1. *Nickel Minerals*

	Ideal formula	% Ni	Color	Crystal system
Sulfides:				
Pentlandite	$(Fe,Ni)_9S_8$	34.22	Bronze-Yellow	Isometric
Millerite	NiS	64.67	Brass-Yellow	Hexagonal
Heazlewoodite	Ni_3S_2	73.30	Bronze-Yellow	Isometric (?)
Polydymite	Ni_3S_4	57.86	Steel-Gray	Isometric
Violarite	$(Ni,Fe)_3S_4$	38.94	Violet-Gray	Isometric
Siegenite	$(Co,Ni)_3S_4$	28.89	Steel-Gray	Isometric
Arsenides:				
Niccolite	NiAs	43.92	Copper-Red	Hexagonal
Maucherite	$Ni_{11}As_8$	51.85	Platinum-Gray	Tetragonal
Rammelsbergite	$NiAs_2$	28.15	Tin-White	Orthorhombic (?)
Gersdorffite	NiAsS	35.42	Steel-Gray	Isometric
Arsenate:				
Annabergite	$Ni_3As_2O_8 \cdot 8H_2O$	29.40	Apple-Green	Monoclinic
Silicate and Oxide:				
Garnierite	$(Ni,Mg)_6Si_4O_{10}(OH)_8$	Variable up to 47%	Green-Gray	Amorphous
Nickeliferous limonite	$(Ni,Fe)_2O_3 \cdot nH_2O$	Low but variable		

Nickel is found also in a number of less common secondary silicate minerals and it is known to substitute for magnesium in certain primary minerals (olivene, hypersthene, hornblende, biotite). Native nickel approaching purity is unknown. Small quantities of nickel combined with iron have been found in meteorites.

In addition to the famous sulfide nickel ores of northern Ontario, important tonnages of similar ore are now being mined at Thompson and Lynn Lake in northern Manitoba. Russia produces nickel from sulfide deposits in the Pechenga (formerly Finnish Petsamo) and Monchegorsk areas near Murmansk and at Norilsk, near the mouth of the Yenisey in Siberia.

Oxide ores, commonly called laterites, are residual concentrates of chemical action by weathering in place of basic igneous rocks high in magnesium and iron and with a small amount of nickel, e.g., 0.2 percent in peridotite, mainly associated with magnesium-rich minerals such as serpentine, olivine, and pyroxene. Nickel can substitute for magnesium in the crystal lattices of these minerals because its atomic radius (0.69 Å) is about equal to that of magnesium (0.66 Å). Depending upon the extent of weathering, two main 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 $(Ni,Mg)_6Si_4O_{10}(OH)_8$ is the most common, and limonitic-type ore, predominately the hydrated mineral goethite, $Fe_2O_3 \cdot H_2O$, in which nickel is dispersed, and iron oxide such as hematite Fe_2O_3. The chemical composition of oxide ores varies widely and, in addition to 1-3 percent nickel, they contain significant amounts of cobalt and chromium. Silicate-type ore in New Caledonia analyzes about 2-3 percent Ni, 0.1 percent Co, 2 percent Cr_2O_3, and 20-25 percent MgO. Cuban ore, primarily of the limonitic type, analyzes in the range of about 1.2-1.4 percent Ni, 0.1-0.2 percent Co, 3 percent Cr_2O_3, and 35-50 percent Fe.

Oxide ores are widely distributed, but occur mainly in the tropical areas of the world and form the largest nickel reserves. Nickel is produced in important quantities from oxide deposits in Cuba, New Caledonia, the USSR, and the United States. Extensive deposits are known in Indonesia, the Philippines, and Central and South America.

The nickel arsenides are of minor importance today as sources of nickel, but are of historical interest. Niccolite (NiAs) is still the principal nickel-arsenide mineral. Others that have received attention at one time or another include bravoite (arsenide of nickel and iron), chloanthite and smaltite (arsenides of nickel and cobalt), gersdorffite (nickel-iron-cobalt sulfarsenide), annabergite (hydrous nickel arsenate), and breithauptite (antmonide of nickel).

Additional information on the mineralogy and geology of nickel is presented by Coleman [25], Lindgren [26], Mellor [27], Dana [28], Hall [29], in a report by the U. S. Bureau of Mines [30], and by Boldt and Queneau [36].

Table 2 gives estimates of known deposits of nickel ore, as quoted by Queneau and Roorda [20], and figure 1 illustrates the geographical distribution of the principal nickel deposits of the world. The Canadian ores of the Sudbury District in Ontario have been the dominant factor in the nickel industry for many years. These ores consist mainly of lenses of mixed pentlandite, pyrrhotite, and chalcopyrite. There is considerable variation from mine to mine, but the average content of the ore is about 1.5 percent each of both nickel and copper. These deposits were discovered in 1884 as a result of excavations made during the building of the Canadian Pacific Railroad [29,29a,31] and subsequent prospecting in the vicinity. Originally the ores were valued primarily for their copper content, and copper today is second only to nickel in importance of products recovered from these ores. Valuable by-products include the platinum metals, cobalt, gold, silver, selenium, tellurium, sulfuric acid, liquid sulfur dioxide, and high-grade iron ore, in the form of sintered pellets.

TABLE 2. *Nickel ore bodies and estimated reserves* [a]

Occurrence	Type	Ore Reserve, Tons	Grade % Ni	Tons Contained Nickel [c]
Canada:				
Int. Nickel Co	Sulfide	325,000,000	1.5	4,875,000
Falconbridge	Sulfide	56,000,000	1.4	785,000
Sherritt Gordon	Sulfide	11,400,000	0.8	90,000
Finland	Sulfide	3,000,000	0.6	20,000
Cuba	Oxide	3,000,000,000	0.8	24,000,000
New Caledonia	Oxide	1,400,000,000	1–5	20,000,000
Indonesia	Oxide	850,000,000	0.5–2	10,000,000
Philippines	Oxide	550,000,000	0.8	4,000,000
Venezuela	Oxide	40,000,000	1.7	700,000
Brazil	Oxide	20,000,000	1–3.5	500,000
Japan	Oxide	30,000,000	0.5	150,000
Greece	Oxide	10,000,000	0.5–1	75,000
Malagasy	Oxide	900,000	5	50,000
USA	Sulfide, Oxide	54,000,000	0.3–1.5	400,000
USSR	Sulfide, Oxide	300,000,000	0.3–1.5	3,000,000
Others [b]	Sulfide, Oxide	1,000,000,000	0.5–2	10,000,000

[a] Estimate from recent publications.

[b] Important tonnages of nickel ore occur in other countries such as in the Dominican Republic, Guatemala, Solomon Islands, Australia, etc.

[c] Figures rounded off.

Sulfide ore similar to the ore of the Sudbury district was found in the Lynn Lake area in northern Manitoba in 1941 [32,33], and was brought into production by Sherritt Gordon Mines, Ltd. in 1953. Deposits of nickel ore have been reported in New Brunswick, Quebec, British Columbia, Northwest Territories, Yukon Territories, and Saskatchewan.

The nickel silicate ores of New Caledonia were discovered by Garnier in 1865, and were the principal source of the world's supply of nickel from 1875 to 1903. The nickel minerals are usually associated in the ore with considerable iron, which is present as hydrated oxide or

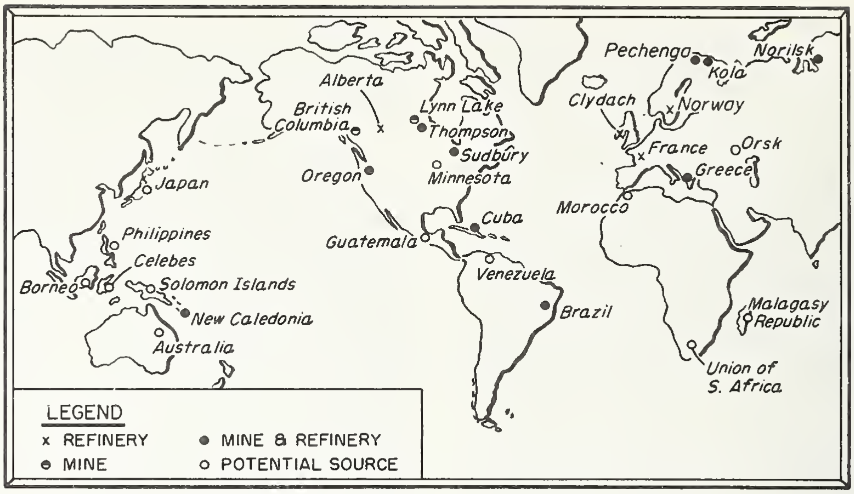


FIGURE 1. *Principal sources of nickel ore in 1965.*

silicate. The ores originally exploited were variable in composition but appreciably richer in nickel than the Canadian ores. Subsequently, attention was paid to ores that were not so rich, and Hall [29] reported that the New Caledonia ores ran 4 to 6 percent of nickel.

The nickel-bearing iron ores of Cuba, in the districts of Mayari, Moa Bay, and San Felipe, are an important group of ores. According to Moldenke [34], the dried Mayari ore contained 49 percent Fe, 11 percent Al_2O_3, 3 percent Si, 1 percent Ni, and 1.5 percent Cr. Williams [35] noted that there are two types of ores in the Nicaro deposits; surface occurrences of limonite containing about 1.25 percent of nickel and 45 percent of iron, underlain by altered serpentine that contains up to 1.6 percent of nickel and down to 12 percent of iron. In contrast to the Nicaro ores, most of the nickel in the Moa Bay ores is in limonite.

In the United States, the silicate and nickel-bearing ores near Riddle, Douglas County, Oregon, are the source of the only appreciable production of nickel. Other locations of nickel ores in the United States are near Fredericktown, Missouri, the Lancaster Gap area in Pennsylvania, in Lake County, Minnesota, in Grant County, New Mexico, and in Alaska.

Minor production comes from the sulfide ores of Africa and the oxide or silicate ores of Greece and the Central Celebes. The sulfide and arsenide ores of southern Norway were the most important nickel ores until competition developed from New Caledonia. An important European source of nickel, according to Boldt and Queneau [36], is in Greece, particularly the magnesium-silicate ores, with the chromium-nickel iron ore (similar to the Mayari ore of Cuba) of less importance. There are sulfide ores in the Transvaal area of the Union of South Africa, and cobalt ores in Morocco.

Other ore bodies are known to exist in Borneo, Solomon Islands, the Philippines, Australia, Malagasy, Brazil, Venezuela and Guatemala.

1.3. Recovery of Nickel from Its Ores

In sulfide-type nickel ores, the sulfides of nickel, copper, and iron occur as distinct minerals, and beneficiation methods such as flotation and magnetic separation generally can be employed after the ore has been crushed and ground sufficiently fine to liberate the sulfide particles from the worthless gangue. With oxide ores, however, the fine chemical dissemination of the nickel content precludes the application of such beneficiation procedures, and except for minor screening or sorting out of barren lumps, the entire ore must be treated by either pyro-, hydro-, or vapo-metallurgical procedures, or by a combination of them.

Electrolytic refining is the final purification step for over half of the world's nickel production. The electrorefining process not only yields nickel of high purity, but facilitates the recovery of elements associated with nickel in the ores, such as the precious metals and cobalt. A variety of beneficiation and extractive metallurgical procedures are employed to prepare crude metal or sulfide anodes for electrorefining.

Some higher-grade sulfide ores may be smelted directly, but usually flotation or magnetic concentrates are produced in the initial beneficiation step. To keep slag losses to a minimum, subsequent smelting operations are conducted in three phases; roasting, smelting, and converting, respectively, which progressively increase the valuable metal content. The concentrates are first roasted in multi-hearth furnaces, sintering machines, or fluidized-bed reactors, to oxidize part of the iron and sulfur constituents. In the ensuing smelting operation, for which blast, reverberatory, or electric furnaces are employed, the iron oxide combines with siliceous flux to form a molten slag which is skimmed off and discarded, while the more valuable metals are collected by the sulfur into a molten 'furnace' matte, which usually contains about 15 to 20 percent nickel-copper, 50 percent iron, and 25 percent sulfur.

The furnace matte is further up-graded by a converting (or Bessemerizing) process, in which molten matte is charged to Pierce-Smith horizontal type converters and air or oxygen-enriched air is blown through it to selectively oxidize the iron and a part of the remaining sulfur. Slag formed in the converters is returned to the primary furnaces to be cleaned of its metal content. The Bessemer matte produced contains about 47 percent nickel, 30 percent copper, and 22 percent sulfur. Several methods are employed by the various nickel companies to separate nickel and copper in the Bessemer matte and produce refined nickel.

At The International Nickel smelter at Copper Cliff, converting is continued until the matte is slightly deficient in sulfur to form sulfides with all the nickel and copper that are present. The molten converter matte is then cast into insulated moulds and cooled slowly over a period of several days, during which time it solidifies and forms discrete grains of copper sulfide, nickel sulfide, and a small amount of a nickel-copper metallic phase. These constituents can be separated by standard beneficiation procedures of crushing, grinding, magnetic separation, and flotation. The metallic phase serves to collect the major portion of the precious metals and, being magnetic, is readily removed for separate treatment. Part of the nickel sulfide flotation concentrate from the matte separation process is roasted in fluidized beds to make nickel oxide sinter containing 75 percent or 90 percent nickel, for direct use by the steel industry. Part is melted and cast into nickel sulfide anodes for direct electrorefining. The major portion is fluid-bed roasted to oxide, a part of it is sent to Clydach, Wales, for refining by the carbonyl process, and the remainder is reduction smelted to crude metal and cast into metal anodes for electrorefining.

At Thompson, Manitoba, where smelter feed contains much less copper, the converter (Bessemer) matte containing about 76 percent nickel, 20 percent sulfur, and small amounts of copper, cobalt, and iron, is cast directly into nickel sulfide anodes which are then electrorefined in the same manner as crude metal anodes. In Falconbridge practice, the converter matte is roasted to oxide, copper is removed from the calcine by acid leaching, and the leached calcine is smelted to nickel anode metal.

Electrorefining is conducted in divided cells, which are separated by porous diaphragms into anode and cathode compartments, respectively. Impure anolyte obtained from dissolution of the crude metal or sulfide anodes is constantly removed from the cells, pumped to a purification section where impurities are removed by chemical treatment, and returned as purified electrolyte to the cathode compartments. Flow through the porous diaphragm from the cathode compartment to the anode compartment is sufficiently restricted to maintain a small hydrostatic head in the former. The constant outflow prevents impurities from reaching the cathodes, where nickel of 99.9+ percent purity is deposited. Pure nickel starting sheets become finished cathodes in about ten days. The purity of nickel from sulfide anodes is similar to that obtained from metal anodes. Sulfur, selenium, tellurium, and the precious metals do not dissolve anodically and may be recovered from the anode sludge. When sulfide anodes are used, this sludge contains about 95 percent sulfur.

As previously mentioned, nickel is also refined at Clydach, Wales, by the carbonyl process discovered by Langer and Mond in 1899. The nickel oxide from Copper Cliff is reduced to crude metal, which is then reacted with carbon monoxide to form gaseous nickel carbonyl. Upon heating, the carbon gas decomposes into its constituents, carbon monoxide and pure nickel, and the latter deposits upon seed nickel pellets in a decomposer. The carbonyl process produces a very high purity nickel in which cobalt is essentially absent.

Nickel is also produced commercially by gaseous reduction of nickel leach solutions derived from both sulfide and oxide ores. While preparatory treatments and leaching procedures vary, nickel is precipitated from a purified aqueous solution by reduction with hydrogen at elevated pressure and temperature.

As practiced by Sherritt Gordon, pentlandite concentrates analyzing about 10 percent nickel, 2 percent copper, 0.5 percent cobalt, 38 percent iron, and 31 percent sulfur are dissolved under elevated temperature and pressure in an aerated ammoniacal solution. The base metals are converted to soluble amines, while the iron remains in the residue as a hydrated ferric oxide. The leach solution is then boiled to recover part of the ammonia and precipitate the copper as sulfide, unsaturated sulfur compounds are destroyed by oxidation and hydrolysis, and the solution is reacted with hydrogen at 30 atm and 200 °C to precipitate nickel powder which analyzes about 99.9 percent nickel. Some of the powder is briquetted and sintered for market.

The Freeport Nickel Company developed a pressure acid leaching process to recover nickel and cobalt from the limonitic type oxide ores of Cuba. The ore is leached with sulfuric acid at elevated temperatures and pressures selected to enhance preferential solution of nickel and cobalt, while leaving most of the iron undissolved. After separation from the residue, the leach solution is treated with hydrogen sulfide to precipitate nickel and cobalt as sulfides. The sulfide slurry is shipped from Cuba to Louisiana, where it is redissolved in acid solution, impurities are removed, and the nickel precipitated as a 99.8 percent nickel powder by reduction with hydrogen at high pressure. The powder is then briqueted for market.

Nickeliferous oxide ores of the silicate type are smelted to ferronickel in several countries, notably in New Caledonia, Japan, Greece, Brazil, and at Hanna Nickel Smelting Company in Oregon. Blast furnaces, rotary kilns, and electric furnaces are used by various producers, with carbonaceous material or ferrosilicon as the reducing agent. Crude ferronickel is refined generally in two stages (oxidizing and reducing), the oxidizing stage removing carbon, silicon, chromium, and phosphorus, and the reducing stage any residual sulfur.

The distribution of nickel ore deposits in the world and their geological background, mining methods for their recovery, and the various beneficiation, pyrometallurgical, hydrometallurgical, and vapometallurgical methods that are presently in use throughout the world for extraction of nickel and associated metals, are described in considerable detail in a recent book by Boldt and Queneau [36], which was produced under the sponsorship of The International Nickel Company.

1.4. Statistics of Production and Consumption

World production of nickel was less than 100 tons per year in 1850 and it did not reach 1000 tons per year until the 1880's. Production began to become commercially important during the 1890's. As shown in figure 2, the production of nickel has increased at a phenomenal rate during the last decade.

In the early years of the century, New Caledonia was the principal source of supply of nickel. Canadian output became greater than that of New Caledonia in 1903. Today approximately 57 percent of the world's production of nickel comes from Canada [42]. The estimated world production capacity for nickel in 1965 is given in table 3. Expansion of productive capacity is in progress by several major nickel producers.

TABLE 3. *Estimated world nickel production capacity* [*20a*]

Country	Million pounds	Type of ore
Canada	538	Sulfide
Soviet Union	190	Sulfide and oxide
Cuba	38	Oxide
France (New Caledonia)	114	Oxide
United States	28	Oxide
Others (South Africa, Finland, Brazil, etc.)	36	Sulfide and oxide
Total	944	

The price of nickel [4] varied from about \$1.70 per pound in 1840 to about \$3.10 per pound in 1845-1846. From then it dropped to about \$1.10 per pound in 1862, then increased to about \$2.30 per pound in 1864, dropped to less than \$1.30 per pound in 1870, and then increased markedly to over \$3.80 per pound, an all-time high. The price of nickel since 1890 is plotted in figure 2. The price as of Nov. 1, 1966 was 85.25¢/lb; this was increased to 94¢/lb on Sept. 15, 1967.

As shown in figure 3, the consumption of nickel in the United States has increased at a steady rate since the end of World War II. Of this total, the stainless steels now consume the largest amounts of nickel. The approximately 350 million pounds of nickel consumed in the United States in 1965 were used as follows [42]:

Stainless steels	30.0%
Other steels	15.7
Cast irons	4.0
Nonferrous	21.6
High temperature and electrical resistance alloys	10.7
Electroplating	11.3
All other uses	6.7

Under this last heading are such uses as catalysts, ceramics, chemicals (other than electroplating), iron-nickel alloys, magnets, metal powder products, welding rods, etc.

1.5. Available Forms of Nickel

The primary forms of nickel that are available to meet the various demands of industry are indicated in table 4. A listing of alloys and forms is given in the Handbook of Huntington Alloys [43] and in a booklet issued by The International Nickel Company, Ltd.[44].

Nickel is marketed in various forms, as follows: (1) nickel pellets, produced by decomposition of nickel carbonyl; (2) electrolytic cathode sheets cut into various sizes; (3) shot, obtained by remelting electrolytic nickel and then casting it into pig molds or pouring it into water without deoxidation; (4) malleable nickel, produced by pouring into ingot molds after deoxidation; (5) nickel rondelles, reduced from the oxide without fusion; (6) nickel salts; (7) nickel oxide; (8) ferronickel; (9) nickel powder; and (10) special alloys for addition to cast irons.

Electrolytic nickel and pellets constitute the most widely used forms of primary metallic nickel. Nickel oxide sinter and ferronickel (of varying Ni content) are also widely used in the steel and foundry industries as alternate forms of primary nickel. These are used in approximately equivalent proportions. Electrolytic nickel, including SD nickel, has gained rapid

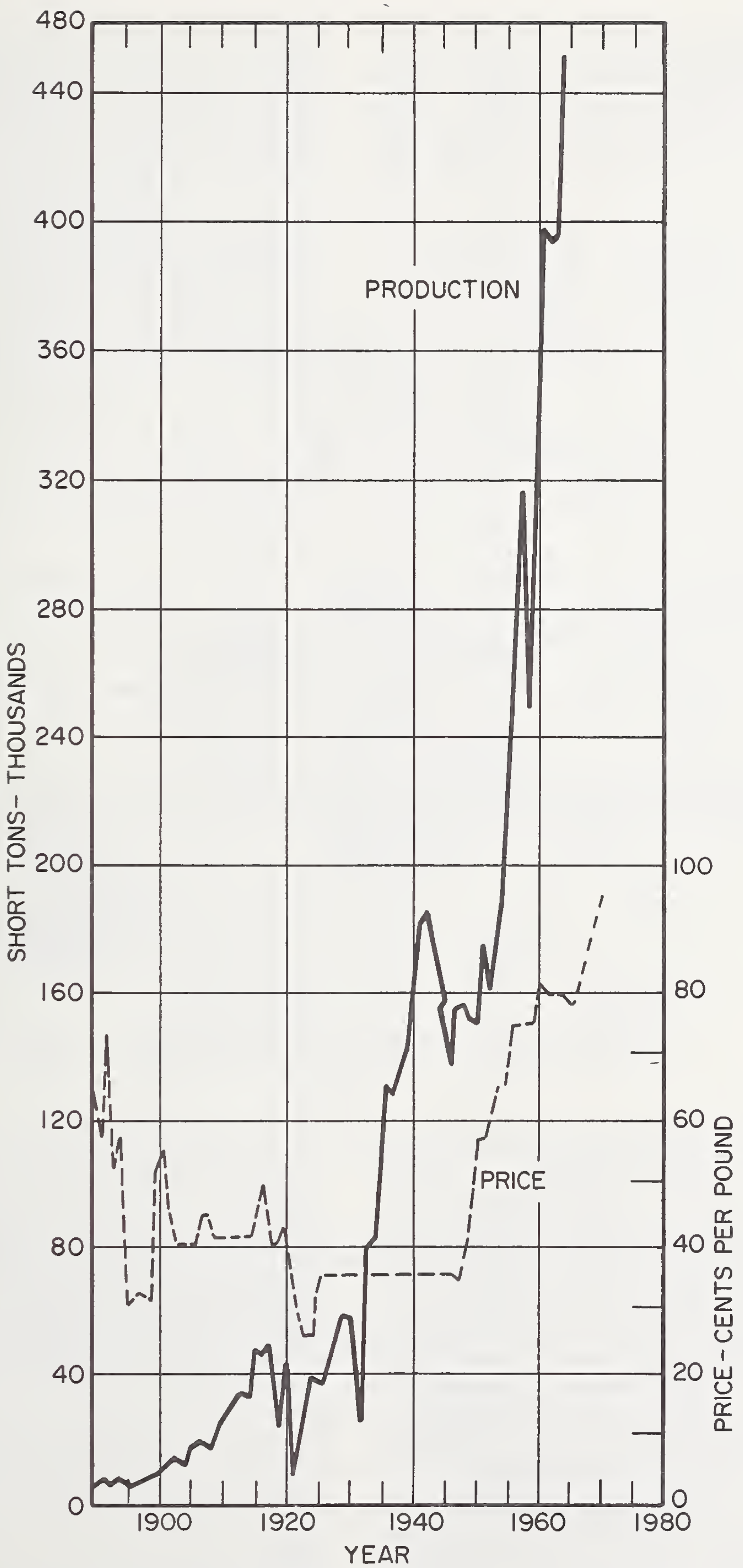


FIGURE 2. *World production and price of nickel* [4,37,38,39,40,41].

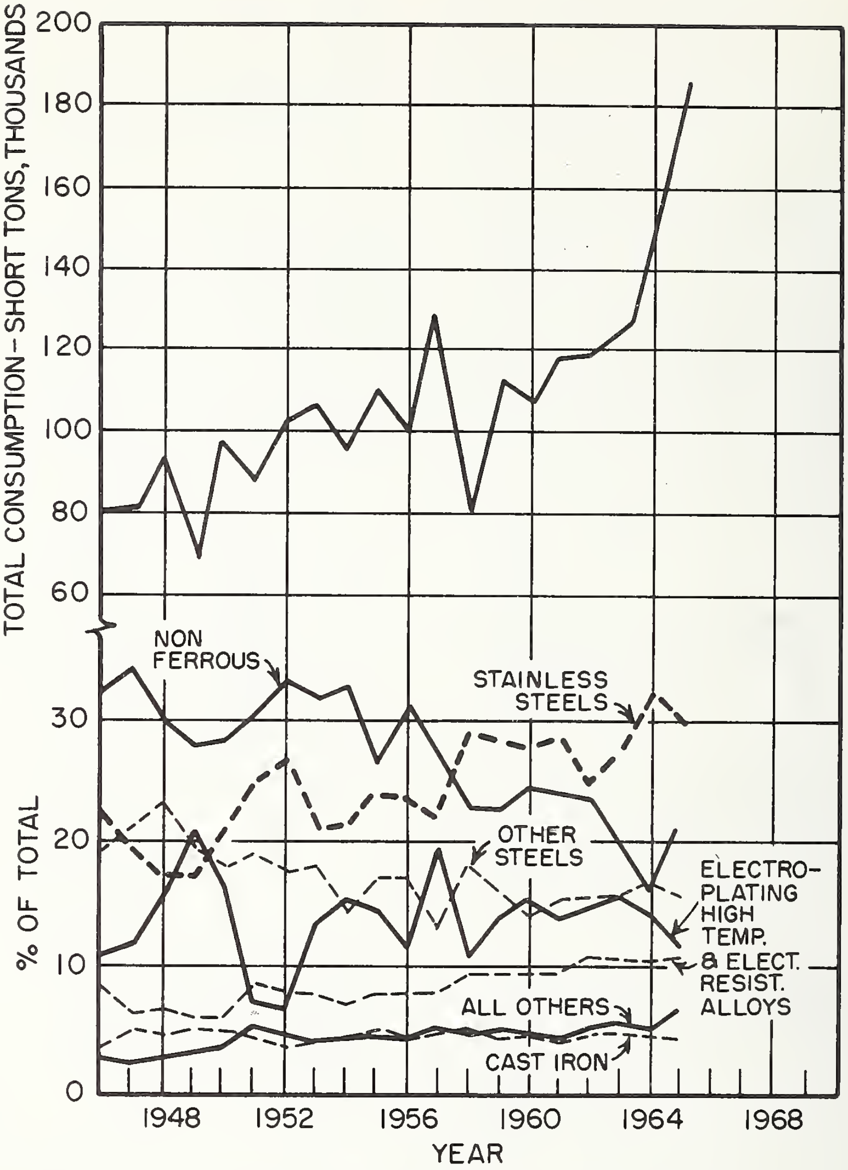


FIGURE 3. *Consumption of nickel in the United States* [*37,38,39,40,41*].

and widespread usage as anode material in electroplating when contained in titanium baskets. Rolled bars and, to a lesser extent, cast anodes, are also used as anode materials in electroplating. Briquetes (as produced from compacted CP powder), XX shot, and rondelles are also utilized to a smaller degree as metallic forms of primary nickel. F shot, nickel-magnesium alloy, and nickel-magnesium-silicon alloy are used for additions to cast iron and for the production of ductile iron. Carbonyl powders find usage in sintered porous plates for batteries and in powder metallurgy parts.

Carbonyl nickel is especially low in cobalt content. The principal impurities are varying amounts of carbon and oxygen from the decomposition of the carbonyl radical.

Electrolytic nickel supplies about one-half of the industrial demand for the metal. The commercial electrolytic refining processes permit the recovery of valuable by-products, such as the platinum metals, and reduce or eliminate most of the impurities. The residual cobalt, less than 0.05 percent, is traditionally counted as nickel because of the chemical and metallurgical similarities of the two metals. Electrolytic nickel is available in full-sized cathodes as deposited, approximately 28 by 38 by 3/8 in and 145 lb in weight, and in smaller sizes, down to 1 by 1 by 3/8 in, prepared by shearing the electrolytic plates.

Nickel shot was used for alloying purposes before the electrolytic refining process was developed, and is still used in small-scale alloy production. Shot is produced today by pouring melted electrolytic nickel into water or by high-pressure steam shotting. "XX" shot passes through a 1-in opening and is retained by an 0.053 in opening; the low-sulfur and high-sulfur grades are steam-shotted, with the maximum particle size 0.053 in for the low-sulfur and 0.071 in for the high-sulfur grade.

Malleable or wrought nickels are produced by treating the molten metal with magnesium and manganese to combine with the sulfur and thereby prevent the formation of brittle films of nickel sulfide. Furnace practice may be varied and additions may be made to meet the requirements of particular uses.

American Society for Testing and Materials recently revised Specification B39 which covers refined nickel primarily produced from ore or matte or similar raw material. The principal commercial forms are cathodes and briquetes. The chemical composition shown in B39 is as follows:

Ni	99.80 min	P, Mn, Si, As, Pb, Sb, Bi, Sn, Zn, less than 0.005 each
Co	.15 max	
Cu	.02 max	
C	.03 max	
Fe	.02 max	
S	.01 max	

TABLE 4. *Primary forms of nickel*

Type	Producer	Approx. Ni content	Main uses	Description
		%		
Electrolytic (cathode)	1,3	99.9	Alloy production, electroplating	Sheared cathodes.
Pellets	2	99.9	Alloy production	Carbonyl nickel.
Briquetes	5	99.9	Alloy production	Compacted hydrogen reduced powder.
Rondelles	4	99.3	Alloy production	Carbon-reduced molded nickel oxide.
Ferronickel	6,4	20 min	Ferrous alloy production	Pyrorefined ingots.
XX shot	1	99.6	Alloy production (ferrous casting)	Molten electronickel shotted in water.
F shot	1	92	Cast iron addition alloy	Cast or shotted pyrorefined nickel-silicon additive.
Nickel oxide sinter 75	1	75	Ferrous alloy production	Product from roasting of refined nickel sulfides.
Nickel oxide sinter 90	1	90	Ferrous alloy production	Product from roasting of refined nickel sulfides.
Powder, carbonyl	2	99.9	Nickel and nickel-containing alloys, via powder metallurgy.	Powder from decomposition of nickel carbonyl.
Powder, chem. pptn. (CP)	5	99.9	Nickel and nickel-containing alloys, via powder metallurgy.	Powder obtained by chemical precipitation methods.
Nickel magnesium additive	1	82	Production of ductile (nodular) iron	Ingot, crushed to various sizes.
Nickel magnesium silicon additive	1	51	Production of ductile (nodular) iron	Ingot, crushed to various sizes.
Nickel oxide acid soluble	1	77	Production of chemicals, ferrites, enameling frits.	Refined form of nickel oxide.

1. The International Nickel Co. of Canada, Ltd., Toronto, Ontario.
2. The International Nickel Co., Ltd. Clydach, England.
3. Falconbridge Nickel Mines Ltd., Toronto, Ontario.
4. La Societe "Le Nickel," Le Havre, France.
5. Sherritt-Gordon Mines Ltd., Toronto, Ontario.
6. Hanna Mining Co., Cleveland, Ohio.

2. Nickel—Properties and Uses

Although nickel can be produced commercially to a purity of 99.99 percent, most of the data reported in the literature are concerned with nickel (plus cobalt) of 99.95+ percent. This degree of purity is satisfactory for the determination of many properties, but certain properties, for instance, electrical resistivity, are very sensitive to impurities in solid solution. A general review of the properties of nickel and its alloys was given by Manly and Bridges [46]. For compositions of the various commercial nickels, see table 31.

2.1. Physical Properties

a. General

(1) *Atomic number and weight—Isotopes.* Nickel is number 28 in the periodic tabulation 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 58.71, representing a composite of the five stable isotopes. The natural abundances of the stable isotopes, as reported by White and Cameron [47] and by Brosi [48], are 67.7 percent for Ni^{58}, 26.2 percent for Ni^{60}, 1.25 percent for Ni^{61}, 3.66 percent for Ni^{62}, and 1.16 percent for Ni^{64}. The isotope with mass 61 has an odd number of neutrons and is probably the only stable isotope that has a nuclear spin other than zero. Ni^{64} is about 10 percent heavier than Ni^{58}, enough to cause appreciable shifts in the energy levels of the atoms as indicated by the values for packing fraction and nuclear binding energy reported by White and Cameron [47], Duckworth and co-workers [49,50], and Wapstra [51]. The technique for separating the stable isotopes was developed by Kelm, and electromagnetically concentrated samples of each isotope are available through the Isotopes Division of the Atomic Energy Commission at Oak Ridge.

Seven radioactive isotopes of nickel have been identified [48,52], with mass numbers 54, 56, 57, 59, 63, 65, and 66. The radioisotopes are produced by cyclotron bombardment of iron, nickel, or cobalt, and have half-lifes as follows:

Ni^{54}—0.16 second
Ni^{56}—about 6 days
Ni^{57}—36 hours
Ni^{59}—approximately 100,000 years
Ni^{63}—about 85 years
Ni^{65}—2.6 hours
Ni^{66}—56 hours

Brosi [48] discussed the decay mechanisms and predicted that Ni^{63} probably will be one of the most valuable radioisotopes; the softness of the radiation is an inconvenience in some respects but a very valuable property in others, e.g., in the study of surface reactions, diffusion, and homogeneity in solids containing nickel.

(2) *Nuclear properties.* The reactions of nickel and its principal isotopes to neutron bombardment were summarized by Bradford [53] from Atomic Energy Commission publications, as shown in table 5. The reaction cross sections (1 barn = $10^{-24}cm^2$) refer to cases in which the neutron is not reemitted, that is, to (n,y) reactions. The absorption cross sections are the particular reaction cross sections that are measured by observing the reaction in which the neutron is absorbed. The activation cross sections are those determined from the radioactivity of the product nucleus as the result of the (n,y) reaction. The scattering cross sections are usually constant with energy in the thermal region, are averaged over the Maxwell distribution, and will depend on the crystalline form of the sample and even upon the size of the crystal grains.

Values for neutron absorption cross section of nickel and some of its isotopes under bombardment by neutrons of different velocities were reported by Harris, et al. [54], Hildebrand and Leith [55], Grimeland, et al. [56], Pomerance [57], Chilton, Cooper, and Harris [58], and Nereson and Darden [59]. Scattering of 1-MeV neutrons were discussed by Walt and Barschall [60] and inelastic scattering of monoenergetic neutrons by Kiehn and Goodman [61].

TABLE 5. *Thermal neutron cross sections of nickel and its isotopes [53]*

Element	Isotope	Reaction cross sections (for neutron velocity of 2,200 m/sec) [a]		Scattering cross sections average
		Absorption	Activation	
		Barns	*Barns*	
Nickel	----------	4.5±0.2	----------	17.5±1.0
	Ni^{58}	4.2±0.3	----------	----------
	Ni^{60}	2.7±0.2	----------	1.0±0.1
	Ni^{61}	1.8±1.3	----------	----------
	Ni^{62}	15 ±3	----------	9 ±1
	Ni^{64}	----------	----------	----------
	Ni^{65}	----------	----------	----------

[a] L. Goldring has stated that bombardment of Ni^{58} with fast neutrons produces an absorption reaction cross section of 0.055 barn and yields Co^{58}.

The effect of bombardment, by neutrons, gamma rays, and beta particles, on the physical and mechanical properties of metals used in reactors was discussed by Convey [62].

(3) *Crystal form and lattice constant.* The normal crystal form of nickel is face-centered cubic. The Metals Handbook [63] gives the value of the lattice constant as 3.5238 Å at 20 °C, although Wise [64], in the same handbook, gives 3.5167 Å. Swanson and Tatge [65] reported the value of 3.5238 in 1953 in recording the x-ray diffraction patterns obtained from powdered nickel. Values given by other investigators are as follows:

Unit cell in angstroms, 25 °C		
1931	Phragmen [66]	3.5255
1932	Owen and Iball [67]	3.5254
1934	Jesse [68]	3.525
1935	Jette and Foote [69, 70, 71]	3.5239
1936	Owen and Yates [72]	3.5247
1941	Lu and Chang [73]	3.5247
1941	Fricke [74]	3.5239
1954	von Batchelder and Raeuchle [75]	3.5238±0.0003

The closest approach of the atoms is given as 2.491 Å by the Metals Handbook [63].

Hazlett and Parker [76] showed that the addition of the solid solution alloying elements tungsten, titanium, iron, and cobalt to nickel effected an expansion of the lattice that was directly proportional to the amount of the added element (fig. 4).

Another crystal form of nickel, hexagonal close-packed, has been observed in thin films of nickel prepared by cathode sputtering or by vacuum distillation [77,78,79], in the mixed structure of certain electrodeposits [80], and as a result of the bombardment of cubic nickel with energy of the order of 12 kV [81]. Thomson [77] reported the values of the axes as being $c = 4.06$ Å and $a = 2.474$ Å. This gives a ratio of 1.64, which is near enough to the ratio 1.633 for closest packing. Finch et al. [82], identified a body-centered cubic structure in translucent nickel films deposited from hot nickel-coated tungsten onto surfaces maintained at 300 to 340 °C. Mild heating, e.g., 1 hr at 400 °C, caused both of these crystal forms unusual for nickel to revert to the normal face-centered cubic form.

(4) *Density.* The Metals Handbook [63] gives the density of nickel as 8.902 g/cm³ at 25 °C. The density, as computed from atomic

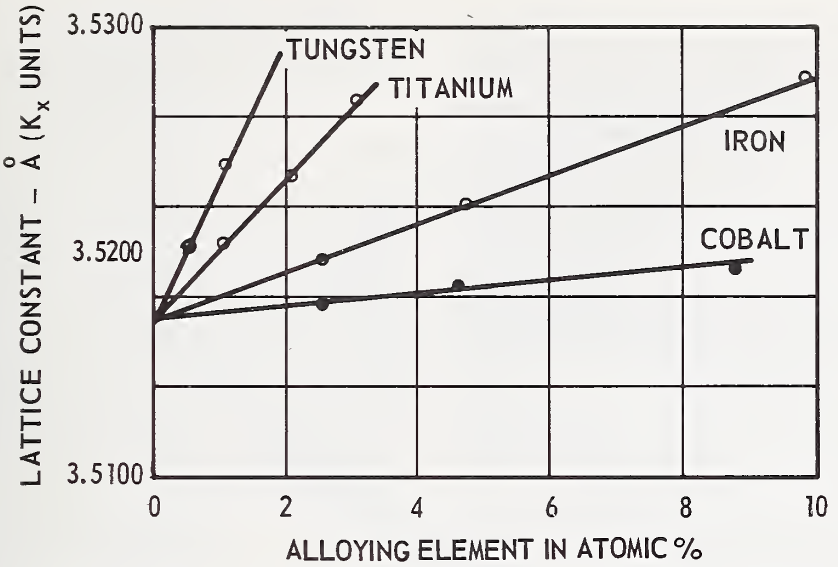


FIGURE 4. *Effect of alloying elements on the lattice constant of nickel at 25° C* [*76*].

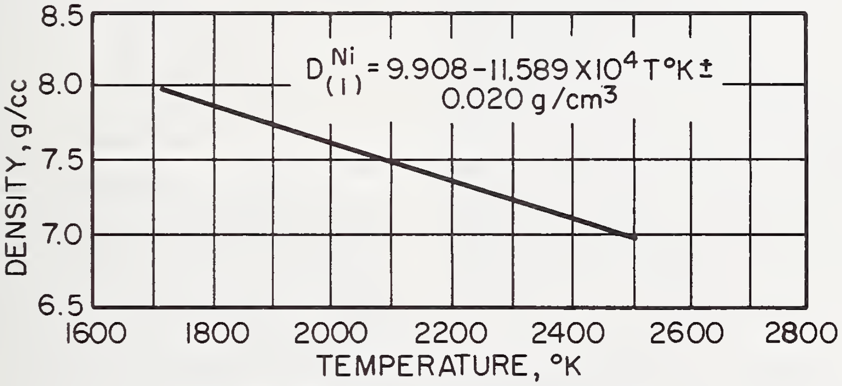


FIGURE 5. *The density of liquid nickel* [*86*].

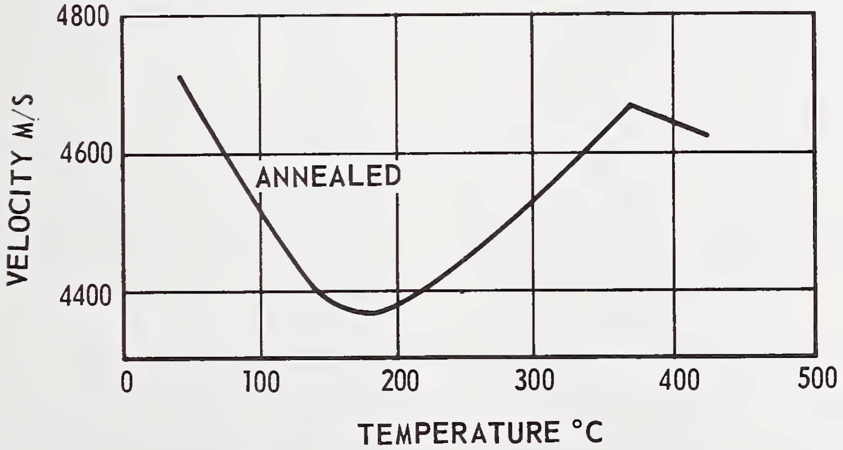


FIGURE 6. *Effect of temperature on the velocity of sound in annealed nickel* [*91*].

data, is 8.908 g/cm^3 at 20 °C, according to Fraser [19]. Direct determinations of the density of nickel are affected by the composition, physical condition, and prior treatment of the material; for example, Jordan and Swanger [83] reported the density of 99.94 nickel as 8.907 g/cm^3 at 23 °C in the cast condition, and as 8.900 to 8.903 g/cm^3 for the same material cold swaged and annealed. Subsequent investigations [84,85] showed that two sudden increments in density, observed on heating plastically deformed nickel, may be attributed to the disappearance of vacancies and to recrystallization.

The density of liquid nickel at its melting point is 7.9 g/cm^3. The effect of temperature on the density of liquid nickel is shown by the curve in figure 5.

(5) *Miscellaneous physical properties.* The surface tension of pure nickel was determined by Kozakevitch and Urbain [87], who reported a value of 1924 d/cm at 1550 °C. Smirnova and Odmont [88] reported that the surface tension of nickel at the melting point was 1756 d/cm.

A study was made of the microwave resonance absorption at a wavelength of 0.86 cm in a single crystal of nickel and in polycrystalline nickel by Barlow and Standley [89]. At 20 °C, the anisotropy constants K_1 and K_2 of the single crystal were both equal to -6.06×10^4 ergs cm^{-3}. The spectroscopic splitting factor, *g*, was determined as 2.19 ± 0.02 both for the single crystal and polycrystalline nickel. This same value was also obtained for nickel-copper alloys containing up to 26 a/o of copper. For nickel-manganese alloys, the *g*-value decreased with increase in manganese, reaching 2.12 at 13.5 a/o of manganese.

The speed of sound in a longitudinal bar of commercial nickel (99.51%) was reported as 4.7×10^5 cm/sec [79]. For ultrasonic frequencies, the transmission rate in electrolytic nickel has been given as 5660 m/sec [90].

The effect of temperature on the velocity of sound in pure nickel was studied by Bell [91]. His results on annealed nickel are shown in figure 6. The sharp maximum at 358 °C is attributed to the Curie temperature, but no explanation was given for the minimum at about 175 °C.

The electron binding energies in metallic nickel are given by Hagstrom et al. [92], as follows:

K	8333	eV
L_I	1012	
L_{II}	872	
L_{III}	855	
M_I	113	
$M_{II,III}$	69	
$M_{IV,V}$	4	

Bearden [93] gives a listing of the x-ray properties of nickel as follows:

Principal x-ray emission lines

KL_{II}	$K_{\alpha 2}$	1.661747 Å±8
KL_{III}	$K_{\alpha 1}$	1.657910 Å±8
$KM_{II,III}$	$K_{\beta 1,3}$	1.500135 Å±8
$KM_{IV,V}$	$K_{\beta 5}$	1.48862 Å±4
$L_I M_{II,III}$	$L_{\beta 3,4}$	13.16 Å±2
$L_{II} M_I$	L_n	16.27 Å±3
$L_{II} M_{IV}$	$L_{\beta 1}$	14.271 Å±6
$L_{III} M_I$	L_e	16.693 Å±9
$L_{III} M_{IV,V}$	$L_{\alpha 1,2}$	14.561 Å±3
$M_{II,III}$ $M_{IV,V}$	------	190. Å±2

[a] Probable error in last digit.

X-ray absorption edges

K	1.4887 Å
L_{II}	14.242 Å
L_{III}	14.525 Å
M_{III}	188.4 Å

b. Optical Properties

The ability of polished nickel to reflect a large percentage of the light incident upon it was summarized by Meyerson [94] as follows: Values for the reflectivity of various forms of nickel increase with increasing wavelength of light, from about 10 percent reflectivity at wavelengths of about 1000 Å to about 90 percent for wavelengths of about 40,000 Å. Some data presented by the Mond Nickel Co., Ltd. [79], are reflectivities of 41.3 percent for 3000 Å wavelength (ultraviolet), 64 percent for 5500 Å (yellow-green), 83.5 percent for 2000 Å, and 87 percent for 3000 Å, the last two representing wavelengths in the infrared region. Roberts [95] reported optical data for nickel at 88, 298, and 473 °K.

The temperature coefficient of reflectivity of nickel was determined by Ward [96], who found that the change in reflectivity was a straightline function of temperature and that there was no significant change at the Curie point. Figure 7 shows his results for wavelengths in the near infrared region of the spectrum.

The emissivity of nickel (and other metals) varies with surface conditions, including the presence of oxide films, and with temperature. The total emissivity of nickel increases approximately linearly with temperatures from 0.045 at 25 °C to 0.19 at 1000 °C. The emissivity for monochromatic light of 0.65 μ wavelength is

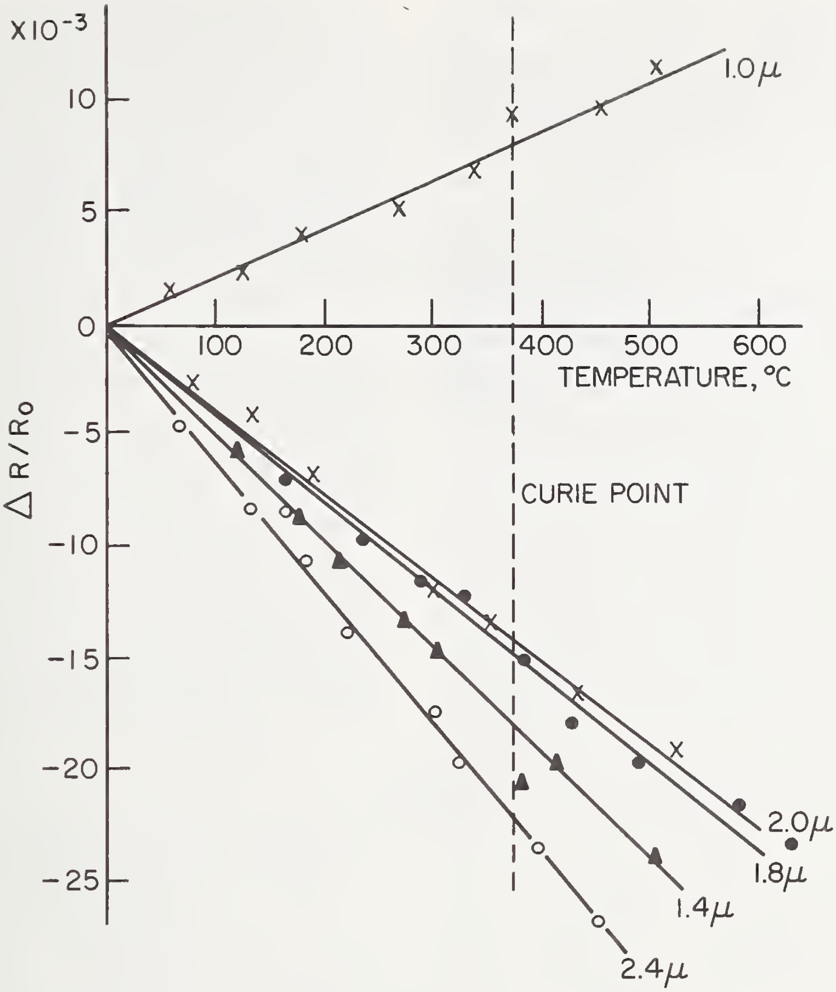


FIGURE 7. *Change in reflectivity of nickel as a function of temperature for several wave lengths of light [96].*

(R_o = room temperature reflectivity and ΔR = the change over T°.)

0.355 [79] and this value is also given by Wise [64]. Lund and Ward [97] presented data for variations in the emissivity of nickel from 1,000 to 1,300 °C. The total emissivity at 1,000 °C was given as 0.19 by Barnes [98].

Nickel films thicker than 100 Å have very nearly the same transmission values for all wavelengths of light in the visible range, but with thinner films there is a slight maximum in transmission at 5000 Å wavelength, imparting a green color to the film [99].

TABLE 6. *Refractive index* (n) *and absorption coefficient* (k) *of nickel for different wavelengths of light [94]*

Wavelength	*n*	*k*	Wavelength	*n*	*k*
Å			*Å*		
4200	1.42	1.79	7500	2.19	1.99
4358	1.41	2.56	7800	2.13	4.43
4600	1.40	2.77	8600	2.24	4.69
5000	1.54	1.93	9400	2.45	4.92
5400	1.54	3.25	10000	2.63	2.00
5461	1.66	3.39	12500	2.92	2.11
5780	1.70	3.51	15000	3.21	2.18
5800	1.73	1.98	17500	3.45	2.25
6200	1.82	1.99	20000	3.70	2.31
6600	1.95	1.98	22500	3.95	2.33
7000	2.03	1.97			

Values for the refractive index and absorption coefficient of nickel for various wavelengths of light are shown in table 6 [94].

The radiation spectrum of nickel is highly complex and contains thousands of individual lines. The most persistent, with a maximum intensity in both arc and spark sources, is at 3414.77 Å. Burns and Sullivan [100] measured 230 lines, in the vacuum-arc spectrum, between 1981 and 221 Å, and Gatterer et al. [101], presented charts of the arc and spark spectra of nickel and other metals.

A tabulation of the wavelengths, between 2000 and 10000 Å, of approximately 500 of the principal lines in the emission spectrum of nickel, is presented in the Handbook of Chemistry and Physics [102]. Moore [103] computed atomic energy levels from analyses of the optical spectrum of nickel.

Spectral lines of short wavelength are emitted from nickel cathodes in an x-ray tube operated at a sufficiently high potential. The most important of these are the K series, with wavelengths of the order of 1.5 Å [104].

c. Thermal Properties

(1) *Melting and boiling points; heat of fusion; vapor pressure.* The Metals Handbook [63] gives the melting (or freezing) point of nickel as 1453 °C (2647 °F). This generally accepted value is based on determinations made at the National Bureau of Standards on 99.94 percent nickel, as reported by Jordan and Swanger [83]. Although they reported 1455 ± 1 °C on the International Temperature Scale of 1927, the value of 1453 °C was assigned to the freezing point as a secondary fixed point on the International Temperature Scale of 1948 [105] because of slight changes in the constants of the radiation equations. The value of 1452 °C (2645 °F) was given by Honig [106]. The presence of the usual impurities or alloying elements tends to lower the melting point of nickel and to change the melting point to a melting range.

The boiling point of nickel is too high to permit direct determinations and is estimated by extrapolation of vapor-pressure data. Wise [64] reported 2730 °C (4950 °F) for the boiling point of nickel. Strangely enough, Honig [106] reported 2839 °C (5142 °F) from vapor pressure data. His vapor pressure data for nickel are shown in figure 8. Some other values for the vapor pressure of nickel are 1.2×10^{-6} mm of mercury at 1000 °C, 9.4×10^{-3} at the melting point, and 213 mm at 2000 °C [79].

The latent heat of fusion of nickel is given as 73.8 cal/g for 99.95 percent nickel [64]. Geoffray et al. [107], gave the value of 4176 ± 54 cal/g-at for the latent heat of fusion.

(2) *Specific heat and heat capacity.* The specific heat of nickel at any temperature represents a combination of lattice vibration, a magnetic effect, and a residual portion. The Metals Handbook [63] gives the value of 0.105 cal/g/°C for the specific heat of nickel at 20 °C. Sykes and Wilkinson [108] determined the specific heat of vacuum-melted Mond pellets from 60 to 600 °C. Busey and Giaque [109] reviewed the low-temperature results reported by others and presented results obtained from very pure nickel over the range 294 down to 12.95 °K.

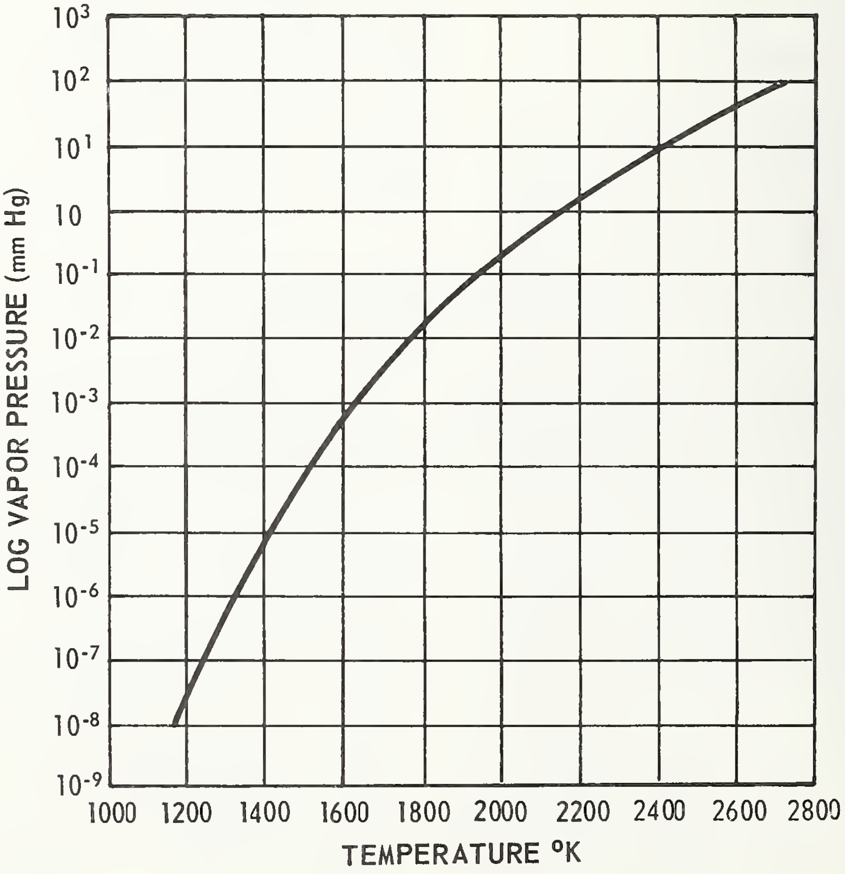


FIGURE 8. *Vapor pressure of nickel [106].*

They give a heat capacity at 15 °K of 0.183 J mole^{-1} deg^{-2}. Krauss and Warncke [110] used vacuum-melted carbonyl nickel of 99.97 percent purity and covered the range from 180 to 1150 °C. The work of these authors has been combined in figure 9, and some of the numerical values used in plotting the curve are recorded in table 7. The sharp maximum at the Curie point occurs at 358 °C according to Sykes and Wilkinson [108], and at 357.2 °C according to Krauss and Warncke [110].

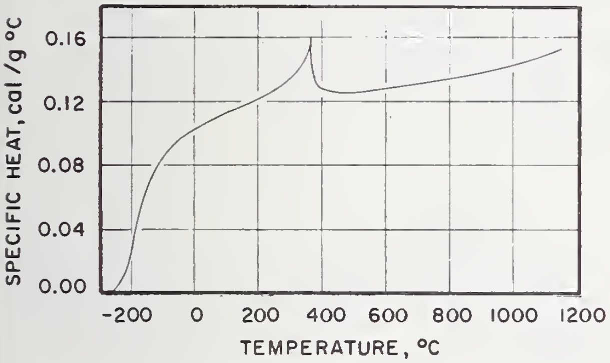


Figure 9. *Specific heat of high-purity nickel [108,109,110].*

Table 7. *Specific heat of high-purity nickel [108, 109, 110]*

Temperature	Specific heat
°C	cal/g/°C
−260	0.00061
−200	.00355
0	.1025
200	.1225
357.5	.1592
500	.1260
700	.1328
900	.1397
1150	.1525

Values for the specific heat of pure nickel, as reported by Valentiner [111], and by Pawel and Stansbury [112], are plotted in figure 10.

Heat capacity measurements have been made below 4.2 °K on 99.9 percent nickel by Rayne and Kemp [113]. They give the curve shown in figure 11, from which they deduce the y value of 7.02 ± 0.06 J mole ($\text{deg}^{-2} \times 10^{3}$). According to these authors, the Debye temperature for nickel (θ) is 441 ± 15 °K. They calculate the heat capacity at 15 °K as 0.183 J mole^{-1} deg^{-2}. Rosenberg [114] gives the value for nickel of 440 °K for θ, and 72.8×10^{4} J mole^{-1} deg^{-1} for γ, the coefficient of the electronic specific heat.

De Nobel [115] gave the following values for the specific heat resistance (W_{spec}) and the specific heat conductivity (λ_{spec}) for 99.4 percent nickel:

Temperature °K	W_{spec} watt^{-1} cm degree	λ_{spec} watt cm^{-1} degree^{-1}
15.12	5.55	0.180
18.15	4.52	.221
21.50	3.65	.274
77.1	1.64	.610
93.1	1.51	.661

Hultgren and Land [116] measured the effect of chromium additions on the heat capacity of nickel; their values for the heat capacity of nickel are given in table 8.

Table 8. *Heat capacity of nickel [116]*

Temperature—°K	Heat capacity—cal per g-atom deg
800	7.44
900	7.60
1000	7.70
1100	7.85
1200	8.08
1300	8.35
1400	8.60
1500	8.80

(3) *Thermal expansion.* Nickel expands with increasing temperature at a regular rate except

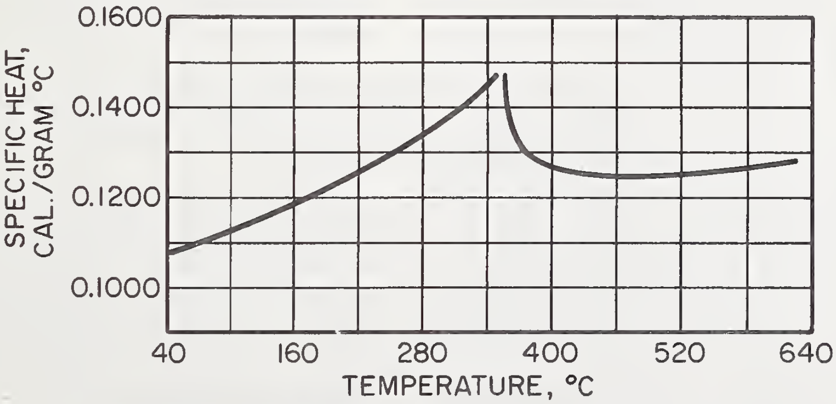


Figure 10. *Specific heat of high-purity nickel [111, 112].*

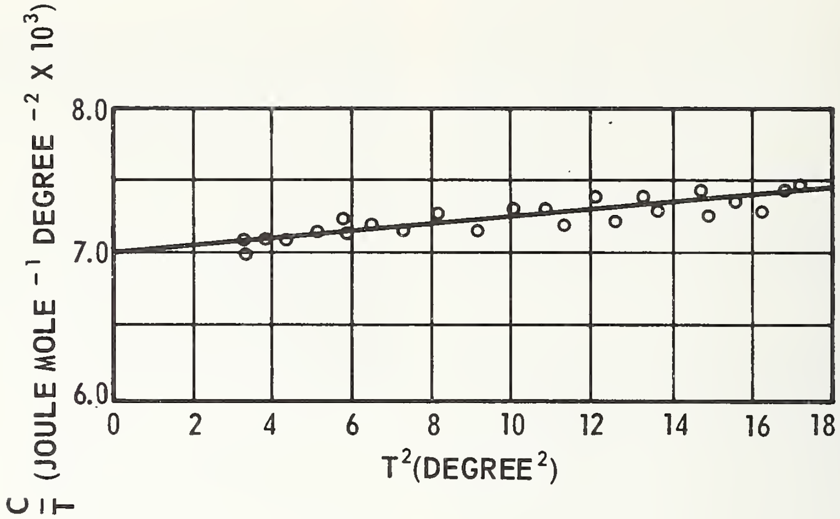


Figure 11. *Atomic heat of nickel* [*113*].

for a sharp maximum at the Curie temperature. Numerical values for thermal expansion are affected by the composition and by physical factors such as the presence of strains, etc. The thermal expansion characteristics of nickel alloys are of much greater practical importance than those of pure nickel and many alloys of closely controlled expansion characteristics depend upon nickel additions.

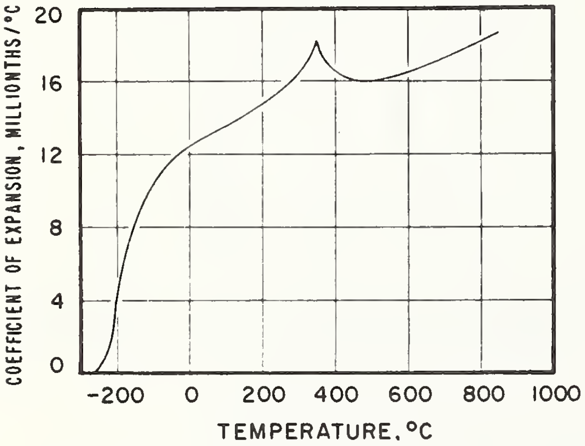


Figure 12. *Thermal expansion of nickel* [*83,117*].

Figure 12 records results obtained on 99.9 percent nickel at low temperatures by Nix and MacNair [117], combined with results obtained by Hidnert for 99.94 percent nickel over the range 25 to 900 °C. The determinations made by Hidnert at the National Bureau of Standards, as reported by Jordan and Swanger [83] and summarized in table 9, have been the basis for numerous summaries of the average coefficient over specific temperature ranges. Owen and Yates [72] reported higher numerical values as a result of x-ray measurements of the lattice constant of 99.98 percent nickel, but a later determination [75] of the lattice constant over the range from 24 to 455 °C confirmed Hidnert's results.

Table 9. *Thermal expansion of 99.94 percent nickel* [*83*]

Temperature range	Average coefficient	Temperature range	Average coefficient
°C	*Millionths per °C*	*°C*	*Millionths per °C*
25 to 100	13.3	25 to 100	13.3
100 to 200	14.4	25 to 300	14.4
200 to 300	15.4	25 to 600	15.5
300 to 350	17.2	25 to 900	16.3
350 to 400	16.4	300 to 600	16.5
400 to 500	15.9	600 to 900	17.8
500 to 600	16.9		
600 to 700	17.1		
700 to 800	17.7		
800 to 900	18.6		

Same values for the spot coefficient at specific temperatures, according to Fraser [19], are

at 20 °C, 12.5×10^{-6} per °C
at 100 °C, 13.5×10^{-6} per °C
at 300 °C, 16.3×10^{-6} per °C
at 400 °C, 16.3×10^{-6} per °C

The Metals Handbook [63] gives the value of 13.3×10^{-6} per °C and 7.39×10^{-6} per °F for the temperature range of 0 to 100 °C (32 to 212 °F).

Arp, et al. [118], made a careful study of the linear contraction relative to 293 °K of several materials, one of which was "A" Nickel (now termed Nickel 200). His values are given in table 10. Corruccini and Gniewek [119] presented a compilation from the literature of the thermal contraction and coefficients of thermal expansion of various metals and alloys at low temperatures. Their values for nickel are given in table 11.

TABLE 10. *Linear contraction of Nickel 200 [118]*

Temperature °K	Contraction $\frac{L_{293}-L_T}{L_{293}}\times 10^5$	Temperature °K	Contraction $\frac{L_{293}-L_T}{L_{293}}\times 10^5$
293	0	160	149
280	16	140	170
273	25	120	188
260	39	100	203
240	63	80	215
220	85	60	223
200	107	40	228
180	129	20	230

TABLE 11. *Linear thermal contraction and coefficients of linear thermal expansion of nickel [119]*

Temperature	$\frac{L_{293}-L_T}{L_{293}}\times 10^5$	$\frac{dL}{L_{293}dT}\times 10^6$	Temperature	$\frac{L_{293}-L_T}{L_{293}}\times 10^5$	$\frac{dL}{L_{293}dT}\times 10^6$
°*K*		*deg*$^{-1}$ *K*	°*K*		*deg*$^{-1}$ *K*
0	224	0	140	171	8.8
20	224	0.2	160	152	9.8
30	224	.5	180	132	10.5
40	223	1.0	200	111	11.0
50	221	1.9	220	88	11.5
60	219	2.8	240	65	11.9
70	216	3.8	260	41	12.2
80	211	4.7	273	25	12.3
90	206	5.5	280	16	12.4
100	201	6.1	293	0	12.6
120	187	7.5	300	−9	12.6

Owen et al.[120], reported on the effect of iron on the thermal expansion of nickel at temperatures up to 500 °C.

(4) *Thermal conductivity.* The thermal conductivity of nickel is lowered by the presence of impurities and irregularities occur near the Curie temperature. The effect of impurities is particularly noticeable at very low temperatures in the varying results reported in 1956 by Kemp et al.[121], who concluded that at these low temperatures thermal conduction in pure nickel is almost completely electronic.

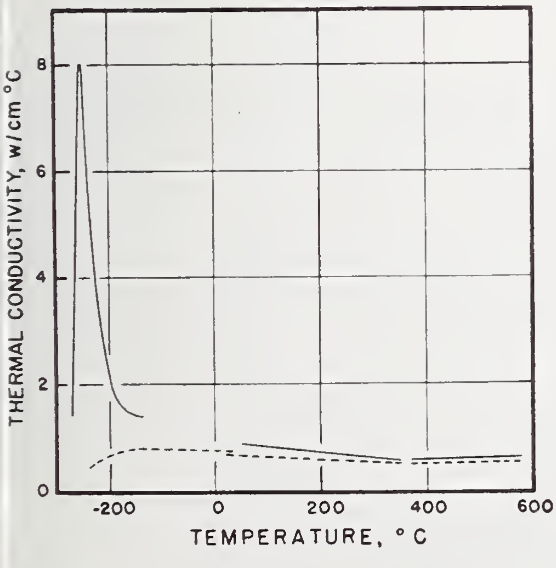


FIGURE 13. *Thermal conductivity of high-purity (solid lines) and commercial-purity (dashed lines) nickel [121,122,123].*

Figures 13 shows results obtained by Van Dusen and Shelton [122] for 99.94 percent nickel over the range 25 to 575 °C and by Kemp et al.[121], for 99.99+ percent nickel at very low temperatures. The two dashed curves for commercial-purity nickel show that the effect of impurities on thermal conductivity is most pronounced at extremely low temperatures. The low-temperature curve for commercial-purity nickel represents data from low-carbon nickel by Powers, Schwartz, and Johnson of Ohio State University according to Powell and Blanpied [123]. The other commercial-purity curve was reported by Van Dusen and Shelton as representing commercial malleable nickel. Some values based in those of Van Dusen and Shelton for 99.94 percent nickel, but expressed [19,79] in calories per second rather than in watts are

at 100 °C, 0.198 cal per cm sec °C
at 200 °C, .175 cal per cm sec °C
at 300 °C, .152 cal per cm sec °C
at 400 °C, .142 cal per cm sec °C
at 500 °C, .148 cal per cm sec °C

The Metals Handbook [63] gives the thermal conductivity of nickel as 0.22 cal/cm^2/cm/sec/°C at 25 °C, which expression may be written as 0.22 cal per cm sec °C. This value is repeated by Wise [64], who also gives the values of 0.198, 0.152, and 0.148 at 100, 300, and 500 °C, respectively.

(5) *Thermionic properties.* Thermionic properties of nickel are those properties that make it useful for ion emission in vacuum tubes. The cathodes used in electron tubes consist of a base material—a nickel alloy having a thin layer of oxides of alkaline-earth elements. When heated to about 700 °C, they emit the stream of electrons used in the amplification process.

Nickel sheet is used for anodes in low-power tubes [129]. Cathodes usually are oxide-coated nickel, but cathodes formed by powder metallurgy techniques from sintered nickel powder and alkaline earth oxides [130] or from carbonyl nickel powder, nickel plus about 4 percent tungsten, or nickel plus 2 percent titanium [131] have been recommended.

Caldwell [132] reported that the thermionic properties of a spectroscopically pure nickel filament became stable only after heat treatment for 1500 hr at temperatures up to 1200 °C. Wohlfarth [133] associated the thermionic emission of nickel with the fact that, with an overlapping *s*-band, there is an increasing transfer of electrons from the *d*-band as the temperature rises. The secondary electron emission of nickel was discussed by Favorin [134] and by Blankenfeld [135]. The amount of carbon present and the rate of its diffusion in nickel are of interest in the activation of oxide-coated thermionic tubes. Lanter et al.[136], reported that the solubility of carbon in nickel between 700 and 1300 °C is expressed by the equation log $S = 2.480 - 4880/T$, where S is the solubility of carbon in grams per 100 g of nickel and T is the temperature in degrees centigrade. The diffusion rate of carbon in nickel is expressed by the equation log $D = 0.909 - 20{,}200/T$, where D is the diffusion coefficient in square centimeters per second.

A review of work carried out to attain precise control over cathode material was written by Acker [137]. The Bell Laboratories developed a method of producing very pure nickel with controlled additions of single alloying elements [138] and material so prepared was used to evaluate the effect of other elements upon the transconductance and total emission of nickel [139].

The thermionic properties of nickel were summarized by Wright [129] as follows:

Work function, Φ, = 5.0 eV,
Temperature, Te, where vapor pressure is 10^{-5} mm = 1330 °K,

$$\frac{\Phi}{\mathrm{Te}} \times 10^3 = 3.78$$

Fomenko [140] gives 4.50 eV as the recommended value for the work function of nickel. He notes that the value varies with crystal face and with temperature.

(6) *Recrystallization temperature.* As with other metals that do not undergo an allotropic transformation, some extraneous factor, such as cold work, is necessary in order for nickel to recrystallize during subsequent heating.

Pure nickel recrystallizes in the temperature range of approximately 300 to 350 °C. The diagram in figure 14 from work by Bollmann [141] shows three general regions for pure nickel cold worked 80 percent; (1) recovery up to 250 °C; (2) primary recrystallization between 250 and 400 °C; and (3) secondary recrystallization above 400 °C. During secondary recrystallization the hardness remains practically unchanged. This figure also shows the recrystallization diagram for two grades of electrolytic nickel.

As a matter of interest, the recrystallization diagram for TD nickel as determined by Inman et al.[142], is included in figure 14. TD nickel consists of a 2 volume percent dispersion of fine thoria particles in a pure nickel matrix. This material was cold worked 93 percent. Its recrystallization diagram indicates that recrystallization occurs at higher temperatures than in pure nickel and that the resultant minimum hardness is considerably higher than that of pure nickel.

Bartuska and Kufudakis [143] presented a recrystallization diagram for nickel showing grain size as a function of temperature and amount of cold work. These authors note that up to about 1050 °C the increase in grain size is very slow and becomes appreciable only above this temperature.

Olsen [144] studied the effect of trace elements on the recrystallization temperature of nickel and noted that the greater the increase in atomic diameter of an added element in rela-

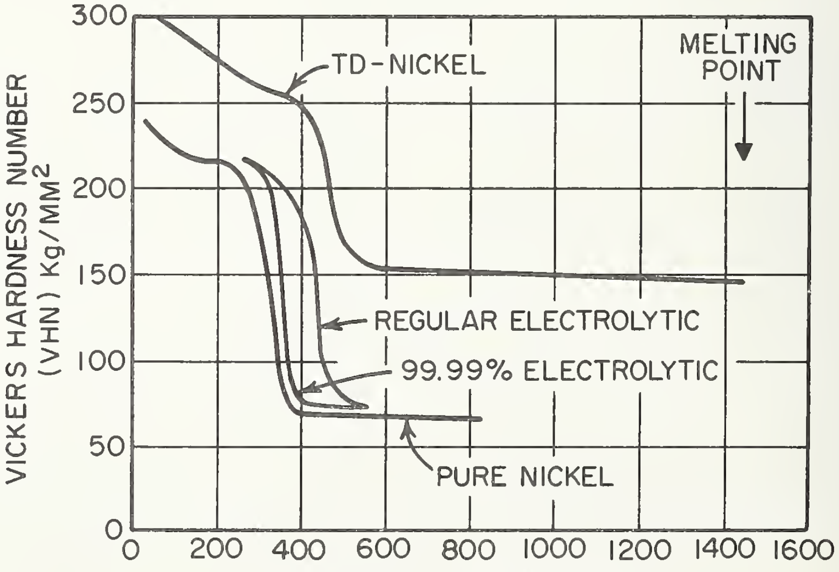
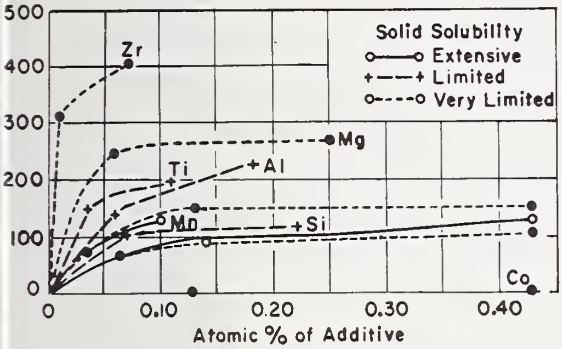


FIGURE 14. *Recrystallization diagram for pure nickel [141], TD nickel [142], 99.99 percent electrolytic nickel [64], and regular electrolytic nickel [64].*

on to that of nickel, the higher is the recrystal-ation temperature. His study showed that the eatest rise resulted from addition of the rgest atoms, magnesium and zirconium. The ost pronounced retardation of recrystalliza-on was produced by addition of 0.1 w/o of rconium, which caused approximately 400 °C se in recrystallization temperature over that pure nickel. Figure 15 shows the effect of



GURE 15. *Increase in recrystallization temperature of high-purity nickel resulting from additions of indi-cated elements [144].*

ace elements on the recrystallization tempera-re of high-purity nickel.

Abrahamson [145] reported that data on the crystallization temperature of binary solid-lution alloys of nickel with up to 0.7 a/o of the rious transition elements showed that all the lditions increase the recrystallization tempera-re of nickel.

d. Electrical Properties

(1) *Electrical resistivity.* The electrical re-stivity of pure nickel is negligible at extremely w temperatures but increases with increasing mperature and with increasing amounts of purities. The resistivity of 99.68 and 99.84 rcent nickel was determined by Pallister 46), who combined his results with those of veral other investigators to yield the curve own in figure 16. The marked change at the urie temperature is evident when values of /dT, derived from the values of ρ (resistivity) near temperatures, are plotted against the mperature (fig. 17).

On the basis of his work and that of others, allister [146] presents estimates for pure ckel as shown in table 12.

The ideal electrical resistivity of 99.99_7 per-nt nickel, according to the data of White and oods [147], is shown in figure 18.

Rider and Brooks [148] studied the effect of ld work on the electrical resistivity of 99 per-nt nickel. Their data gave the curve shown in figure 19, where the logarithmic reduction η is defined by $\eta = 1\mathrm{n}(A_0/A)$, where A_0 is the initial cross-sectional area (i.e., as annealed) and A is the cross-sectional area after cold reduction.

TABLE 12. *Estimate for electrical resistivity of pure nickel [146]*

Temperature	Resistivity	$\rho/\rho273$	$d\rho/dT$
°*K*	*Microhm cm*		
0	<0.03	<0.005	<0.0005
20	<.04	<.006	.001
50	<.18	<.029	.008
100	<1.02	<.16	.023
200	3.70	.60	.031
273	6.15	1.00	.0365
300	7.16	1.165	.0385
400	11.55	1.88	.0505
500	17.5	2.85	.068
550	21.05	3.42	.077
600	25.2	4.10	.0905
650	29.6	4.815	.050
700	31.7	5.16	.0365
800	35.0	5.70	.031
900	38.0	6.18	.0285
1000	40.75	6.62	.027
1100	43.35	7.05	.0255
1200	45.85	7.45	.0245
1300	48.3	7.85	.0235
1400	50.6	8.23	.023
1500	52.85	8.59	.0225
1600	55.05	8.95	.022
1700	57.25	9.30	.0215

Wise [64] gives the value of 6.84 microhm-cm for the resistivity of nickel at 20 °C, and 25.2 percent IACS for the electrical conductivity. The marked effect of slight impurity is indicated by the value of 9.5 microhm-cm for the electrical resistivity at 20 °C and 18 percent IACS for the electrical conductivity for "A" nickel [149]. Figure 20 depicts the ratio of electrical resistance of nickel to the resistance at 0 °C.

Reichelt [150] noted that the resistivity of very thin films, for example, vapor deposited on glass, is 3 to 10 times that of bulk metal.

Bridgman [151] found that the resistivity of a single crystal of high-purity nickel decreased with increasing pressure, as follows:

Pressure	Relative resistivity
kg/cm²	R/R_0
0	1.000
10,000	.982
50,000	.918
80,000	.880
100,000	.858

Changes in the electrical resistivity of a stressed nickel wire can be used to determine Poisson's ratio [152], and the strain coefficient of resistivity of nickel can be qualitatively explained by the free-electron theory [153]. Broom [154] found that the resistivities in the longitudinal and transverse directions in cold-rolled nickel are equal. According to Potter

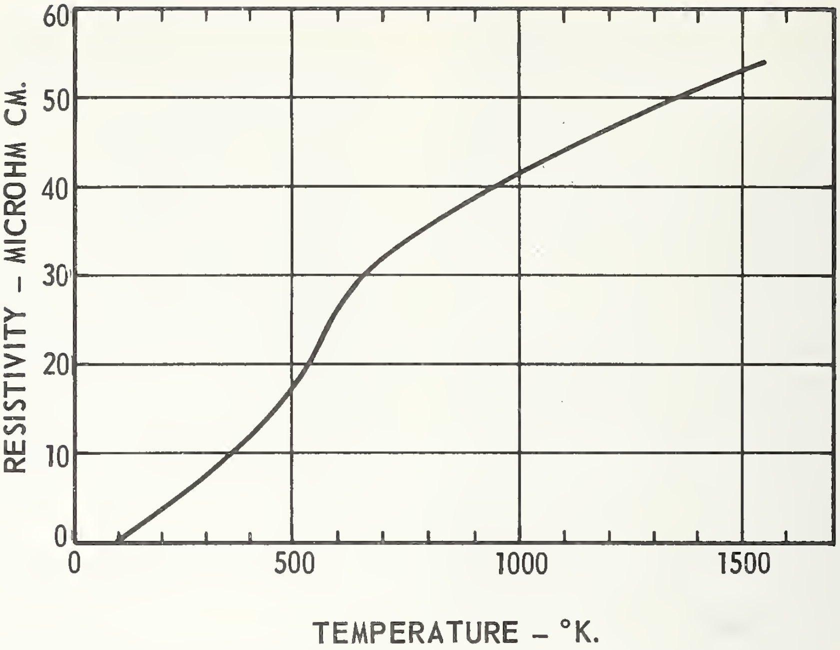


Figure 16. *Electrical resistivity of nickel [146].*

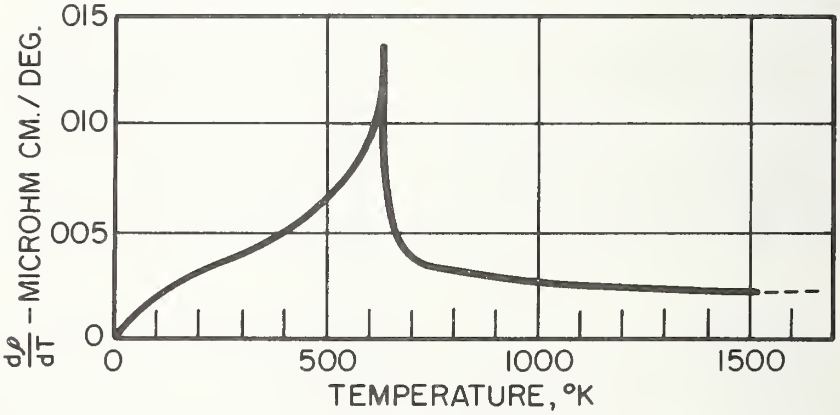


Figure 17. *Change in electrical resistivity of nickel as a function of temperature [146].*

[155] and Matuyama [156], increases in the resistivity of nickel because of the presence of longitudinal magnetic fields are most noticeable at very low temperatures and fade out as the temperature rises above ambient. Smit [157] reported that the resistivity of pure nickel at low temperatures increases with increasing strength of the magnetic field. Tabulated data for the increase of resistivity of nickel due to transverse magnetic fields are presented in tables 488 and 489 of the Smithsonian Physical Tables [158].

Values for the temperature coefficient of electrical resistance of high-purity nickel, from 0 to 100 °C, range from 0.00658 to 0.00692 per °C [19]. Wise [64] gives the value of 0.0069 m crohm-cm per °C for the temperature coefficier of resistivity. That of "A" nickel is given a 0.00474 microhm-cm per °C [149]. The tempe ature coefficient of very thin films of nickel negative, passing through zero and becomin positive as the thickness of film increases [15 160,161]. Belser and Hicklin [162] reporte that the temperature coefficients of resistance substantially pure metallic films (nickel was in cluded) were in the range of 1/3 to 2/3 those the respective bulk metals, irrespective of th substrate used.

Impurities have a marked effect upon th electrical resistivity of nickel. The increase i

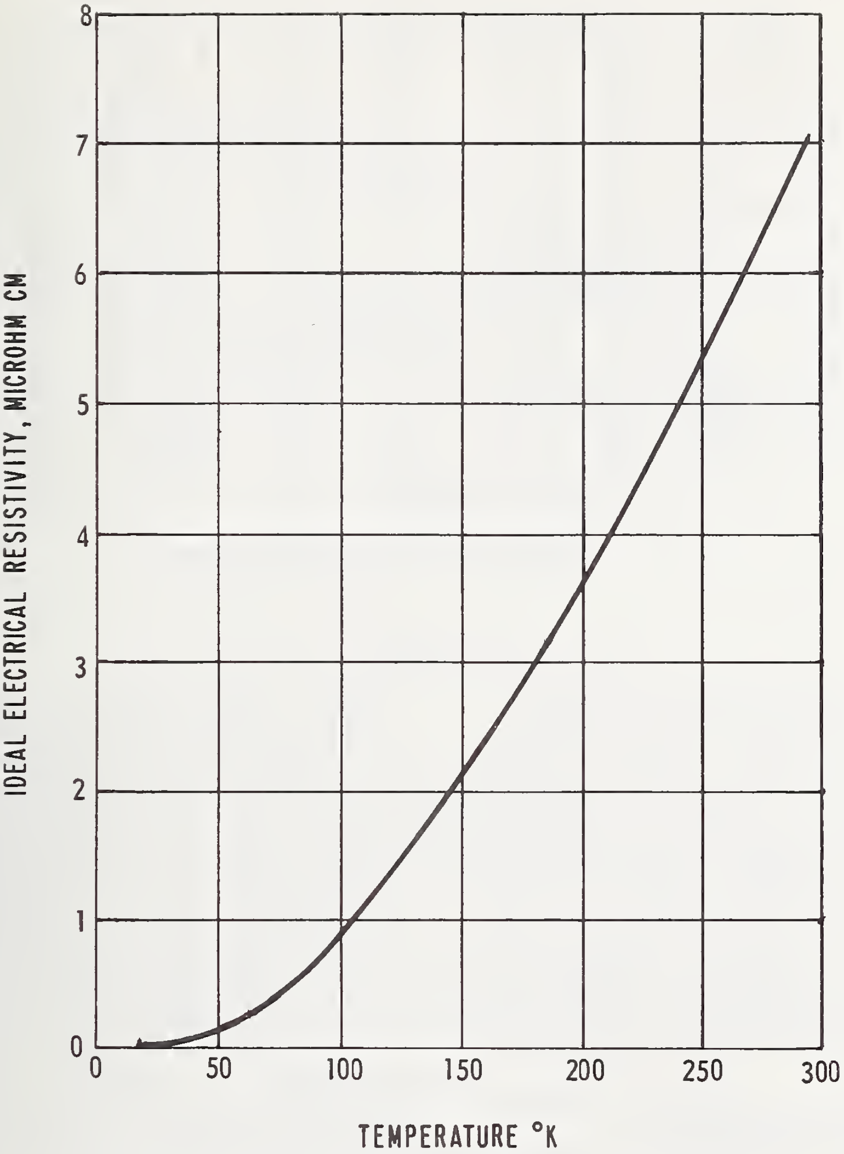


FIGURE 18. *Ideal electrical resistivity of pure nickel* [*147*].

istivity caused by small amounts of other ments is indicated in figure 21.

(2) *Thermal electromotive force.* Nickel is rmoelectrically negative to platinum, i.e., in simple thermoelectric circuit of these two tals the current at the cold junction flows m the platinum to the nickel. Iron, copper, d, silver, and numerous other metals, which positive to platinum, all develop higher emf h nickel than they do with platinum, but in te of this, nickel is not one of the most com- n thermocouple elements because of excessive dation at the higher temperatures. It is, how- r, an alloying element in many thermo- ples.

Values for the thermal emf of nickel with tinum, silver, and iron at various temperatures are shown in figure 22. Values for nickel-copper thermocouples, reported by Pecheux [165], are very similar to the values shown for nickel-silver. Mortlock [166] observed the effect of elastic tensile strain on the thermoelectric power of high-purity nickel from 20 to 400 °C. Bridgman [167] showed that pressures up to 12,000 kg/cm^2 had a slight but consistent effect on the thermal emf of nickel. The effect of magnetic fields of different intensities was studied by Yamanaka [168]. The effect of magnetization on the thermoelectric power of a single crystal of 99.2 percent nickel is always positive near the Curie point, but varies with different orientations within the crystal [169].

Effects associated with the development of thermal emf in nickel and other metals, i.e., the

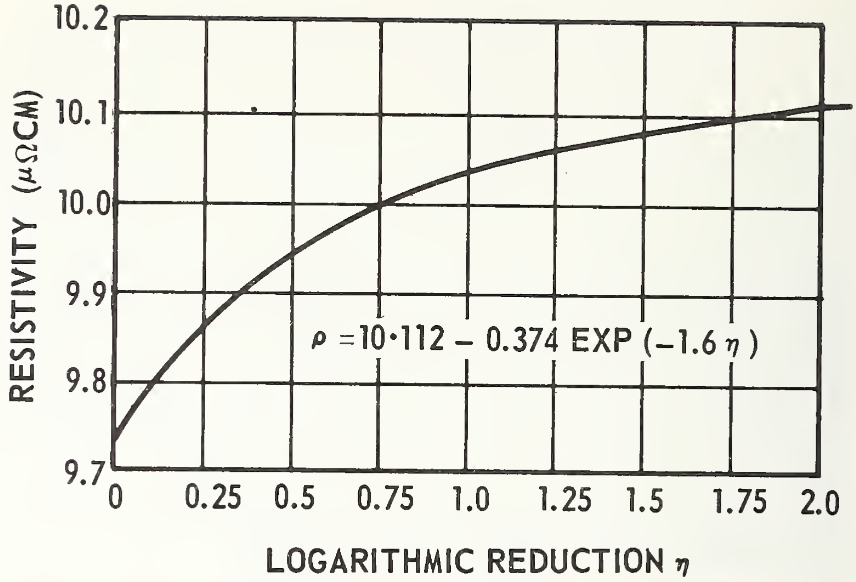


FIGURE 19. *Effect of cold work on the electrical resistivity of 99 percent nickel [148].*

Peltier and Thomson effects, are discussed in the Smithsonian Physical Tables [158].

Berry and Martin [170] studied the thermoelectric stability of various thermocouple materials and found that the high-purity grade of nickel was quite stable in air up to 780 °C.

Considerable information exists in the literature on the compositions, properties, and uses of thermocouples in which nickel is either a major or a minor alloying element. Potts and McElroy [171] investigated the effects of cold working, heat treatment, and oxidation on the thermal emf of the nickel-base thermoelements indicated in table 13.

TABLE 13. *Nickel-base thermoelements investigated by Potts and McElroy [171]*

Material	Al	Cr	Fe	Si	Ni	Other elements
	%	%	%	%	%	%
Hoskins Alloy No. 875	6.0	22.5		0.5	bal	
Hoskins Alloy No. 827		20	8.0	2.0	bal	
Hoskins Alloy No. 717		20		.25	bal	
Chromel A		20		1.5	bal	
Geminol P		18	.7	.8	bal	1.0 Nb
Chromel P		9.46	.2	.4	bal	
Chromel P+Nb		9.41	.2	.35	bal	.2 Nb
Kanthal P		9.11	.05	.37	bal	
Alumel	1.6		.10	1.2	bal	1.75 Mn
Geminol N				2.75	bal	
Kanthal N			.02	2.4	bal	
Alumel special			.26	1.23	bal	
Nickel					bal	
Nickel-1% Si				1	99	
Nickel-2% Si				2	98	
Nickel-3% Si				3	97	
Nickel-4% Si				4	96	
Nickel 5% Si				5	95	

e. Magnetic Properties

(1) *General.* Nickel is one of the three elements (iron and cobalt are the others) that are strongly ferromagnetic at ambient temperature. Typical normal induction curves of anneal samples of the elements iron, nickel, and coba of comparatively high purity are shown in fi ure 23. Pure nickel is seldom used itself as magnetic material except for certain speci purposes, such as magnetostriction applicatio and as a calibration standard in susceptibili measurements. However, many nickel alloys a exceedingly important and often are superior all other magnetic materials for many applic tions. The magnetically preferred axes of sing crystals are the body diagonals (111), as show in figure 24. Bozorth discussed the theories ferromagnetism as applied to nickel in his boo [174] and in a subsequent paper [175] ar showed Beth's curve relating the exchange e ergy of magnetization of nickel to the distan between atom centers, with fixed diameter active shell. The formation of ferromagnet domains in single crystals of nickel, their ident fication through Bitter patterns, and the effe of grain boundaries have been reported by se eral other investigators [176,177,178,179,180]

The magnetic properties of thin films of pu nickel have been studied by several investig tors. Although their conclusions are inconsi tent, the latest studies indicate that the ma netic properties of really clean and pure film are the same as for the bulk nickel [181].

(2) *Curie point.* The Curie point for nicke the temperature at which the change from fe romagnetism to paramagnetism occurs, is a fected by numerous factors, including the pri mechanical and thermal treatment of the spec men, the nature and amount of impurities pre ent, and the method of determination.

The Curie point for high-purity nickel occu between 350 and 360 °C. A value of 353 °C wa

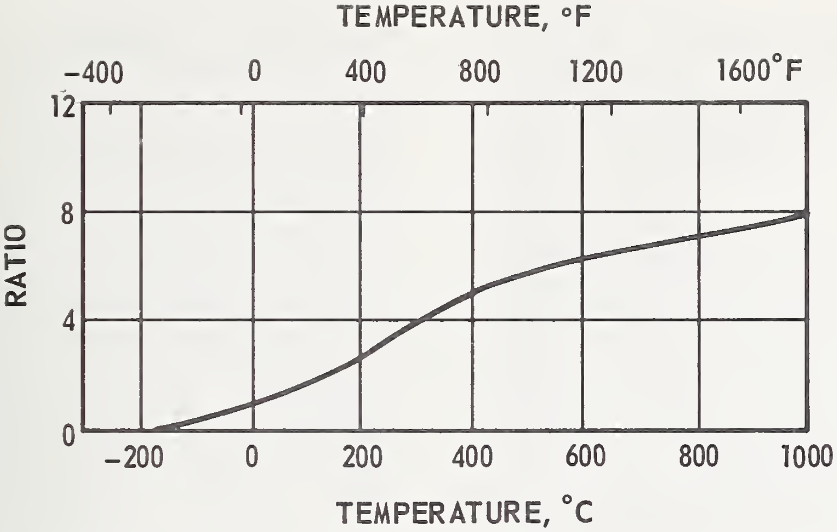


FIGURE 20. *Ratio of electrical resistance of nickel to resistance at 0 °C [64].*

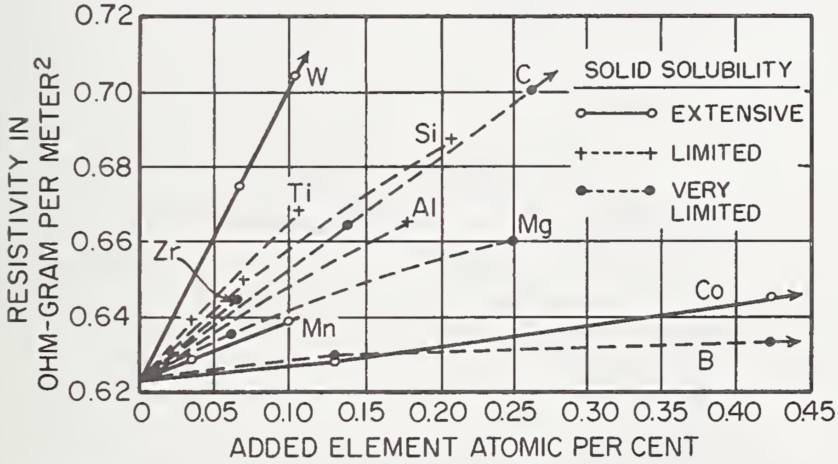
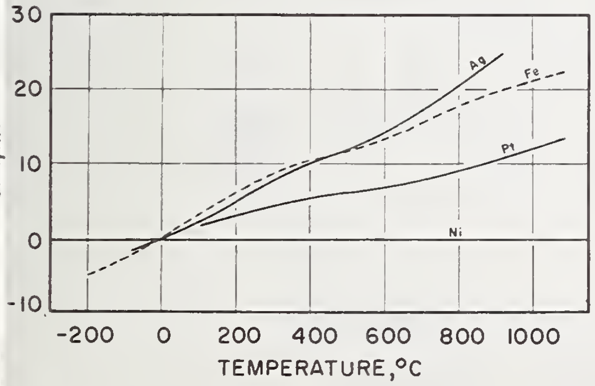


FIGURE 21. *Effect of trace elements on the change in electrical resistivity of high-purity nickel wire (annealed ½ hour at 800 °C) [144].*



IGURE 22. *Thermal electromotive force of nickel against platinum [83], silver [163] and iron [164].*

reported for 99.94 percent nickel, 360 °C for "A" nickel [19,79,182], and 357 or 358 °C for high-purity nickel [108,110]. Wise [64] gives the value of 353 °C for 99.95 percent nickel. The Curie point is lowered slightly by tensile stresses [183] and is raised by pressure at the rate of 0.35 °C per 1,000 atm [184]. Bader [185] correlated pressure effects on the Curie temperature with the introduction of *d*-electrons and the accompanying changes in interatomic distances. Most alloying elements lower the Curie point of nickel but cobalt and iron are exceptions, as shown in figure 25. Small heat changes accompany the magnetic transition [187] and this effect for nickel has been reported by various observers as 0.65, 1.33, and 2.01 cal/g [188]. At relatively high field in-

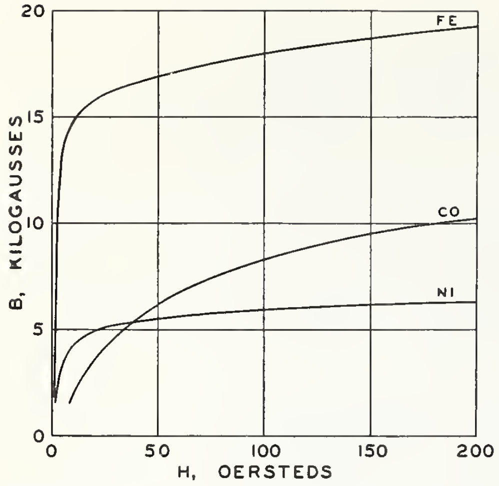


FIGURE 23. *Typical normal induction curves of annealed samples of iron, nickel, and cobalt [172].*

tensities the magnetocaloric effect is mainly reversible; in low positive fields there is a marked cooling effect, which is associated with large irreversible changes in magnetization [189].

(3) *Saturation.* The intrinsic saturation induction value for high purity nickel (99.98%) is approximately 6170 G[3] and for "A" nickel is approximately 600 G [19,79]. The saturation induction of nickel at various temperatures is shown in figure 26 according to Bozorth [174]. The effect of tension in decreasing the magnetic saturation of nickel was explained by Buhl [190] on theoretical grounds.

(4) *Permeability.* The initial permeability of high-purity nickel is approximately 200 and the maximum permeability is 2,000 to 3,000 with H = 1 Oe. For "A" nickel the initial permeability is approximately 200 and the maximum permeability, $H = 20$ Oe, is approximately 1,000 [19,79]. The theoretical effect of temperature on the permeability of nickel was compared by Kersten [191] with the vaulting of the Block walls.

(5) *Coercivity.* The coercivity of nickel is given from 0.7 to 2.7 Oe [19,175]. It is greatly affected by its fabrication and heat treatment. The effect of plastic deformation on the tem-

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[3] This value, not yet published, was obtained by R. E. Mundy at the National Bureau of Standards in 1966.

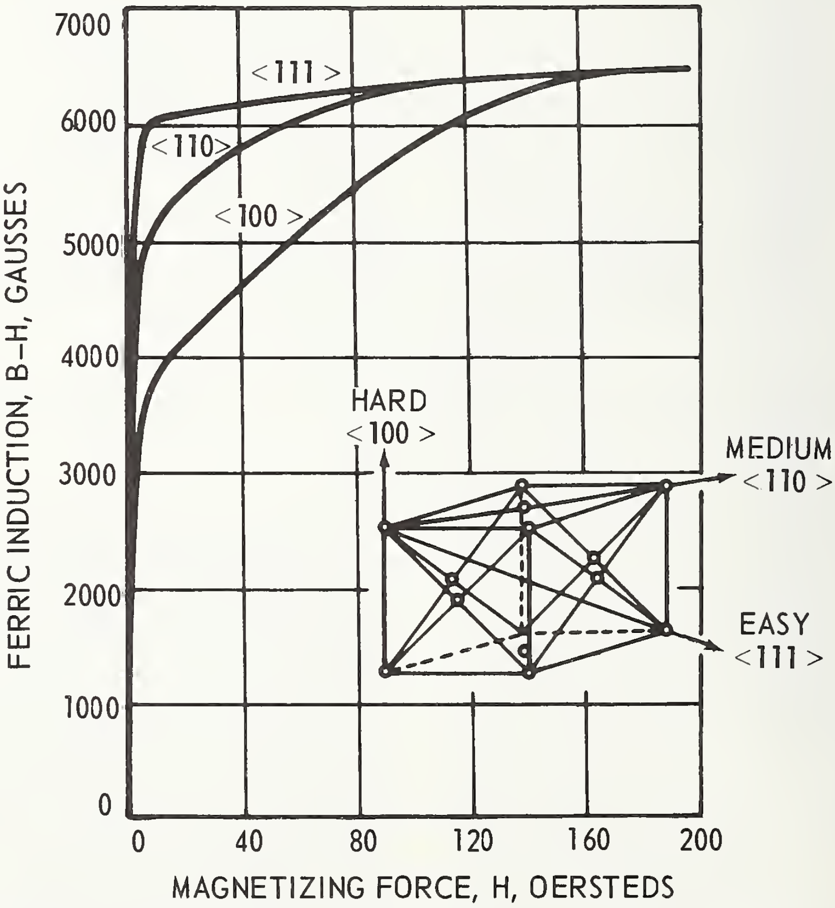

FIGURE 24. *Crystal structure of nickel and types of magnetization curves obtained in crystallographic directions [173].*

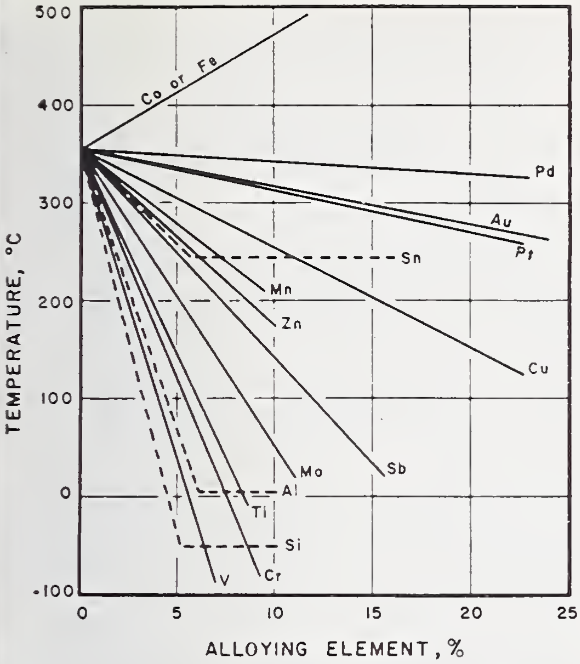

FIGURE 25. *Effect of single alloying elements on the Curie point of nickel* [186].

perature dependence of the coercivity, through the temperature range —195 to +360 °C, is reversible on annealing [192]. Nickel rods sintered above 1,000 °C show an increase in coercivity with decreasing temperature, and the increase is proportional to the square root of the crystal energy or the anisotropy constant [193].

(6) *Magnetostriction.* Magnetostriction is the change in dimensions of a body resulting from magnetization. The most important magnetostrictive effect is the fractional change in length of the order of a *few parts* in a million on magnetization, known as the Joule effect. The reverse phenomenon, in which change of magnetization is produced by the application of mechanical strain, is known as the Villari effect. Pure nickel has, in conjunction with other desirable properties, one of the largest magnetostrictive effects available in commercial materials and is extensively used in devices when this effect is required.

According to the domain theory of magnetization, magnetostriction develops in nickel as follows: each small domain is always magnetized to saturation in any one of the six easy directions of magnetization. In the absence of

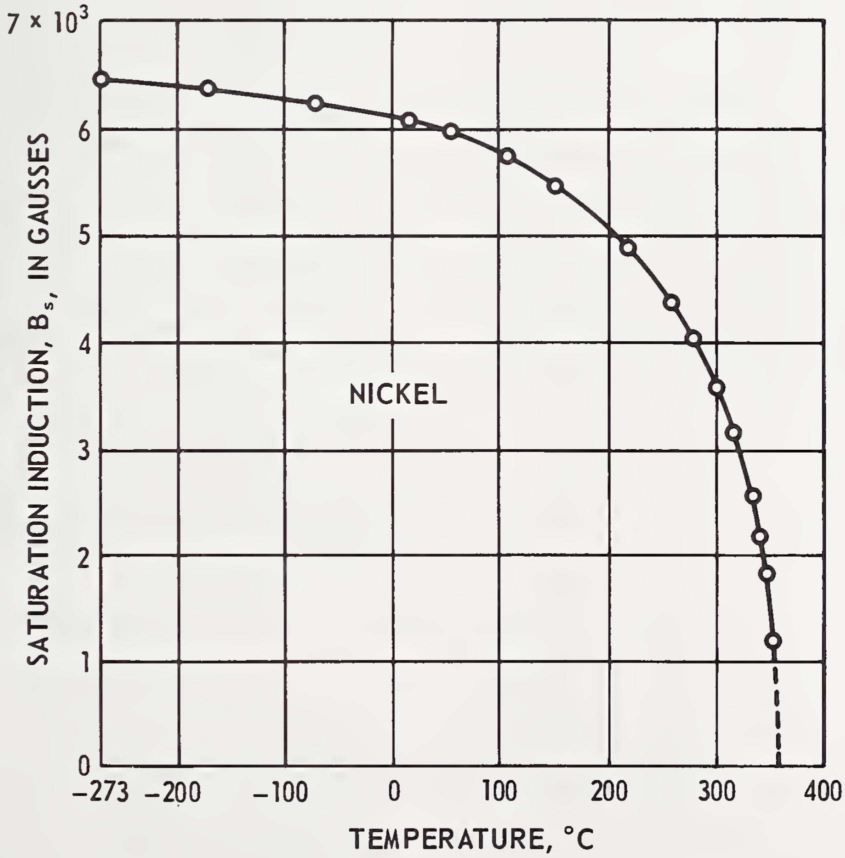

FIGURE 26. *Saturation induction of nickel at various temperatures* [174].

an external field, the random orientation of the 100,000 domains in a crystal of average size results in a net magnetic effect of zero for the crystal. However, if a weak magnetic field is applied, some of the favorably oriented domains grow in size at the expense of others. As the field is increased the growth process continues until each crystal becomes one domain, magnetized along an easy direction of magnetization that approximates the direction of the field. On further increase of the applied field, the large domain rotates until it is parallel to the field, and it is during this process that the material expands or contracts its dimensions, thus exhibiting magnetostriction.

Nickel contracts in all magnetic fields whereas iron expands in a low field and contracts slightly in a high field as shown by figure 27. The nickel-iron alloy system is interesting in the wide range of magnetostrictive properties available, as shown in figure 28. A few percent of nickel makes iron exhibit positive magnetostriction at all magnetic field strengths. At about 30 percent nickel the longitudinal magnetostriction drops to zero, but the volume magnetostriction reaches its maximum in alloys containing about 35 percent of nickel. At about 45 percent nickel there is a peak in positive magnetostriction that is comparable in size to the negative magnetostriction of pure nickel. The 63-percent nickel alloy is the most strain-sensitive of these alloys, i.e., it shows the greatest change in magnetization for a given change in stress, and the effect can be further increased by special heat treatment. At 81 percent nickel the magnetostriction goes through zero, and at higher nickel contents the negative magnetostriction ultimately reaches its maximum value at pure nickel.

Ferromagnetic iron-nickel alloys lose their magnetism as the temperature is increased to the Curie point, and this loss of internal magnetism causes the alloy to contract if the magnetostriction is positive. In the Invar alloys, the volume contraction due to loss in magnetization almost neutralizes the thermal expansion due to the forces of thermal agitation, with the result that these alloys have extremely low thermal expansion over a considerable temperature range.

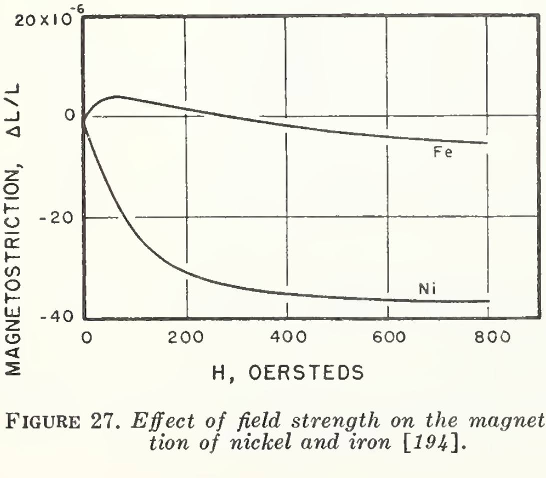

FIGURE 27. *Effect of field strength on the magnetostriction of nickel and iron* [*194*].

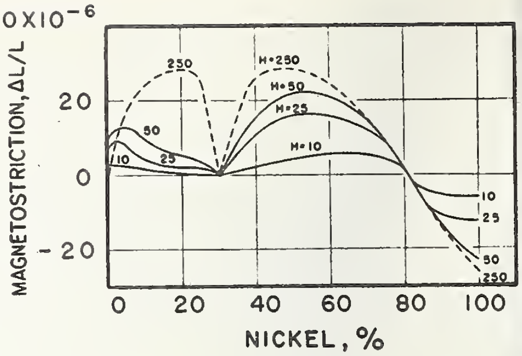

FIGURE 28. *Magnetostriction in iron-nickel alloys at different field strengths* [*194*].

The actual change in length that accompanies magnetostriction is small; even in nickel the maximum change in length is less than 40 ppm. However, even this small dimensional change is sufficient to make nickel very important in the construction of transducers for the conversion of electrical to mechanical energy, particularly in the ultrasonic range. The magnetostrictive properties of nickel or its alloys make it useful for transducers vibrating in the range of 10-100 kHz and of vital importance in equipment used in many and diverse fields, including Sonar and related devices for echo sounding and underwater detection; electrical filters, e.g., a band pass filter for use in commercial receiving sets; the purification of water and killing of bacteria; acceleration of chemical reactions and cavitation effects; strain gages, vibration and engine detonation; phonograph pickups; frequency control of oscillators; dust precipitation; the drilling and machining of hard materials like tool steels and refractories; detection of flaws, and many other uses.

An extended discussion of the theory and practice of magnetostrictive effects, with an appendix of pertinent references, is contained in two booklets of The International Nickel Company, Inc. [194,195].

2.2. Chemical Properties

a. Behavior in Corrosive Media

The resistance of nickel to tarnish and corrosion in the atmosphere and in many corrosive media was established in the early history of the nickel industry and was responsible for the first large use of nickel in nickel plating. Nickel requires the presence of an oxidizing agent, such as dissolved air, for most of its corrosion reactions. Reducing conditions usually retard the corrosion of nickel, while oxidizing conditions usually accelerate it. However, nickel has the ability to protect itself against certain forms of attack by development of a corrosion resisting, or passive, oxide film and consequently, oxidizing conditions do not invariably accelerate corrosion.

The surface finish and the use of polishing agents, such as chalk, tripoli, and the oxides of iron, chromium, and aluminum, have effects on the initial rates of corrosion but the differences disappear as corrosion proceeds [196]. Yamaguchi [197] found that nickel lapped to a mirror finish with an aqueous colloidal suspension of aluminum oxide exhibits remarkable corrosion resistance, retaining its finish even after longtime immersion in a saturated aqueous solution of hydrogen sulfide. In contrast, a chemically or electrochemically polished surface was immediately attacked in the hydrogen sulfide solution. A bibliography of the literature concerned with the corrosion products on nickel and its alloys was published in 1960 [198].

(1) *Water.* Nickel is highly resistant to corrosion by waters, such as distilled water, ordinary tap water, and natural fresh waters (including those containing hydrogen sulfide or free carbon dioxide). It is resistant to corrosion by water even at 500 °F under pressure of 2000 psi and at velocities up to 30 fps [199].

In sea water, conditions of agitation or flow are favorable to nickel, but local attack may occur under barnacles or other attached solids in low-velocity exposure. In general, salt and brackish waters are more corrosive than fresh waters, but nickel alloys find many uses under marine conditions. An evaluation of nickel and many nickel-containing materials for marine usage was made by Tuthill and Schillmoller [200].

Although Friend [201] reported, on the basis of 4-year exposure tests, that 99.84 percent nickel was second only to tin in resistance to Bristol Channel waters, other sea water exposures have shown that nickel is subject to pitting [201a]. A report by May and Humble [202] stated that crevice corrosion of nickel in quiet sea water can be prevented by cathodic protection.

(2) *Mineral acids, alkalies, and salts.* Nickel is fairly resistant to sulfuric acid in concentrations of less than 80 percent at room temperature, the rates varying from less than 5 mpy in air-free acid to about 50 mpy in air-saturated acid. It is not useful in contact with hot sulfuric acid of concentrations greater than about 15 percent [203]. Aeration increases corrosion rates, particularly in dilute acids; in concentrated acids aeration decreases corrosion rates. Increasing temperature increases corrosion rates and hot aerated solutions are very corrosive. In boiling solutions the use of nickel should be confined to concentrations below 5 percent. At 5 percent concentration, the corrosion rate of Nickel 200 in boiling (216 °F) sulfuric acid is 34 mpy [204]. At 10 percent, the rate increases to 120 mpy. The kinetics of nickel corrosion in sulfuric acid were reported by Pitt and Wadsworth [205]. Nickel is corroded severely by sulfurous acid, except the very dilute solutions such as are used to preserve foods.

With cold hydrochloric (muriatic) acid, the rates of attack vary according to the air content, from 10 to 40 mpy in dilute acid to 60 to 80 mpy in concentrated acid. Figure 29 shows the effect of hydrochloric acid concentrations and aeration on the corrosion rates of nickel at 86 °F. Nickel may find some applications in low concentrations of acid, especially in unaerated solutions at room temperature. Nickel is rarely useful in handling hot hydrochloric acid of more than 2 percent concentration [203,206].

Nickel is resistant to pure unaerated phosphoric acid at room temperature but is cor-

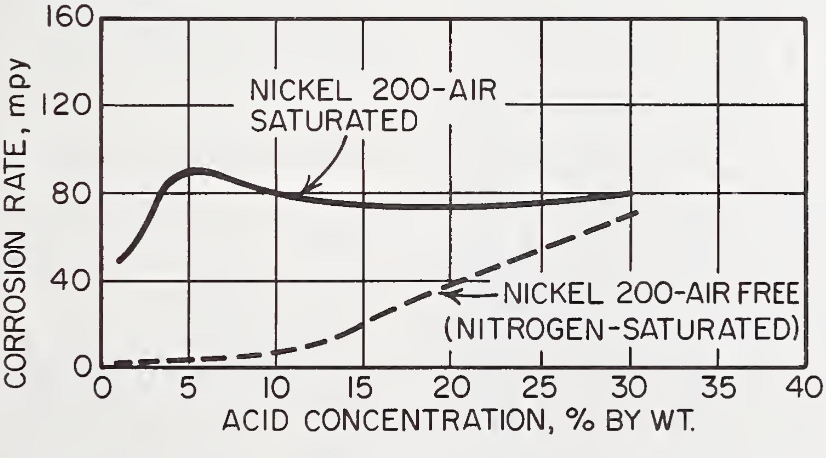

FIGURE 29. *Corrosion of Nickel 200 in hydrochloric acid solutions at 86 °F [204].*

roded when the acid contains oxidizing impurities such as ferric compounds. In hot phosphoric acid, corrosion rates are high.

Nickel 200 shows excellent resistance to anhydrous hydrofluoric acid even at elevated temperatures [204]. In aqueous solutions, however, exposure is usually limited to temperatures below 180 °F.

Strongly oxidizing acids, such as nitric acid, corrode nickel. Berg [207] showed that the rate of solution in nitric acid was proportional to the square root of the concentration up to 3.5 *N*, but at higher concentrations the equation is complex and results are difficult to reproduce. Nitric acid of greater than 0.5 *N* concentrations rapidly attacks Nickel 200.

Nickel is strongly resistant to alkali solutions. For example, in boiling 50 percent sodium hydroxide (caustic soda) the rates of corrosion are less than 1 mpy [203,208,209], and in concentrations greater than 75 percent, nickel is second only to silver in resisting attack. The resistance of nickel to corrosion by molten sodium hydroxide was used by Probst et al. [210], as a base for attempting to develop nickel alloys having similar corrosion resistance but having greater high-temperature strength. Anhydrous ammonia does not corrode nickel, but ammonium hydroxide is appreciably corrosive in concentrations greater than about 1 percent. Molten carbonates are corrosive to nickel [211]. The well-known ability of molten sodium hydroxide containing about 2 percent of sodium hydride to remove oxide scale from nickel without attacking the underlying metal led to numerous investigations of the possibility of using nickel to contain sodium hydroxide as a heat transfer agent in nuclear reactors [212,213,214, 215]. These investigations showed that molten sodium hydroxide can be handled in nickel containers at all temperatures up to about 1000 °F, but at 1200 to 1500 °F the circulating system becomes plugged with deposited nickel. The Research and Development Department of The International Nickel Company, Inc., reports that, in commercial production of caustic, nickel containers are useful at 1200 °F.

Nickel resists corrosion by neutral and alkaline salt solutions, with rates usually less than 5 mpy. Nonoxidizing acid salts are only moderately corrosive, with rates seldom higher than 2 mpy. Oxidizing acid salts, such as ferric chloride, and mixtures of oxidizing salts with mineral acids, are likely to corrode nickel severely, and the same is true of oxidizing alkaline salts, such as hypochlorites, with which nickel should not be used when the available chlorine content exceeds 3 g per liter. Gurovich [216] reported that the magnitude and rate of corrosion in molten alkali chlorides varied with the cation ratio; nickel lost 1.3 g/m^2/hr in KCl and 4 g/m^2/hr in LiCl. He also reported on reactions of nickel with molten nitrates of the alkali metals [217]. Treseder and Wachter [218] stated that the use of nickel is required when a liquid mixture of $AlCl_3$ and $SbCl_3$ is used as a catalyst in petroleum processes.

Alkaline solutions containing hydrogen peroxide do not corrode nickel and are not decomposed by it.

(3) *Organic acids and compounds.* With a few exceptions, organic acids are weak and nonoxidizing. Nickel 200 has excellent resistance to organic acids of all concentrations if the aeration is not high. Natural and alkaline organic compounds have virtually no effect on nickel.

Nickel is not attacked by fatty acids or soap and is widely used in their processing [219, 220]. The corrosion of nickel by acetic acid is very slight [219]. In the production of low- and medium-priced jewelry, watch bracelets, for example, Mairs and Williams [221] note that no single substitute has yet been found with the general usefulness of nickel in resistance to synthetic and natural perspiration.

Steverding [222] reported that rapid intergranular corrosion of nickel by kerosene-type fuels does not occur below 550 °C, and that cold-worked metal offers greater resistance to corrosion than nickel of equiaxed grain structure.

Nickel is not corroded appreciably by chlorinated solvents or by mixtures of these with water.

(4) *Atmospheres.* When exposed indoors, Nickel 200 will remain reasonably bright and free of tarnish, being superior to silver, copper, and brass in this respect. Outdoors, it becomes dull and acquires a thin adherent corrosion film which is usually a sulfate. Rate of corrosion is extremely slow although corrosion does increase with increases in the sulfur dioxide content of the atmosphere. Marine atmospheres and rural atmospheres cause comparable corrosion rates, both very slow.

The 20-year atmospheric exposure tests conducted by the American Society for Testing and Materials included exposure of plates of 99+ nickel at industrial locations (Altoona, Pa., and New York City), a marine location receiving

TABLE 14. *Results of ASTM 20-year atmospheric exposures of 99 + nickel [223]*

(Specimen size 9 x 10 x 0.035 in.)

Location	Original weight, avg	Loss in weight, avg				Corrosion rate	
		10 yr		20 yr		10 yr	20 yr
	g	*g*	%	*g*	%	*mil/yr*	*mil/yr*
Altoona	566	47.90	8.5	140.73	25.2	0.164	0.222
New York	564	40.56	7.2	93.28	16.6	.137	.144
Sandy Hook	562	9.35	1.7	------	------	.0313	------
Key West	562	1.49	.3	2.55	.5	.0050	.0041
La Jolla	564	1.38	.2	3.32	.6	.0047	.0058
State College	565	1.95	.3	5.44	1.0	.0066	.0085
Phoenix	563	.38	.1	.88	.2	.0013	.0015

considerable industrial pollution (Sandy Hook, N. J.), marine locations (La Jolla, Calif., and Key West, Fla.), and two rural locations (State College, Pa., and Phoenix, Ariz.). The results of these long-duration exposures, reported by Copson [223] and summarized in table 14 and figure 30, showed that nickel is very resistant to corrosion at marine and rural locations. In all cases the corrosion was constant with time, and the corrosive attack was essentially uniform in nature, i.e., nonpitting.

Copson's report of the ASTM tests contained supplementary data from exposures of sheet and screen specimens in the industrial atmosphere of Bayonne, N. J., for periods ranging up to 20 years. The corrosion rates corresponded with those of the ASTM locations, but the Bayonne results showed that sheltered specimens corroded more than unsheltered exposed specimens, and that screen and wire corrode faster than sheet. Pitting was not observed in any of the screen specimens but was observed in two of the sheet specimens; the average maximum pit depth was 3.4 mils for a sheet exposed 12 years in the exposed vertical position and 1.4 mils for a sheet exposed for 20 years in the sheltered vertical position. The faster corrosion of screen and wire, because of such factors as increased pickup of pollution per unit area, was discussed by Copson in another publication [224].

(5) *Wet and dry gases.* Dry gases are not actively corrosive to nickel at atmospheric temperatures, but wet gases such as nitric oxide, chlorine and other halogens, sulfur dioxide, and ammonia are appreciably corrosive. Nickel is resistant to dry chlorine and hydrogen chloride at temperatures up to about 1,000 °F [203]. The approximate temperature at which a given corrosion rate is exceeded in short-time tests in dry chlorine for Nickel 201 is as follows [204]:

30 mpy	950 °F
60 mpy	1000
120 mpy	1100
600 mpy	1200
1200 mpy	1250

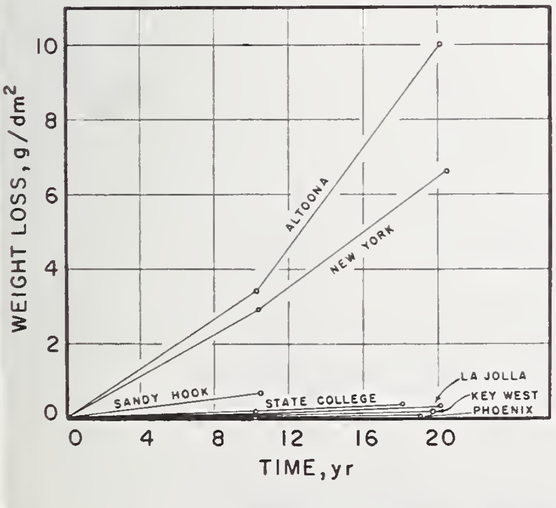

FIGURE 30. *ASTM 20-year atmospheric exposures of 99+ nickel plate [223].*

In wet hydrochloric acid vapor, corrosion begins at isolated points, which increase in number with increasing time [225]. Nickel is resistant to fluorine and fluorides, but this resistance is decreased in the presence of moisture and the consequent formation of hydrofluoric acid [226,227]. At temperatures above 375 °C, nickel is subject to general and intergranular attack by gases that contain sulfur and sulfur compounds. The extent of the attack is less in an oxidizing environment (SO_2) than in a reducing environment (H_2S), and the resistance of nickel to attack by sulfur is considerably improved by the presence of up to about 5 percent of manganese [203]. Nickel begins to react with sulfur dioxide at about 460 °C to form nickel sulfide, Ni_3S_2; the reaction goes nearly to completion at about 700 °C, and may reverse at higher temperatures [228]. The reaction of nickel and molten sulfur follows a parabolic law between 205 and 445 °C, forming Ni_3S_2 or Ni_6S_5 [229].

(6) *Oxidation.* When heated in oxidizing atmospheres, nickel forms a superficial, tightly adherent scale at temperatures below 1400 °F, and its resistance to excessive oxidation makes nickel useful at higher temperatures [203]. The rate of oxidation of nickel in air or oxygen essentially follows a parabolic law, and the purer the nickel the lower the rate [230,231, 232].

Gulbranson and Andrew reviewed the early literature relating to the oxidation of pure nickel [233] and reported studies on oxidation at temperatures up to 1050 °C [234]. They reported that protective oxidation failed at about 900 °C, at which temperature the parabolic law constant has a value of 1.88×10^{-11} $(g/cm^2)^2/sec$ and a film thickness value of 400 to 600 $\mu g/cm^2$. Their curves for the oxidation of nickel are shown in figure 31.

Many studies of the oxidation of nickel have been reported [235,236,237,238,239,240,241,242, 243,244]. Uhlig et al.[237] ascribed the discontinuity in oxidation rate at the Curie temperature to a slightly higher work function above the Curie temperature, which explains a slightly higher activation energy for oxidation above the Curie temperature. Doerr [240] reported that for 99.99 percent nickel heated in oxygen at 1200 °C, the parabolic-rate constant was 2 mg $cm^{-2}hr^{-1/2}$. Baur et al.[242] studied the effect of oxygen pressures ranging from 6.5×10^{-3} atm to 20.4 atm at temperatures up to

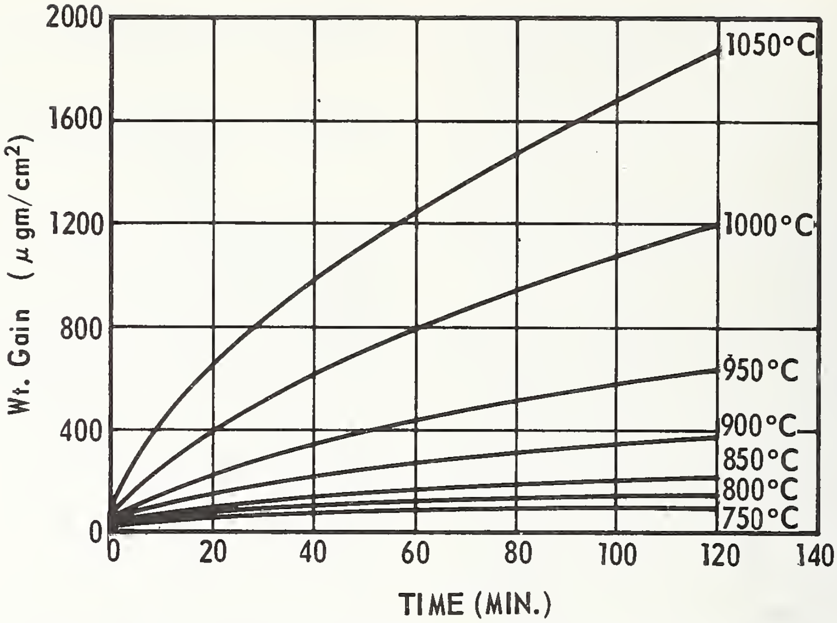

Figure 31. *Effect of temperature on the oxidation of nickel in oxygen; pressure = 7.6 cm Hg [234].*

1200 °C; they found the oxidation rate to be proportional to the one-fifth power of the oxygen pressure. Fueki and Wagner [243] determined activation energies for oxidation ranging from 36.3 to 43.6 kcal/mole, depending on the test atmosphere.

Zima [245] combined his data (at 76 cm of Hg) with those of Gulbranson and Andrew [233] (at 7.6 cm of Hg) to give the oxidation rates at temperatures from 550 to 1260 °C as presented in table 15. The combined data yielded an activation energy of 45.1 kcal/mole for the oxidation of nickel. Rosenberg [246] reported that TD nickel wire exhibited parabolic oxidation kinetics, with the resultant formation of a tenacious oxide (NiO) film on the surface. No internal oxidation, or effects of stress on oxidation, were noted. The effect of small amounts of lithium in decreasing the oxidation of nickel was studied by Hagel [247]. He determined a parabolic rate constant (at 1200 °C) of 2.75×10^{-10} g^2 cm^{-4} sec^{-1} for nickel containing 0.6 a/o lithium, as compared with one of 2.00×10^{-9} g^2 cm^{-4} sec^{-1} for carbonyl nickel; i.e., the oxidation rate was decreased by a factor of seven. Even a barely detectable amount of lithium (<0.4 a/o) provided a rate constant of 5.65×10^{-10} g^2 cm^{-4} sec^{-1} (rate-reduction factor, 3.5).

Table 15. *Rates of oxidation of 99.95% nickel [233, 245]*

Temperature	Oxygen pressure	Parabolic rate law constant
°C	*cm of Hg*	*g^2 cm^{-4} sec^{-1}*
550	7.6	1.08×10^{-14}
600	7.6	5.23×10^{-14}
625	7.6	6.83×10^{-14}
650	7.6	1.46×10^{-13}
700	7.6	5.08×10^{-13}
980	76	1.14×10^{-10}
1096	76	5.48×10^{-10}
1260	76	34.1×10^{-10}

Fueki and Ishibashi [248] showed that the addition of small amounts of aluminum (about 1%) improves the oxidation resistance of nickel at temperatures from 700 to 900 °C.

b. Adsorption and Diffusion of Gases and Metals

Hydrogen is strongly adsorbed and other gases, such as carbon monoxide, carbon dioxide, and ethylene, are adsorbed by nickel. This ability of nickel to combine with certain gases without forming stable compounds is important in electroplated nickel and is particularly important in the use of nickel as a catalyst. In general, the amount of gas taken up by nickel increases markedly with increasing temperature and mildly with increasing pressure, but the mechanism of the adsorption and absorption reactions has not been completely clarified. Baker et al. [249] concluded that the contact of nickel with hydrogen, at temperatures from +20 to —183 °C, results in dissociation at the surface with subsequent solution of atoms in the bulk phase. This involves activation energy and the existence of lattice vacancies or macrocrystalline spaces, but probably does not involve lattice solution. Baker and Rideal [250] reported that at —183 °C carbon monoxide is absorbed by nickel, but at higher temperatures, surface reactions form carbon dioxide and nickel carbide (or carbon). Carbon dioxide can replace hydrogen chemisorbed by nickel, but hydrogen cannot replace carbon monoxide. Gundry and Tompkins [251,252] studied the equilibrium properties of the hydrogen plus nickel and carbon monoxide plus nickel systems and the kinetics of sorption of these two gases on nickel films below —78 °C. They concluded that the slow rate of sorption was due to an activated diffusion process over the nonuniform surface of the metal film. The ratio of amount of carbon monoxide adsorbed to that of hydrogen, under comparable conditions, was about 1.5.

The amounts of hydrogen and other gases adsorbed by nickel are greatly in excess of their true solubilities. Meyerson [94] presented results from numerous sources to show that the solubility of hydrogen in solid nickel varies from about 0.0002 w/o at 300 °C to 0.0008 w/o at 900 °C.

Edwards [253] determined that the diffusion rate of hydrogen in nickel followed the equation $D = Do \exp(^{-b}/T)$, where $Do = 1.07 \times 10^{-2}$ cm^{-2} sec^{-1} and $b = 5100$ °K. His plot of the variation of diffusion rate with temperature is shown in figure 32. Olsen and Larkin [254] found the diffusion coefficient of hydrogen in nickel at 25 °C to be 3.9×10^{-10} cm^2/sec and reported that the diffusion constants showed the activation energy to be about 9500 calories per mole. They found that the total amount of hydrogen liberated at this temperature was approximately 0.0001 percent. Wortman et al. [255], reported that the diffusion of hydrogen

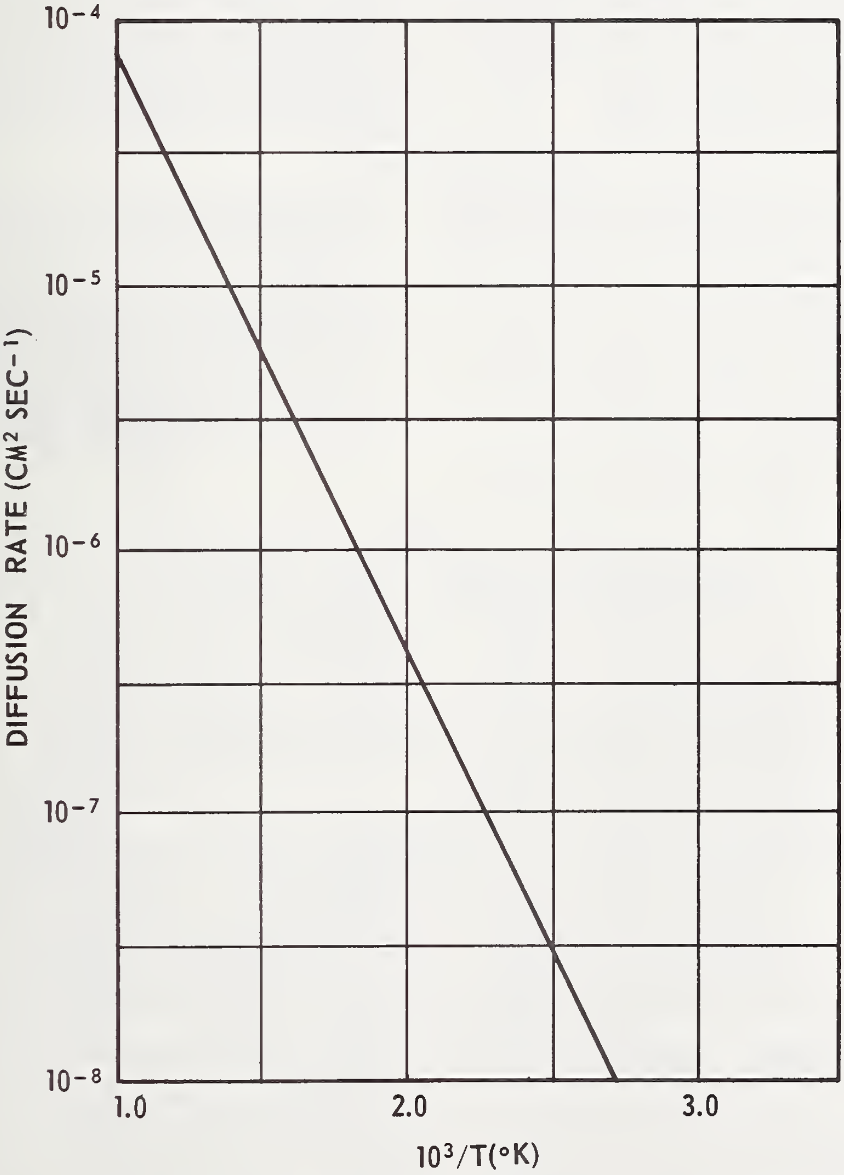

FIGURE 32. *Variation of diffusion rate of hydrogen in nickel with temperature [253].*

in nickel occurs with an activation energy of 7000 ± 1000 calories per mole in the chemisorbed layer.

Some gases, notably hydrogen, can diffuse through solid nickel. It is reported [256] that hydrogen at a pressure differential of 1 atm diffused through certain thin-walled nickel tubes at 950 °C at a rate of 250 ml/min. Hill and Johnson [257] studied the diffusion of hydrogen through nickel at temperatures from 380 to 1,000 °C. They concluded that the entropy of activation was negative and that the diffusion was accompanied by little, if any, distortion of the nickel lattice.

Grimes [258] observed that deformations up to 10 percent caused no significant change in the diffusion coefficient for hydrogen through unstrained nickel, which he gave as 0.0095 exp $(-10{,}300/RT)$ cm^2 sec. He noted that this finding agrees with theoretical analysis of interstitial diffusion in strained systems.

The permeability of hydrogen through nickel is rapid, even at temperatures approaching room temperature [259]. Gorman and Nardella [260] measured the hydrogen permeation rate in nickel and reported the following values for the permeation coefficient (U):

at 700 °K, $U = 19.1 \times 10^{-2}$ μ liters cm^{-1} sec^{-1} atm$^{-1/2}$

at 1000 °K, $U = 3.32 \times 10^{-2}$ μ liters cm^{-1} sec^{-1} atm$^{-1/2}$.

Their curves for hydrogen permeation through nickel are shown in figure 33.

Weinstein and Elliott [261] reported that, at 1600 °C and 1 atm, 40.7 ppm of hydrogen was soluble in liquid nickel. The effect of temperature on the solubility of hydrogen, according to these authors, is shown in figure 34. Busch and Dodd [262] found that, at 1600 °C and one atmosphere, 3.82×10^{-3} w/o of hydrogen was soluble in nickel.

Selwood [263] discussed the theory of nitrogen adsorption on nickel at low temperatures and demonstrated that there is no true chemisorption of nitrogen on nickel. However, Kokes, and Emmett [264] reported that pure nickel catalysts will chemisorb nitrogen to a slight extent at about 250 to 300 °C. Amounts chemisorbed at high temperatures correspond to 5 percent surface coverage calculated as molecular nitrogen; the low temperature chemisorption corresponds to as much as 28 percent surface coverage. The nitrogen absorbed at —195 °C is easily removed by evacuation at room temperature.

Busch and Dodd [262] reported that nitrogen was insoluble in pure liquid nickel, but Humbert and Elliott [265] note some slight solubility at 1600 °C and 1 atm (0.001 ± 0.001 w/o).

The solubility of oxygen in molten nickel, according to Wriedt and Chipman [266], varies from 0.294 w/o at 1450 °C to 1.63 w/o at 1691 °C. In a later paper [267], these authors discuss equilibrium of hydrogen and oxygen with molten nickel, iron, and their alloys. Tankins

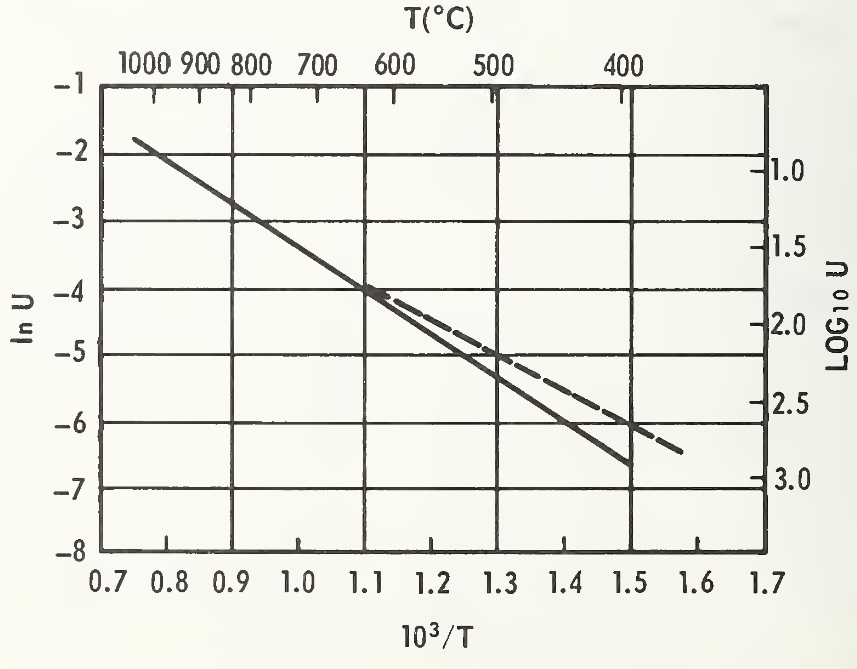

FIGURE 33. *Hydrogen permeation through nickel* [*260*].
Solid line—heavy-walled sample. Dotted line—thin-walled sample.

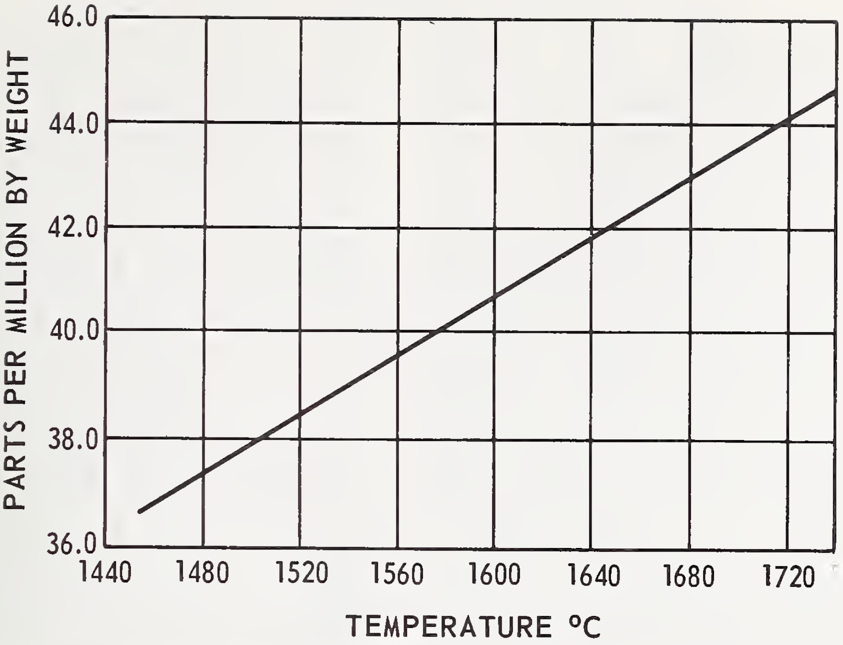

FIGURE 34. *Effect of temperature on the solubility of hydrogen at one atmosphere pressure in pure nickel* [*261*].

et al.[268], gave the following figures for the maximum solubility of oxygen in nickel:

0.44% at 1550 °C
.62 at 1600
.88 at 1650
1.23 at 1700

Sedles and Danielson [124] computed the thermal diffusivity of 99.95 percent nickel at 25 °C as almost 0.23 cm^2/sec, and of 97.92 percent nickel as 0.12. Hoffman et al.[125], studied the self-diffusion coefficient of high-purity nickel over the range 870 to 1248 °C and found that the measured activation energy correlated with the melting point and the heats of fusion and sublimation. Studies of the diffusion rates of nickel in other metals, and vice versa, have been reported [126,127,128].

Surface self-diffusion measurements on nickel between 800 and 1200 °C were made by Blakely and Mykura [269]. They found that the self-diffusion constant (D_s) depended strongly on surface orientation, the dependence being greatest at the lower temperatures. Variation of diffusion constants with temperature for surfaces orientated within 25° of the (111) surface was given by $D_s = Do \exp ({}^{-Q}/KT)$, with $Do = 5\ (\pm 3) \times 10^{-4}$ cm^2/sec and $Q = 0.62\ (\pm 0.08)$ eV.

Upthegrove and Sinnott [270] studied the grain boundary self-diffusion of nickel. They reported that the lattice self-diffusion coefficient of nickel in the temperature range 850 to 1100 °C is $D_L = 0.48 \exp (-65{,}800/RT)$. The ratio of the grain boundary diffusion coefficient to the lattice diffusion coefficient (D_B/D_L) varies from 10^3 to 10^7 for boundary angles from 5° to 80° over the temperature range 700 to 1100 °C. The ratio increases with increasing angular misfit and with decreasing diffusion temperature. The activation energy for grain boundary diffusion is independent of misfit angle for $20° < \theta < 70°$; the value is 26.0 ± 1.5 kcal/g mole. Beyond these limits the activation energy approaches 65.9 kcal/g mole, the lattice diffusion activation energy.

The surface self-diffusion coefficient on nickel single crystals was measured by Pye and Drew [271] over the temperature range 400 to 1000 °C. They found that the activation energy for surface diffusion was the same on the (111), (110), and (100) planes, amounting to about 0.60 eV. The values for the diffusion coefficient (D_s) at constant temperature varied with crystallographic orientation as follows:

$D_s\ (111) > D_s\ (110) > D_s\ (100)$. Their data are plotted in figure 35.

Murarka et al.[272], gave the diffusion coefficient of chromium in nickel in the range 600 to 900 °C as:

$D_{Cr/Ni} = 0.03 \exp (- 40{,}800\ R/T$ cm^2 sec and in the range 350 to 600 °C as $D_{Cr/Ni} = 5.45 \times 10^{-9} \exp (- 13{,}700\ R/T)$ cm^2 sec.

The diffusion rates of magnesium, silicon, and molybdenum in nickel were measured as a function of temperature by Swalin et al.[273], and are shown in figure 36.

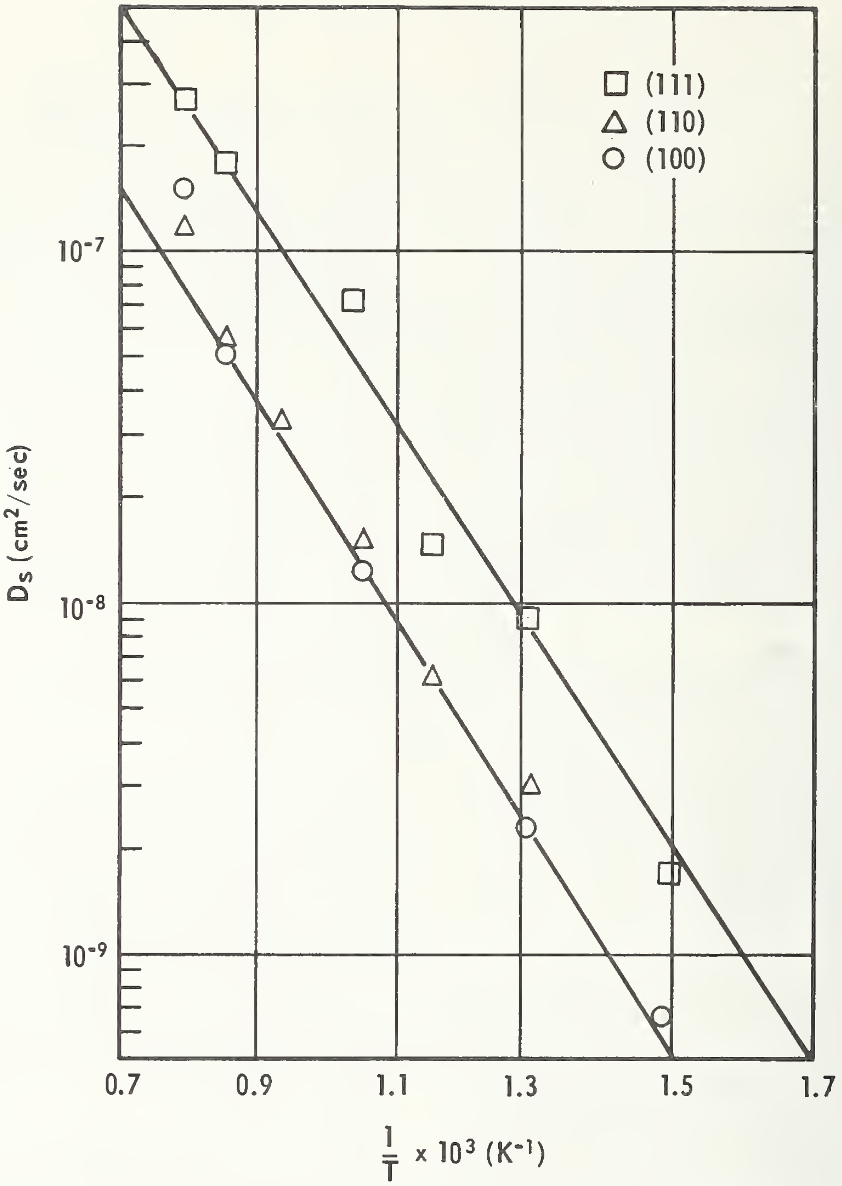

FIGURE 35. *The temperature dependence of the self surface diffusion of nickel [271].*

Barnes and Mazey [274] reported no change in the rate of diffusion of copper into nickel as a result of pressure up to 2500 lb/in^2.

The interdiffusion of uranium and nickel was studied by Aas and Steinegger [275] who found that at 500 and 600 °C the penetration of nickel into uranium was about four times more rapid than that of uranium into nickel. The activation energy for the temperature range 400 to 600 °C was determined as 17.1 kcal.

c. Catalytic Action

About 1818 Thenard observed the catalytic effect of nickel in a study of the decomposition of hydrogen peroxide, and Marchand in 1842 decomposed ethylene over heated nickel. Mond and Langer produced hydrogen in commercial quantities by the action of nickel catalysts on mixtures of carbon monoxide, hydrocarbons, and steam. In 1896 Sabatier and Senderens started their classical work on the catalytic hydrogenation of unsaturated hydrocarbons and other organic compounds. Most of the reactions catalyzed by nickel involve hydrogenation or dehydrogenation of organic compounds. The preparation of edible oils and fats accounts for more than two-thirds of the consumption of nickel as a catalyst. Fraser [276] in 1937 listed approximately 40 fields in which nickel catalysts

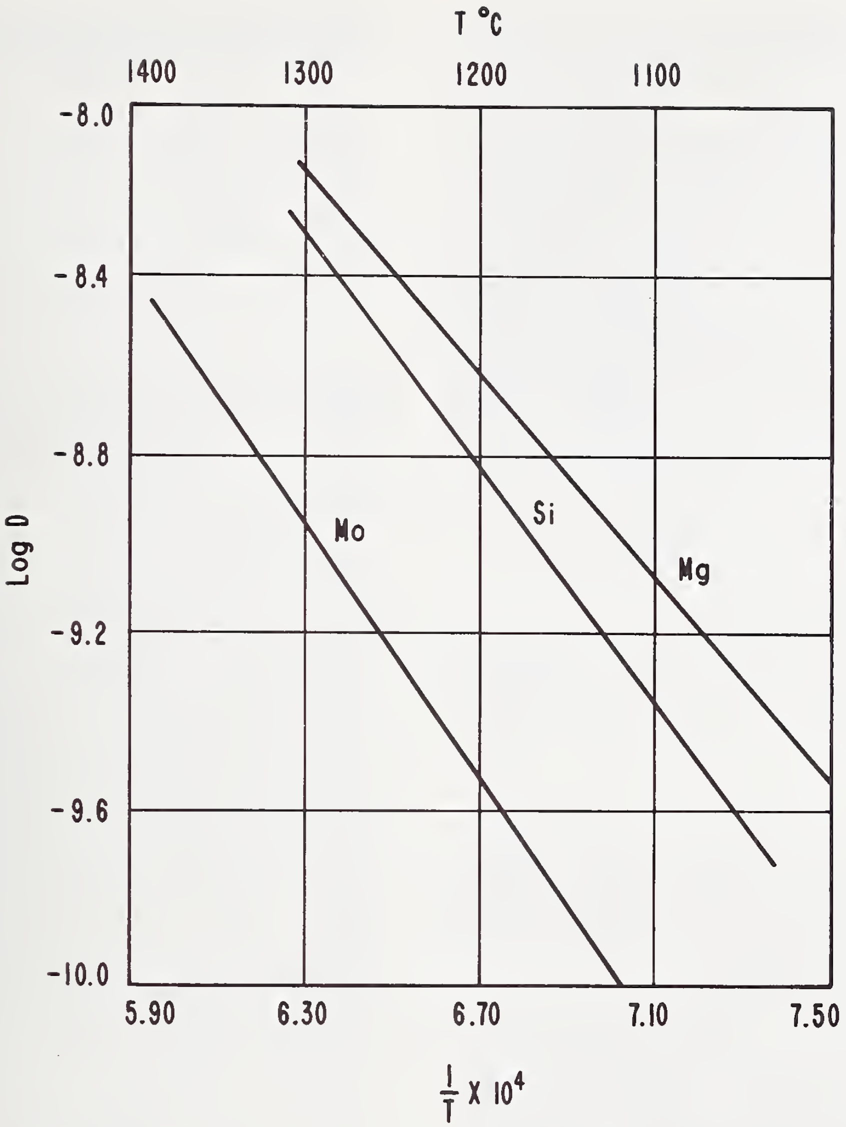

FIGURE 36. *Relation between temperature and diffusion of molybdenum, silicon, and magnesium in nickel [273].*

were used, and the list was still growing. Among these fields are the artificial aging of liquors, drying oils, bleaching, waste-water purification, the removal of organic sulfur compounds from coal gas, the manufacture of alcohol from gas oil, cracking of ammonia, reactions of carbon monoxide with aromatic halogen compounds, and the manufacture of hydrazine from urea. Dinickel phosphide, prepared by reduction of nickel orthophosphate in excess hydrogen, is a highly active heterogeneous catalyst for the vapor-phase reduction of nitrobenzene with hydrogen to analine and water [277]. Alloys of nickel and copper are used as catalysts to hydrogenate carbon dioxide to methane rather than to carbon monoxide [278].

The catalytic action of nickel is primarily a surface reaction and consequently maximum surface with respect to mass is desirable in nickel catalysts. The traditional procedure, from the days of Sabatier's experiments, was to disperse small particles or flakes of nickel throughout the reacting mixture, but the modern Raney catalyst is much more active than Sabatier's flake nickel. To prepare the Raney catalyst, according to Adkins and Billica [279], a nickel-aluminum alloy is digested in aqueous NaOH at 50 °C, producing a sludge, which is washed successively with distilled water, ethanol, and absolute alcohol. The centrifuged sludge may be stored wet in a refrigerator for about two weeks before its activity becomes appreciably affected. Ipatieff and Pines [280] reported that catalysts thus prepared contained about 21 percent of Al_2O_3, instead of being simply nickel and residual aluminum as reported by Adkins and Billica. Raney catalysts prepared from nickel-magnesium, instead of from nickel-aluminum, were reported by Pattison and Degering [281]. The mechanisms of the reactions of Raney catalysts, particularly in hydrogenation reactions, has been thoroughly studied. The factors affecting the catalytic activity were discussed by Pattison and Degering [281] and were reviewed by Yasumura [282], who cited some 60 references. Baker, Jenkins, and Rideal [249] believed that chemisorption and energy of activation were important factors and that solution in the lattice was not involved, although vacancies might be. Smith et al. [283] reported that the catalytic activity is highest for those freshly prepared catalysts that have the highest hydrogen contents, and assumed that the hydrogen atoms are attached to nickel in metastable fashion. In film catalysts, available evidence indicates the presence of a catalytically active nickel-hydrogen layer [284].

The catalytic activity of Raney catalysts may be reduced, i.e., the catalysts may be "poisoned" by sulfur, chlorides, or bromides, and particularly by iodides [281] or by an excess of alkali [285].

d. Electrolytic Solution Potential—Passivity

Values for the electrolytic solution potential of nickel are —0.227 ± 0.002 V at 20 °C [286], and —0.231 ± 0.002 V at 25 °C [287]. Values of —0.2508 V at +18 °C and —0.2496 at 25 °C were reported for powdered nickel in $1N$ solution of nickel sulfate [288].

Under most conditions the tendency for nickel to become passive, i.e., to behave like a noble metal, is not dependable and is not of practical importance. The passivity developed by simple immersion may be destroyed by slight changes in the composition or concentration of the solution, or by mechanical means such as scratching the surface. Anodic passivity is affected by the presence of impurities in the metal or electrolyte; chloride ions are particularly effective in destroying anodic passivity, and use is made of this in maintaining the activity of nickel in electroplating.

The passivity of nickel in acid solution was studied by Markovic and Ahmedbavic [289], who concluded that in the case of acid solution, the dissolution mechanism and formation of the passive film are explicable by the reaction $Ni_3O_4 + H^+ \rightleftharpoons Ni_2O_3 + Ni^{2+} + OH^-$ where the basic potential $U_H = +0.38$ V. Osterwald and Uhlig [290] found that the critical potential for passivity of nickel in deaerated $1N$ sulfuric acid at 25 °C followed the relation $E_H = 0.125 + 0.059\ pH$. The critical current density (ma/cm^2) followed the relation $\log i = -0.76\ pH + \log 27$. Sato and Okamoto [291] also studied the passivation of nickel in sulfuric acid solutions and proposed that the mechanism for formation of passive film involves the successive reactions:

$$Ni + OH^- \rightarrow NiOH^+ + 2e;$$
$$3NiOH^+ + OH^- \rightarrow Ni_3O_4 + 4H^+ + 2e.$$

Markovic [292] found that, in neutral and alkaline solutions, the formation and dissolution of the surface film involves the mechanism

$$Ni_3O_4 + H^+ \rightleftharpoons Ni_2O_3 + Ni^{2+} + OH^- \text{ with } U_H = 0.38 \text{ V.}$$

Davis and Barker [293] reported that nickel becomes passive in alkaline solutions by the formation of about one layer of $Ni(OH)_2$ on the surface. In borate solutions, 1-2 molecular layers are necessary for passivation. Further polarization causes the $Ni(OH)_2$ to become oxidized to Ni_2O_3.

Kronenberg et al.[294], determined the energy of activation for the anodic dissolution process to be approximately 15 kcal/mole.

Janz and Conte [295] conducted potentiostatic studies to establish data on the electrochemical behavior of nickel over the range 600 to 700 °C. The steady state potential for nickel was — 1166 mV when referred to a Ag/Ag reference half-cell. The anodic potentiostatic polarization curve at 600 °C was characteristic of metal passivation; a primary passive potential was observed at —1015 ± 5 mV, but the protection conferred appeared to be far from complete.

Other studies on the passivity of nickel have been made by Piontelli and Serravalle [296], Piontelli, Seravelle, and Sternheim [297], Schwabe and Dietz [298], Okamoto, et al.[299], and Greene [300].

e. Hygienic Significance

The hygienic significance of nickel is confined to industrial operations for the production and utilization of nickel and its salts or compounds, and is further confined to poisoning from nickel carbonyl or to dermatitis produced in individuals sensitive to nickel, for example in electroplating operations [301]. It was shown over 40 years ago [302] that the preparation of food in nickel or nickel-plated utensils is entirely safe, and the extensive use of nickel in pasteurizing equipment and in commercial food processing has never created any problems [303]. The small amounts of nickel that are naturally present in food products, or may be introduced by processing or cooking operations are in general promptly and completely excreted [304]. Early in the 20th century nickel sulfate, chloride, and bromide were sometimes prescribed for tonic purposes, although in some cases overdoses produced nausea and vomiting [302].

Some operators of industrial electroplating equipment have suffered from eczematous dermatitis in varying degrees from contact with nickel-containing solutions and fumes [302, 305], and there have been occasional reports of nickel poisoning resulting from the inhalation of dust, for example, in polishing operations [302], or in the production of alkali-cadmium-nickel storage batteries [306]. Modern knowledge of industrial hygiene, improved ventilation, and the use of protective equipment have practically eliminated the danger of nickel poisoning in such operations.

An extremely toxic industrial nickel compound is nickel carbonyl, $Ni(CO)_4$, which is prepared in large quantities for subsequent thermal decomposition to yield a high-purity nickel powder. It has found extensive industrial application as a carbonylation reagent for producing acrylic acid from acetylene. When nickel carbonyl is present in human lungs, the presence of moisture causes the compound to dissociate into carbon monoxide and finely divided nickel. Small amounts of the dissociation products are readily eliminated by the human system, i.e., the effects are not cumulative, but a number of fatalities have occurred because of single exposures to lethal doses in producing plants and in laboratories [301,302,307]. The threshold limit of one part of nickel carbonyl per billion parts of air has been established by the American Conference of Governmental Industrial Hygienists. The compound known as BAL (2,3-dimercaptopropanol) has been found to be an excellent antidote for nickel-carbonyl poisoning [308]. An excellent review of the toxicity of nickel carbonyl was prepared by Rea [309].

The utilization or handling of radioactive forms of nickel obviously requires observance of the precautions used in handling any radioactive material. The tissue-damaging properties of gamma and beta radiation from irradiated nickel (and other metals) are discussed by Wise [310].

2.3. Mechanical Properties

The mechanical properties of nickel, in common with other metals, are greatly influenced by the purity, temperature, and the previous thermal and mechanical history of the specimen. As in the case with pure metals in general, the values for many of the mechanical properties of pure nickel are lower than those of commercially pure or alloyed metal, particularly the low-alloy, age-hardening nickels. With decreasing temperature below room temperature there is a marked increase in tensile strength, and a less pronounced increase in yield strength, hardness, modulus of elasticity, elongation, and fatigue resistance. The effects on the reduction in area, impact values, and compressibility are inconsistent.

Nickel, with its face-centered cubic lattice, does not show the embrittlement and abrupt change from ductile to brittle behavior with decreasing temperature that is encountered in so many ferritic materials with body-centered cubic lattices. Elevated temperatures produce softening and weakening of most metals, including nickel. The previous thermal and mechanical history affect the grain size, structure, and physical condition, including the presence of strains, all of which affect mechanical properties. For these reasons, values cited in the ensuing paragraphs are general. A comprehensive coverage of the mechanical properties of nickel is contained in a booklet published by The International Nickel Company, Inc. [86]. Slunder and Hall [311] summarized the mechanical properties of wrought nickel in various forms and conditions.

a. Tensile and Compressive Properties

The tensile strength of annealed nickel of high purity, 99.99 percent [186] and 99.94 percent [83] was reported as 46,000 psi. Brenner [312] gives a value of 1.8 percent elastic strain for nickel whiskers, which, using a modulus of elasticity of 30,000,000 psi, converts to a tensile stress of 540,000 psi. Wise and Schaefer [186] summarized the tensile strengths of commercial nickel as follows: by suitable choice of hot rolling, annealing, and cold drawing or cold rolling, tensile strengths ranging from 65,000 to 115,000 psi can be had in rods and bars, as high as 130,000 psi in strip, and 160,000 psi in wire. ASTM Specifications B160–61 for nickel rods and bars, B161–61 for pipe and tubing, and B162–61 for plate, sheet, and strip require minimum tensile strengths of 55,000 psi for annealed 99 percent nickel and 50,000 psi for annealed low-carbon (0.02% max.) 99 percent nickel, with higher values for worked material.

Studies of annealed 99.85 percent nickel, with an average grain diameter of 0.045 mm, have been reported by the National Bureau of Standards in a series of papers [313,314,315]. Figure 37, plotted from the data of Jenkins et al. [315] shows that the tensile strength of 99.85 percent nickel decreases smoothly and rapidly with increasing temperature. The value at room temperature was 51,800 psi. Small irregularities in the vicinity of the Curie temperature were reported by Zackay and Hazlett [316]. Foley [317] reported that the tensile strength of nickel increased with decreasing temperature, from 65,000 psi at room temperature to 97,500 psi at —120 °C. Additional data at temperatures down to —320 °F are given by International Nickel [86]. At this low temperature the tensile strength of annealed Nickel 200 is given as 103,000 psi. Wessel [319] investigated the tensile properties of commercially pure nickel over a wide range of temperatures. Mc-

TABLE 16. *Effect of temperature on the tensile properties of annealed Nickel 200 [86]*

Temperature	Tensile strength	Yield strength (0.2% offset)	Elongation in 2 in	Reduction of area
°F	*psi*	*psi*	%	%
Room	67,000	21,500	47.0	------------
200	66,500	22,300	46.0	------------
300	66,700	21,700	44.5	------------
400	66,500	20,200	44.0	------------
500	67,500	19,600	45.0	------------
600	66,200	20,200	47.0	------------
650	62,000	18,100	47.0	------------
700	52,500	17,000	61.5	------------
800	44,000	16,500	65.0	------------
900	37,000	15,000	66.0	------------
1000	31,500	13,500	69.0	------------
1100	26,500	11,500	72.0	------------
1200	21,500	10,000	76.0	------------
1400	14,000	7,000	89.0	------------
1500	12,200	6,300	98.5	98.5
1600	8,200	3,600	110.0	99.3
1800	5,400	2,300	198.0	99.5
2000	3,500	1,400	205.0	99.6

Clintock and Gibbons [319] reviewed the literature on the mechanical properties of materials at low temperature; their curves for nickel are reproduced in figure 38. Table 16 gives the tensile properties of annealed Nickel 200 as listed by The International Nickel Co., Inc.[86]. Their data for annealed Nickel 201 are shown in table 17.

Anker and Parker [320] reported that the tensile strength of nickel increased regularly with increasing amounts of deformation at room temperature followed by a recovery anneal at 800 °C. They believed that the hardening effect of the recovery treatment, i.e., the sharpening of the angular dislocations produced by the room-temperature deformation, was greater than the softening effect resulting from the annihilation of internal barriers. The tempera-

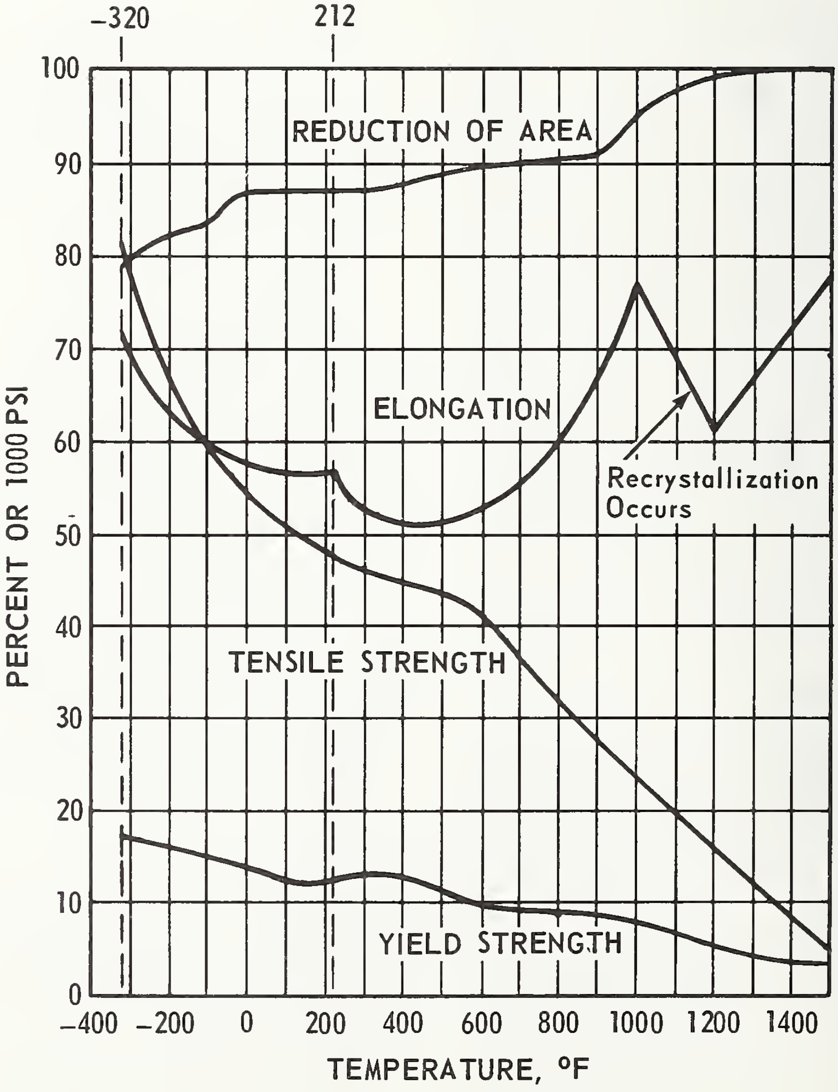

FIGURE 37. *Effect of temperature on the tensile properties of annealed 99.85 percent nickel [315].*

TABLE 17. *Effect of temperature on the tensile properties of annealed Nickel 201* [86]

Temperature	Tensile strength	Yield strength (0.2% offset)	Elongation in 2 in	Modulus of elasticity
°F	*psi*	*psi*	*%*	*psi*
Room	58,500	------------	50.0	30,000,000
200	56,100	20,700	45.0	29,600,000
300	54,000	15,700	45.5	29,100,000
400	54,000	18,000	43.5	28,600,000
500	54,000	16,200	41.0	28,000,000
600	52,500	18,700	42.0	27,400,000
700	47,000	14,000	------------	26,900,000
800	41,500	13,500	------------	26,200,000
900	37,500	13,000	------------	25,600,000
1000	33,000	12,000	------------	25,000,000
1100	27,000	11,500	------------	24,300,000
1200	22,000	9,000	------------	23,700,000

ture of heating after cold working has a marked effect on the room temperature tensile properties of nickel, as shown in table 18.

Makin [321] investigated the effect of neutron irradiation at 100 °C with 5 × 10^{19} neutrons/cm^2 on the mechanical properties of nickel over a range of temperatures; he reported a small increase in tensile strength but a large increase in yield stress as a result of irradiation. At room temperature, the tensile strength was increased about 5,000 psi and the yield strength about 25,000 psi; these increases became proportionately greater at the lower temperatures. The increase in strength was re-

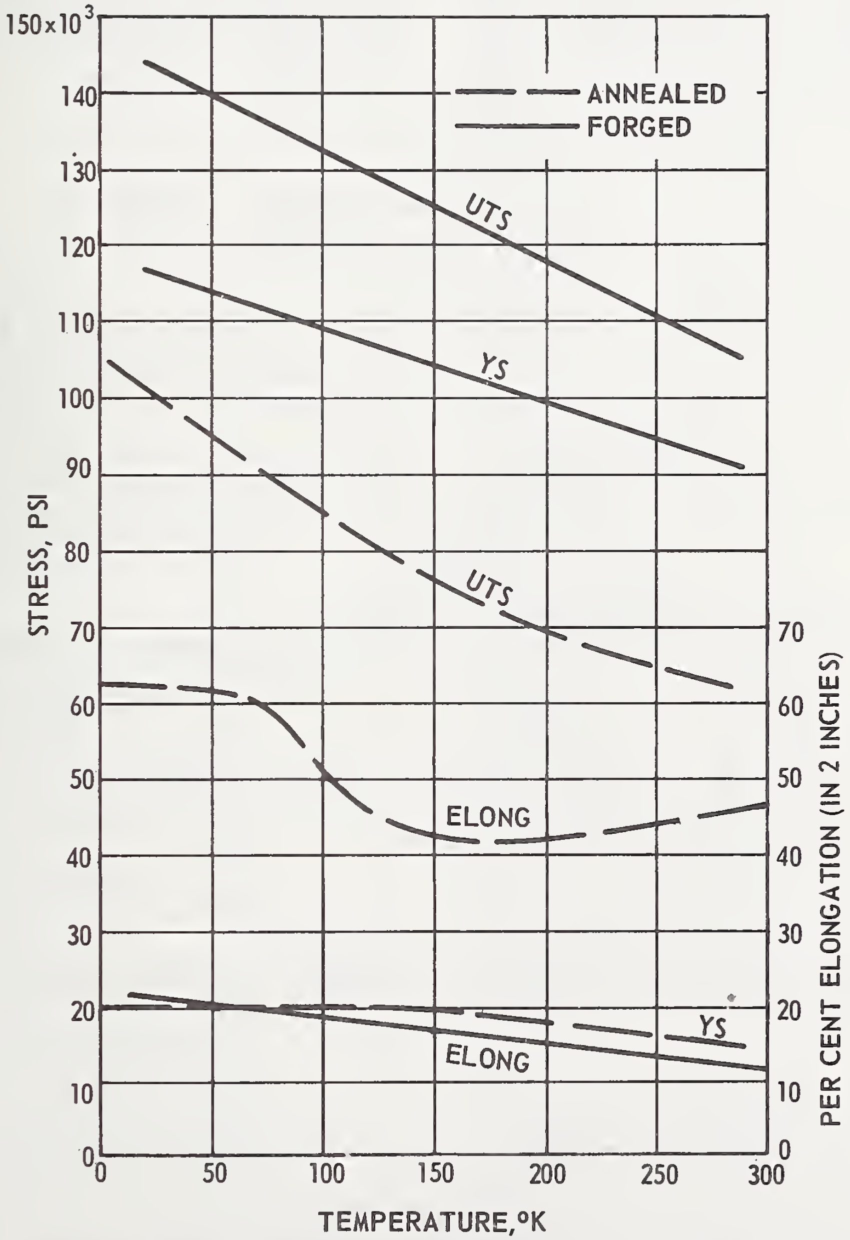

FIGURE 38. *Effect of temperature on the tensile properties of nickel* [319].

Table 18. *Effect of heating on room-temperature tensile properties of hot-rolled and annealed Nickel 200 after 22 percent stretching at room temperature* [86]

Temperature	Tensile strength	Yield strength	Elongation in 2 in	Reduction of area
	psi	*psi*	%	%
No heating	89,400 89,200	82,500 80,400	20.5 25.0	61.3 68.1
200	89,300 89,400	81,600 81,700	22.5 21.5	90.5 70.5
400	97,300 97,300	80,700 81,900	21.0 18.5	62.1 60.2
600	98,200 99,000	78,900 78,200	21.0 20.0	62.4 65.3
800	95,000 95,800	70,700 70,600	22.0 23.0	68.3 70.6
1,000	89,800 89,600	58,000 57,700	26.0 25.0	70.6 71.4
1,200	83,700 84,400	42,700 42,400	30.5 32.0	68.3 69.1

moved by annealing between 340 and 400 °C. His curves are reproduced in figure 39. Paine, Murphy, and Hackett [322] reported that, after irradiation at fast flux levels of the order of 10^{20} nvt, increases in yield strength of Nickel 200 were as high as 500 percent. Tensile strength was increased up to 70 percent. The rate of change in these properties decreased with increased radiation. For the flux levels tested, irradiation generally leaves Nickel 200 in a more ductile condition than does cold working to a comparable strength.

The yield strength of annealed 99.95 nickel, according to Wise [64] is 8,500 psi. Jenkins et al. [315] reported values of 11,100 and 12,500 psi at 75 °F for annealed 99.85 percent nickel; their data for the effect of temperature are plotted in figure 37. ASTM Specifications B160–61, B161–61, and B162–61 require minimum

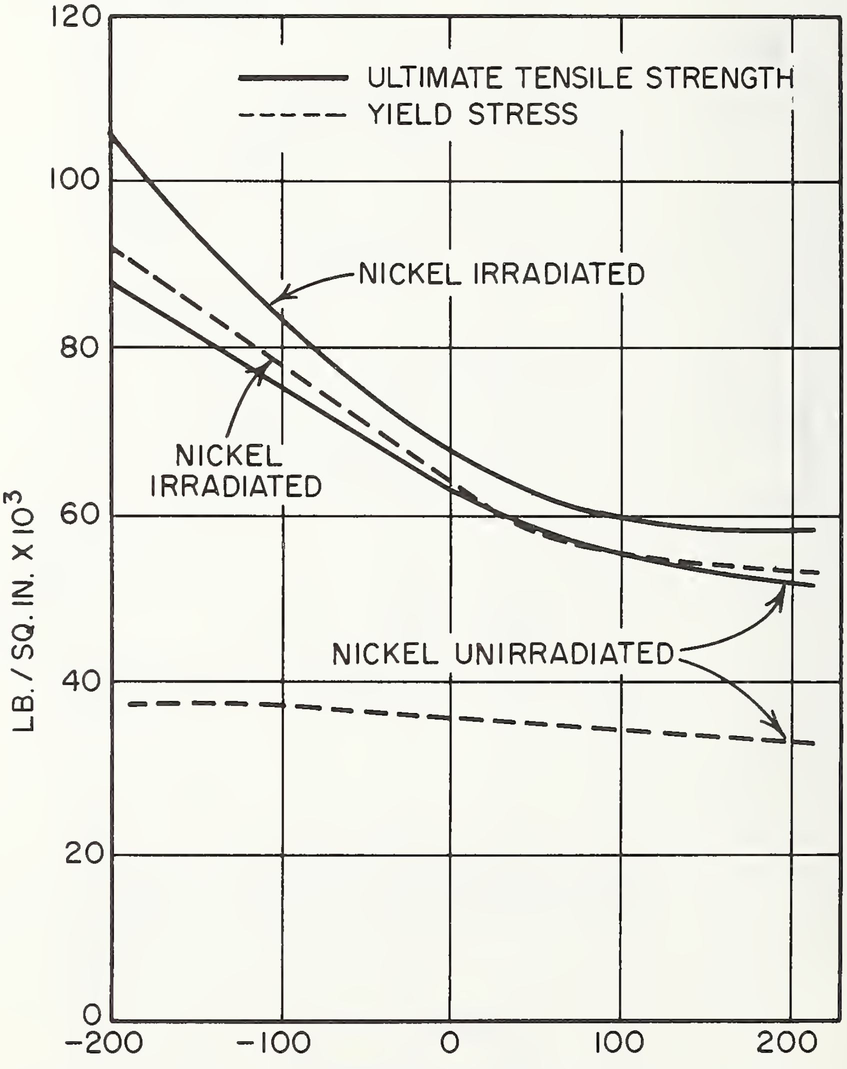

Figure 39. *Effect of neutron irradiation on the tensile properties of commercially pure nickel* [321].

yield strengths of 15,000 psi for annealed commercial nickel and 10,000–12,000 psi for annealed low-carbon nickel, depending upon the product. The effect of temperature on the yield strength of nickel is also shown in figure 38 and in tables 16 and 17.

Rosenberg [323] reported that the yield strength of cold-drawn commercial 99.4 percent nickel was 97,000 psi at room temperature and 112,000 psi at − 78 °C. Meyerson [94] quoted values for yield strength in compression (0.2% offset) of "A" nickel as 23,000 psi for hot rolled, 58,000 psi for cold drawn and stress relieved, and 26,000 psi for annealed material. Slunder and Hall [311] give the following values in compression:

	Yield strength (0.2% offset)	Proportional limit
	psi	*psi*
Hot rolled	23,000	18,000
Cold drawn 24%	58,000	41,000
Annealed	26,000	15,000

The yield point in stress-strain curves of single crystals of nickel was discussed by Haasen and Kelly [324]. The marked effect of irradiation on the yield strength has already been noted (fig. 39).

The strength of "A" nickel in double shear is given as 52,300 psi annealed, 57,550 psi half-hard, and 75,300 psi hard [149]. Data on the shear and bearing strengths of Nickel 200 are given in tables 19 and 20.

Table 19. *Shear strength of Nickel 200 bars [86]*

Temper	Shear strength (double shear)	Tensile strength	Hardness, Rockwell B
	psi	*psi*	
Annealed	52,000	68,000	46
Half-hard	58,000	79,000	90
Full-hard	75,000	121,000	100

Table 20. *Bearing strength of Nickel 200 sheet* [a] *[86]*

Condition	Tensile properties			Bearing properties		Ratio of bearing to tensile properties	
	Tensile strength	Yield strength (0.2%)	Elongation in 2 in	Ultimate strength (tearing out)	Yield strength [b]	Tensile	Yield
	psi	*psi*	%	*psi*	*psi*		
Soft	59,600	28,700	39.0	125,500	50,300	2.11	1.75
Half-hard	67,600	55,500	30.0	151,500	97,900	2.24	1.77
Full-hard	99,000	88,900	18.0	179,000	133,500	1.81	1.50

[a] 0.062 x 1.25 x 2.5 in material having a $\frac{3}{16}$ in hole at a hole center-to-edge distance of $\frac{3}{8}$ in.

[b] 2 percent enlargement of hole diameter in sheet.

b. Elastic Properties

Studies of single crystals revealed pronounced anisotropy in the elastic properties of nickel [325,326,327,328]. For example, the anisotropy factor is $2\ C_{44}/(C_{11} - C_{12}) = 2.63$, according to Bozorth [325], and values for Young's modulus, according to Yamamoto [328], are $E_{(100)} = 1.198$, $E_{(110)} = 2.008$, and $E_{(111)} = 2.592 \times 10^{12}$ d/cm². Measurements made on polycrystalline specimens with random orientation represent a balance between anisotropic values; computations made by Yamamoto [327] showed good agreement between his results obtained from single crystals, by magnetostrictive vibration methods, and measured values for polycrystalline nickel.

Average values for Young's modulus of elasticity are 30,000,000 psi for 99.95 percent nickel [64] and also for annealed "A" nickel [149]; 31,200,000 psi for cold-drawn nickel [323], and 21,500,000 psi for sand-cast "A" nickel [149]. Bennett and Davies [329] concluded, from a comparison of their own results with those of other investigators, that purity had less significant effect than thermal treatment (there was no significant difference in results from 99.97 and 99.2 nickel), that the temperature of annealing was more significant than the time, and that Young's modulus decreased regularly with increasing temperature, except in the vicinity of the Curie temperature, until the value at 600 °C was about 80 percent of the value at room temperature. The effect of temperature on the elastic modulus, according to several investigators, is shown in figure 40. Additional data are given in table 17.

Young's modulus of nickel is dependent on magnetization as well as temperature. Figure 41 [174] shows the effect of various degrees of magnetization on the modulus of nickel.

The modulus of elasticity in compression is the same as in tension, about 30,000,000 psi for all commercial forms of nickel [94].

The modulus of elasticity in torsion, also known as the modulus of rigidity and the modulus of shear, was reported as 11,000,000 psi for "A" nickel [79]; 12,000,000 psi for annealed 99.2 percent nickel and 11,600,000 psi for the same material before annealing [333]; and as 11,270,000 for hot-rolled nickel [334].

Poisson's ratio, i.e., the ratio of transverse contraction to longitudinal extension under tensile stress, is 0.31 for nickel [158].

c. Hardness

Values as low as 35 Rockwell B and 64 Vickers have been reported for the indentation hardness of annealed high-purity nickel [94]. The hardness of annealed Nickel 200 rod and bar has been given as 45–70 Rockwell B [86]. Cold work and the presence of impurities increase the hardness. ASTM Specification B162–61 for

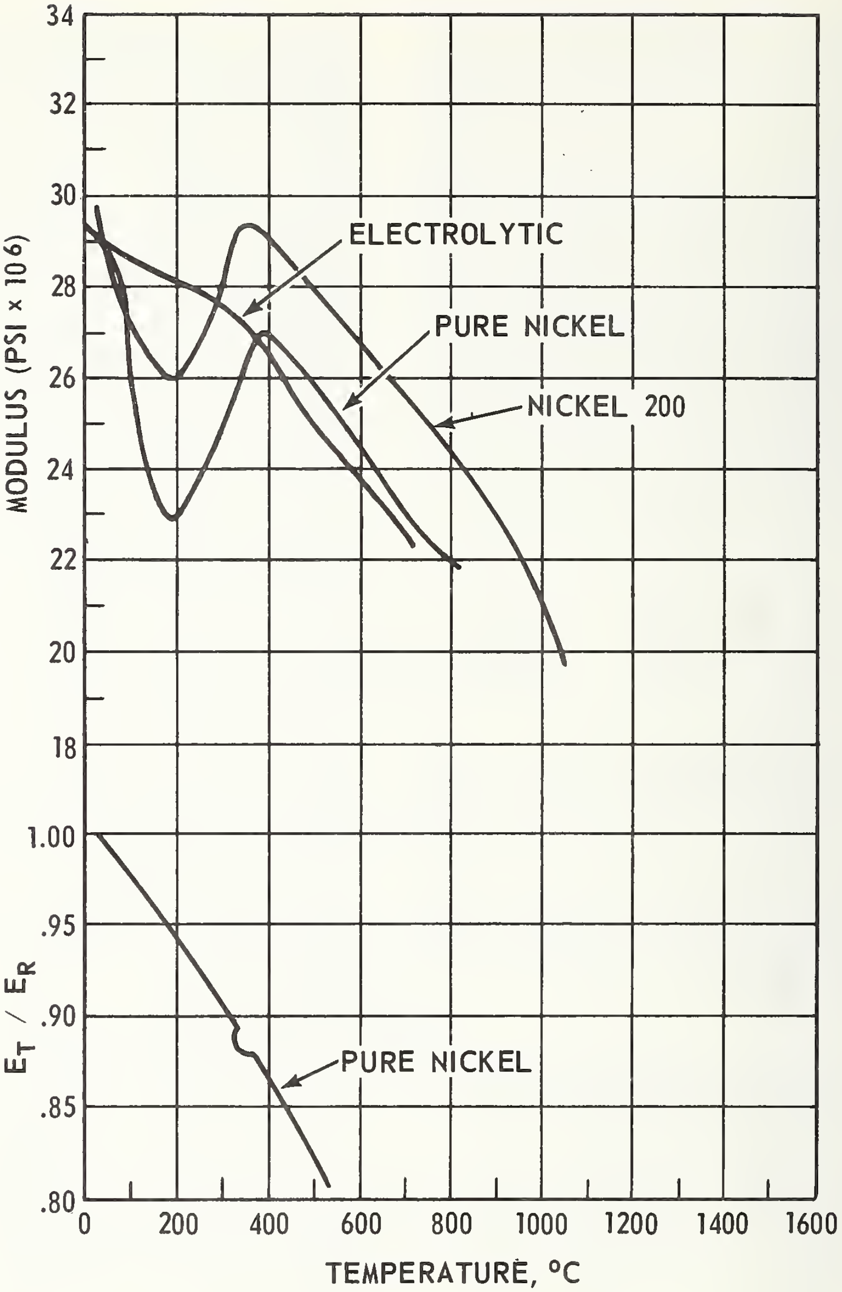

Figure 40. *Effect of temperature on the elastic modulus of nickel* [*329,330,331,332*].

nickel plate, sheet, and strips lists Rockwell B numbers ranging from 64 maximum for annealed "A" nickel (Nickel 200) and 55 maximum for annealed low-carbon nickel (Nickel 201) to 90 minimum for hard cold-rolled and 95 minimum for spring-temper cold-rolled strip. The effect of cold work on the hardness of nickel is shown in figure 42.

The hardness of electrolytic nickel as deposited ranges from 100 to 425 Vickers [335]. The effect of annealing temperature on the Vickers hardness is slight up to about 300 °C; above this temperature the hardness drops sharply as shown in figure 43.

Pile irradiation of 10^{19} nvt increased the Brinell hardness of annealed nickel by 110. The increase in Brinell hardness was smaller for partially hardened material [336].

A general relationship exists between the hardness and the tensile properties of nickel, as shown in figure 44.

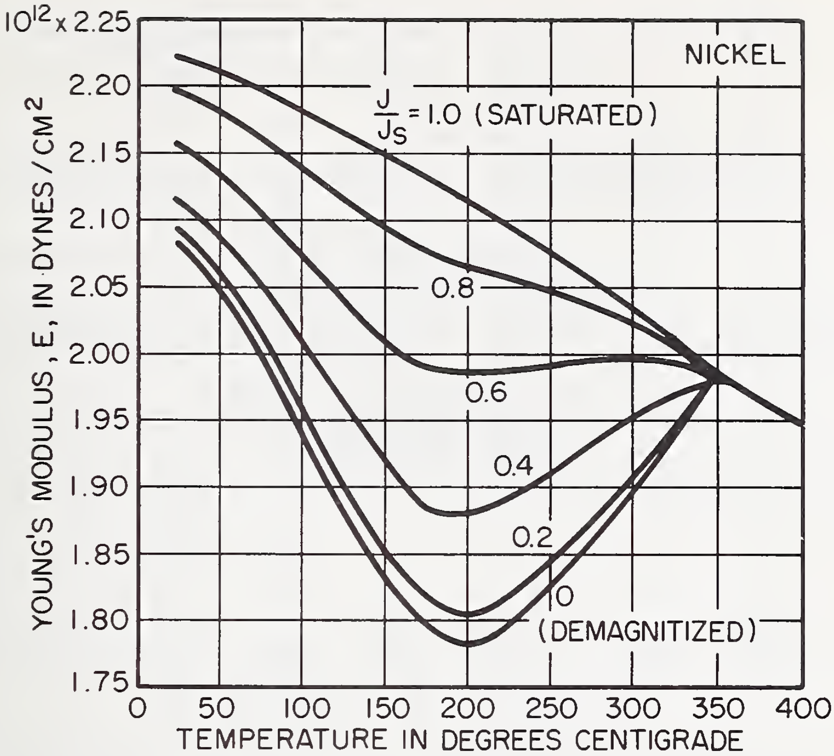

FIGURE 41. *Young's modulus of nickel as dependent on magnetization and temperature* [*174*].

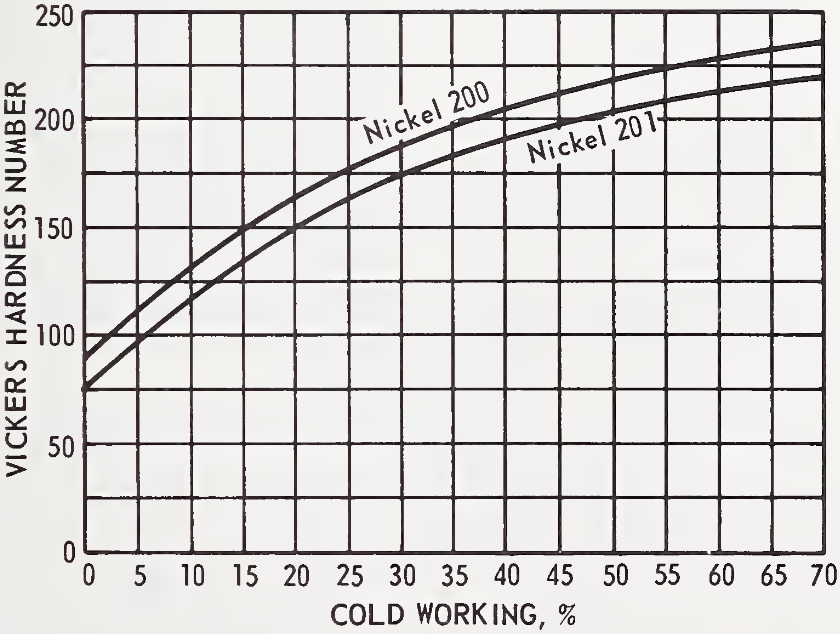

FIGURE 42. *Effect of cold work on the Vickers hardness of annealed nickel* [*86*].

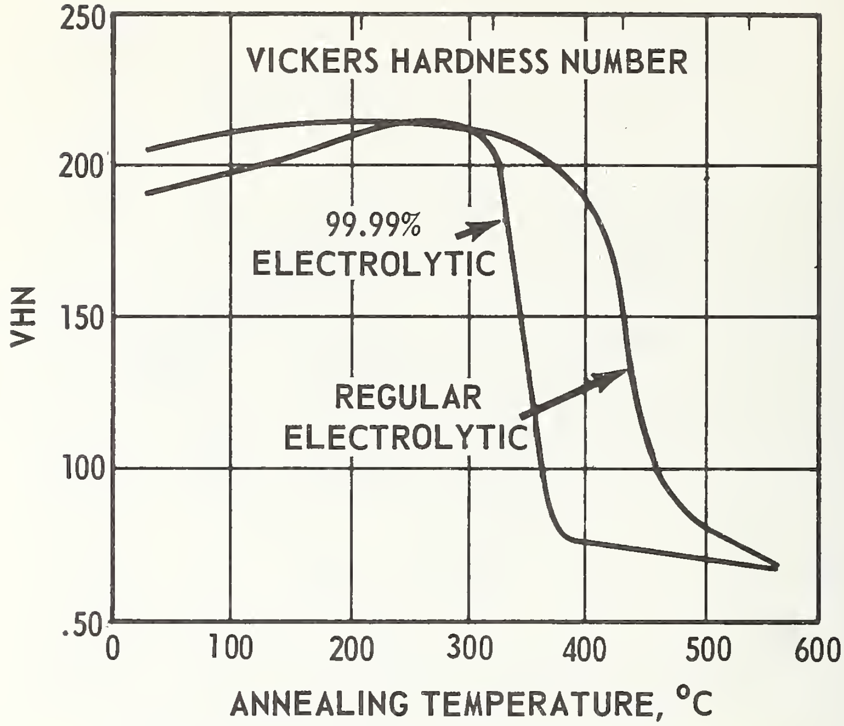

FIGURE 43. *Effect of annealing temperature on the hardness of electrolytic nickel* [*64*].

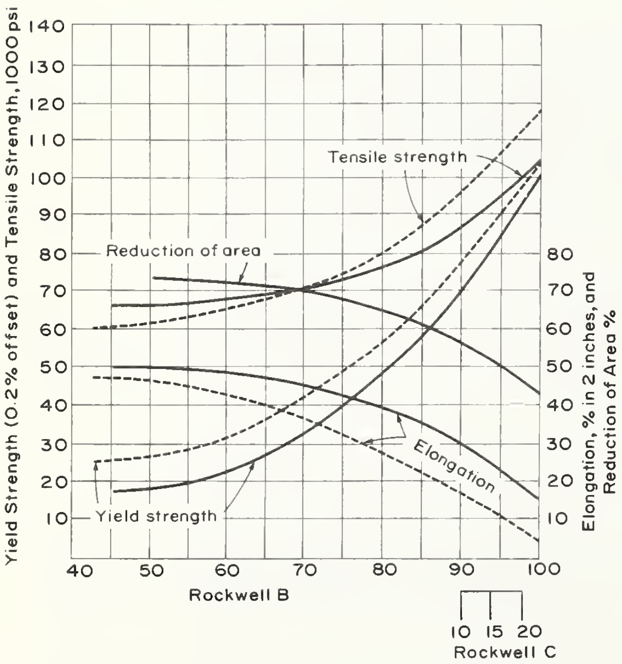

FIGURE 44. *Relationship between hardness and tensile properties of nickel 200* [*86*].

d. Impact

Nickel is an extremely tough metal as measured by the notched-bar impact test, and it maintains this toughness even at low temperatures. For "A" nickel at room temperature, Charpy values were reported as 222 ft-lb annealed, 197 ft-lb hot rolled, 195 ft-lb cold drawn, and 60 ft-lb as sand cast; Izod values were 120 ft-lb for annealed, hot-rolled, or cold-drawn material, and 85 ft-lb for sand cast [149]. Some low-temperature Charpy impact values for "A" nickel are recorded in table 21. Rosenberg [323] reported similar Charpy V-notch values for cold-drawn commercial nickel, 204 ft-lb at room temperature and 216 ft-lb at −78 °C.

TABLE 21. *Charpy impact values of 99.51 percent nickel at low temperature* [*79*]

Temperature	Hot rolled	Cold drawn	Annealed
°C	*ft-lb*	*ft-lb*	*ft-lb*
Room	195	185	216
−80	236	205	235
−190	227	210	234

McClintock and Gibbons [319] published the graph shown in figure 45 to illustrate the effect of temperature on the impact properties of commercial nickel.

Additional data on the impact properties of Nickel 200 are presented in table 22.

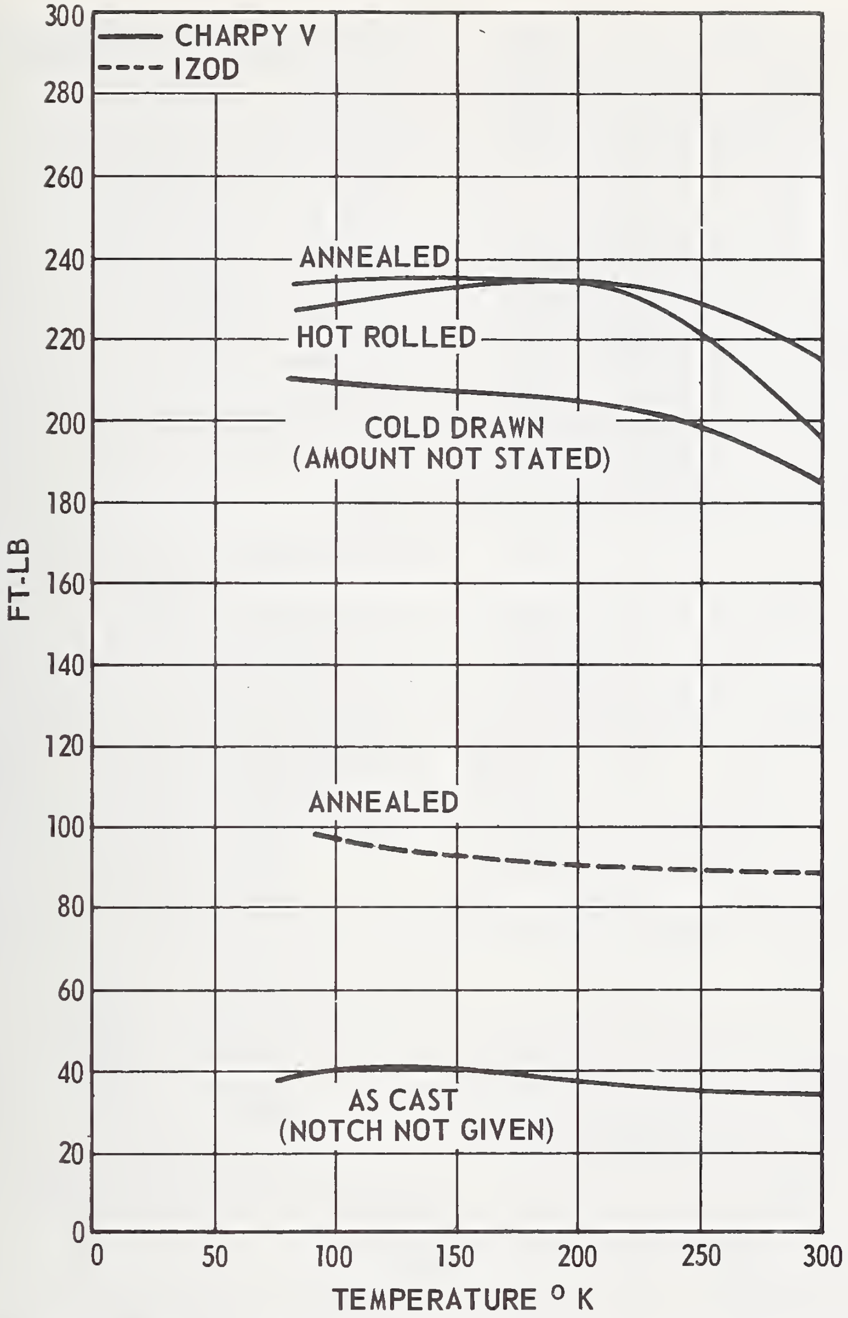

FIGURE 45. *Effect of temperature on the impact energy of commercial nickel* [*319*].

TABLE 22. *Impact values of Nickel 200* [*86*]

Condition	Brinell hardness number	Izod impact		Charpy V notchimpact	Charpy torsion		Charpy tension		
		ft-lb	ft-lb/in.^{2}	ft-lb	ft-lb	twist-degree	ft-lb	Elong. in 3.54 in.	Reduction of area
								%	%
Hot rolled	107	120	932	200	29	103½	98	20.0	83.1
Cold drawn 24% reduction, stress relieved	177	120	966	204	35	102	88	19.5	71.2
Cold drawn, annealed 3 hr at 1350 °F	109	120	980	228	29	103	113	33.0	75.1

e. Fatigue

Results for the endurance limit for 100,000,000 cycles were compiled for "A" nickel by Meyerson [94] as follows: 24,000 psi annealed, 30,000 psi hot rolled, and 42,500 psi cold drawn.

Greenall and Gohn [337] found that rolling 24-gage "A" nickel sheet to reductions of 4 or 8 B and S numbers raised the endurance limit from 25,000 to 40,000 psi. Betty [338] found that polishing the surface of a cold-drawn nickel specimen increased the endurance limit almost 50 percent. Alternate tension and compression softened cold-drawn nickel but produced strain-hardening in annealed specimens [339].

The combined effects of corrosion in several waters and fatigue on the endurance limit (10^8 cycles) of annealed "A" nickel were determined by McAdam [340] to be 21,000 to 24,000 psi in carbonated tap water, and 20,000 to 22,000 psi in brackish water, in comparison with 33,000 psi in air.

Gideon et al. [341] observed that the fatigue life of "A" nickel, at both 10^5 and 10^6 cycles, increased as the temperature decreased below room temperature. The effect of elevated temperatures and of vacuum on the fatigue life of nickel has been studied at temperatures as high as 1500 °F [342,343]. In vacuum, the fatigue strength initially increases with increasing temperature, due to greater ductility, up to 600 °C. The fatigue strength subsequently decreases and the mechanism of damage and crack initiation undergoes a transition in this temperature range due to the appearance of diffusion-controlled processes such as dislocation climb and grain-boundary sliding.

f. Creep

Creep curves for nickel, as for metals in general, exhibit three stages: an initial rapid rate of primarily elastic extension, a second stage where the combination of elastic and plastic behavior produces a low and fairly constant rate of extension, and a final stage where the extension increases rapidly until fracture occurs. Because of the complicated nature of these curves and the difficulty of deriving equations to describe such curves completely, it has been the practice to summarize the results obtained from a family of curves in terms of the stress required to produce a specified strain in a specified number of hours. Recent investigations have been concerned with the behavior in certain portions of the curves, and with the explanation of these behaviors in terms of atomic forces, dislocations, etc. [343a].

Jenkins, Digges, and Johnson [344] conducted an exhaustive study of the creep behavior of 99.85 percent nickel in tension at temperatures up to 650 °C (1200 °F). They found that discontinuous flow occurred in each of the three stages and was affected by temperature, strain rate, and prior strain history. Strain aging was especially prominent at 300 °F, producing an appreciable creep life in specimens stressed in excess of the short-time tensile strength at this temperature. The influence of stress on the average creep rate is shown in figure 46. Some of their results may be summarized as follows: at 300 °F the rate of extension in the second stage was very low for all stresses up to slightly above the normal tensile strength; at higher temperatures fracture occurred as follows:

Temperature	Stress	Time to fracture
°F	*psi*	*hr*
700	21,330	21,000
700	32,000	22
900	18,670	153
900	20,000	57
1,200	4,010	6,800
1,200	6,670	224
1,200	9,330	32

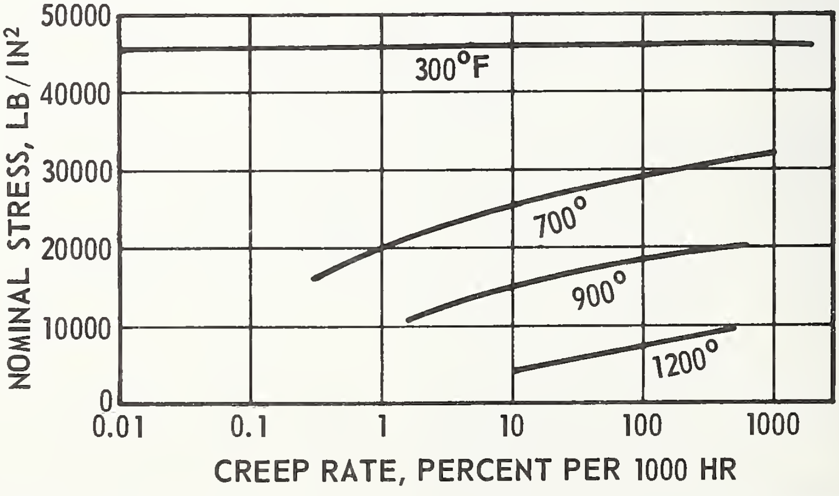

FIGURE 46. *Influence of stress on the average creep rate of nickel during the second stage of creep* [*344*].

For hot-rolled nickel rod, it was reported that at 427 °C a stress of 20,000 psi produced an extension of 0.25 percent in 1,000 hr; at 538 °C a stress of 10,000 psi produced an extension of 0.28 percent in 1,000 hr [345]. The creep of annealed nickel was studied by Jenkins and Johnson [346].

Jenkins and co-workers [347,348] found that cold drawing increased the creep resistance of nickel below the recrystallization temperature, but had little effect above that temperature. Colden et al. [349] noted that, at relatively low temperatures, internal strain induced by cold work can raise the creep strength of nickel substantially. As the test temperature increases, strain becomes less important. The recrystallization temperature is the limiting factor for improving strength by this mechanism. Davies et al. [350,351], also reported that prestrain increases resistance to creep. Yim and Grant [352] observed that the creep strength at 700 and 1300 °F of prestrained nickel appears to be related to the arrangement and density of preinduced dislocations. The greater the dislocation density, the stronger was the nickel during creep. In contrast to tensile prestrain, compressive prestrain decreases both the creep resistance and fracture life [353]. Davies [354] reported that in pure nickel the creep rate in compression at 500 °C was between two and three times as rapid as in tensile creep at the same stress.

Weertman and Shahinian [355] measured minimum creep rates of nickel in the stress region 2.5×10^7 to 2.8×10^9 d/cm^2 in the temperature range 400 to 1100 °C. They reported that the creep rate appeared to be proportional to the 4.6 power of the stress at stresses below 7×10^8 d/cm^2 and that the activation energy of creep is approximately 65,000 cal/mole. Landon, et al. [356], reported that the activation energy for creep increased with rising temperature from a low value of about 3,000 to 5,000 cal/mole at 78 °K (−195 °C) to that for self-diffusion at the highest temperatures.

The effect of environment on the creep of nickel has been studied extensively [357,358, 359,360,361,362]. The stress-rupture life at 1500 °F was slightly less in sodium hydroxide than in argon, and somewhat less in argon than in air [357]. At low rates of strain and at high temperatures, the strength of nickel was higher in air than in vacuum; at high strain rates and low temperatures the strength was higher in vacuum [358]. It was found that at high temperatures an oxidizing atmosphere gave the highest strength but that it gave a lower strength at lower temperatures [360]. It was also reported that the strength in nitrogen was lower than in vacuum [360]. Cass and Achter [361] explained the higher strength in oxidizing atmospheres as being due to an oxide bonding.

Dennison and Wilshire [363] found that both the creep resistance and rupture life of nickel increased with decrease in purity.

g. Ductility

Values for elongation and reduction in area are the usual indications of ductility, with certain other determinations to show ductility or deformability under particular conditions. Nickel, being a face-centered metal, is inherently ductile. Tensile tests have shown high-purity nickel to have elongation in 2 inches of 56 percent at room temperature and 72 percent at −320 °F [315]; corresponding values for reduction in area were 88 percent and 78 percent; true strain at complete fracture was 2.173 and 1.543. Additional values for elongation and reduction of area are shown in tables 16, 17, 18, and figure 44.

The amount of cold work that may be done without intermediate annealing is indicated by the Olsen (Erickson) test. Using a ⅞-in diam ball and a 1⅝-in diam die, the following values were reported for nickel [86]:

Thickness	Condition	Depth to fracture	Load to fracture
		in	*lb*
0.062	Annealed	0.650	10,000
.062	Hard	.325	7,000
.031	Annealed	.500	3,400
.031	Hard	.300	3,000

Kramer and Macklin [364] reported that subzero ductility of nickel decreases linearly with increase in prior strain history.

Ellis [365] determined the malleability of cold-drawn nickel rods at various temperatures by measuring the reduction in height caused by forging blows of known energy. His results showed that the malleability increased slowly up to 600 °C and rapidly thereafter up to 1,100 °C, with irregularities at about 850 °C. In the practice of the International Nickel Company, the temperature range for hot rolling and hot forging is 650 to 1260 °C. Brittleness at elevated temperatures has been shown to be due to minor amounts of sulfur [366, 367].

Bridgman [368] reported that nickel remained ductile under pressures up to 30,000 kg/cm^2.

The flexure of nickel wire was determined by MacBride [369] by cantilever tests in a Tour-Marshall tester. The results showed that the load to produce a given angular deflection increased progressively with cold-drawing 1 and 3 B&S numbers, and that this stiffening effect was reduced by annealing at 500 °C and eliminated by annealing at 700 °C.

h. Friction

The coefficient of friction in rubbing contact was reported by Tichvinsky [370] as follows: With nickel as the moving contact, the coefficient with nickel was 0.53, with glass 0.56, and with mild steel 0.66. With nickel stationary and mild steel moving, the coefficient was 0.49. Tamai [371] found the coefficient of friction of nickel on nickel to be 0.60.

Simon et al. [372] determined the coefficient of static friction of two unlubricated surfaces of nickel as 0.51 at 4.2 °K (liquid helium) and 0.65 at 77 °K (liquid nitrogen). Higher values were obtained in vacuum, 0.82 at 4.2 °K, 0.77 at 77 °K, and 0.69 at 300 °K. The results were cited as substantiating the adhesion theory of friction.

2.4. Effect of Minor Constituents on Properties

In general, minor constituents or impurities that exist in solid solution in nickel tend to increase the hardness, strength, and electrical resistivity, decrease the thermal expansion and thermal conductivity, and except for iron and cobalt, lower the Curie temperature. According to Kornilov [373], nickel will form solid solutions with elements whose atomic radii differ from that of nickel by not more than 11 percent. Impurities that are present in excess of the solid solubility in nickel chiefly affect the workability, particularly the hot workability, and may affect the resistance to corrosive attack. When impurities or alloying elements are deliberately added to produce specific effects, the product is technically an alloy even though the alloy content is small, for example, in the age-hardening nickels or high-sulfur shot.

a. Carbon

Carbon exists in nickel in solid solution or as graphite formed by the decomposition of the carbide, Ni_3C, which exists at temperatures above 1500 °C but is exothermic and unstable. The solubility of carbon in nickel is as follows [136,374]:

0.03 w/o at 500 °C
.14 w/o at 780
.245 w/o at 1,030
.65 w/o at 1,318 (the eutectic temperature).

The solubility of carbon in liquid nickel is given by Elliott [375] as follows:

12.5 a/o at 1,550 °C
11.9 a/o at 1,500
10.9 a/o at 1,450
9.5 a/o at 1,350
8.9 a/o at 1,314 (which he gives as the eutectic temperature).

The diffusion coefficient of carbon in nickel ranges from 4.0×10^{-9} cm^2/sec at 727 °C to 4.1×10^{-7} at 1,020 °C [136].

Carbon in solid solution in nickel increases the ease of hot working because of increased toughness and lower susceptibility to edge cracking at these temperatures. However, the initial hardness, strength, and tendency to work harden, as a result of the presence of carbon, increase the difficulty of cold working. The low-carbon malleable nickel (Nickel 201) was developed to facilitate spinning and deep drawing operations.

Small amounts of carbon do not appreciably affect the Curie temperature [374], but the diffusion of even small amounts of carbon in nickel is of interest in the activation of thermionic oxide-coated cathodes [136]. The malleability of nickel is adversely affected by the presence of graphite or carbon in excess of the solid solubility.

b. Cobalt

The great bulk of nickel, i.e., nickel produced from Canadian ores by processes other than the carbonyl process, has had an average cobalt content of about 0.5 percent. Such amounts of cobalt produce slight increases in electrical resistivity and in the Curie temperature but otherwise have no appreciable effect on the properties of nickel. Consequently, it has been the accepted commercial practice to count the cobalt as nickel and to express analytical results in a single value for nickel plus cobalt. The current demand for cobalt, and the development of improved processes for recovering nickel from its ores, have resulted in lowering the average content of cobalt in nickel to about 0.1 percent, from the 0.5 percent which had previously represented the practical economic limit of separation of nickel and cobalt in commercial production.

It has been reported [376] that cobalt increases the oxidation rate for nickel but the effect is small below 11 percent of cobalt.

c. Copper

Copper usually is present in nickel in amounts less than 0.1 percent and such amounts do not have a noticeable effect on the properties.

d. Iron

Iron is present in commercial nickel either because it was present in the ore, or because of contamination from iron equipment during the recovery and refining processes. The iron content of electrolytic cathodes usually is less than 0.05 percent, whereas melted electrolytic nickel and the malleable nickels may contain up to 0.25 percent. Such amounts of iron have no appreciable effect on the properties of nickel.

e. Magnesium

Magnesium was the first metal used to control the harmful effects of sulfur and it is still important for this purpose. It has the indirect effect, through fixing of sulfur by the formation of the high melting point compound MgS, of increasing the ductility of nickel and of decreasing the tendency for hot shortness.

f. Manganese

The equilibrium diagram of the nickel-manganese system according to Lacy [377] indicates a solubility of at least 20 percent of manganese in solid nickel.

In the production of malleable nickel, small amounts of manganese and magnesium are added to combine with the sulfur present as nickel sulfide, and thereby to improve the malleability, surface characteristics, and appearance of ingots. Additions of manganese in excess of the requirements for sulfur fixation mildly increase the strength and hardness without appreciable effects on the ductility, increase the resistance to oxidation, and decrease the susceptibility of nickel and its alloys to damage from sulfur in the fuels used to heat these materials for hot-working and heat-treating operations.

Additions of 10 to 20 percent of manganese markedly increased the electrical resistance of annealed nickel [378]. Ten percent of manganese lowers the Curie temperature to about 200 °C, as shown in figure 25. In the common commercial alloys, each percent of manganese up to 15 percent reduces the density of nickel by about 0.02 g/cm^3.

g. Oxygen

Oxygen is the only gaseous element that has any significance in nickels that have been melted. Electrolytic nickel, as deposited, contains variable amounts of hydrogen and other gases, which contribute to the hardness and brittleness of some electrodeposits, but these gases are greatly diminished by heat treatment and disappear on melting, particularly when melting is done under oxidizing conditions.

Oxygen is soluble in molten nickel in increasing amounts as the temperature rises above the melting point. According to Wriedt and Chipman [266], the solubility is 0.294 w/o of oxygen at 1,450 °C and 1.63 w/o at 1,691 °C. The presence of oxygen lowers the melting point of nickel progressively until the eutectic composition (0.22% of oxygen) is reached, with a melting point 20 °C lower than that of pure nickel [379]. According to Seybolt [380], the solubility of oxygen in solid nickel is exceptional in that it increases with decreasing temperature as follows:

0.012%	at 1,200	°C
.014	at 1,000	
.019	at 800	
.020	at 600	

Oxygen has little effect on the properties of nickel, even when it is present in amounts in excess of the solid solubility. Merica and Waltenberg [381] showed that nickel may contain up to 1.1 percent of nickel oxide and still be malleable hot or cold. Agents such as titanium and boron may be added to correct the minor effects on the malleability of oxides and of gases such as carbon monoxide, nitrogen, and hydrogen. Nickel oxide, which is readily detectable microscopically, may be encountered in nonmalleable nickels, such as shot for alloy additions, but is generally eliminated in the preparation of malleable nickels.

h. Silicon

Additions of silicon lower the melting point of pure nickel until the eutectic composition (about 11.5% of silicon) melts at 1,152 °C. The solubility of silicon in solid nickel decreases with decreasing temperature from 9.3 percent at 1,125 °C to about 6 percent at 600 °C [382].

Silicon is present in furnace-melted nickels, up to 0.10 percent in electrolytic shot, and up to about 0.25 percent in some of the malleable nickels. Age-hardening nickels contain up to 0.50 percent of silicon, and casting nickels contain up to 1.5 percent. The amounts of silicon present in the malleable and electrolytic nickels have little, if any, effect on the properties, but amounts in excess of 1 percent increase the hardness and stiffness, and reduce the malleability. According to Okamoto and Iwase [383], 1 percent of silicon lowers the Curie temperature from 362 to 320 °C and 6 percent lowers it to —45 °C.

i. Sulfur

Sulfur lowers the melting point of nickel; the eutectic composition (21.5% of sulfur) melts at 644 °C [384]. The solubility of sulfur in solid nickel is about 0.005 percent [381]. Amounts in excess of the solid solubility exist as sulfides which can be identified by metallographic procedures [385].

The only property of nickel that is appreciably or seriously affected by the amounts of sulfur ordinarily present is the malleability, both hot and cold. The brittleness of nickel encountered in the very early days of the industry, and the discovery by Fleitman in 1879 that additions of manganese and magnesium improved the malleability of nickel, were explained by Merica and Waltenberg [381]. These investigators found that sulfur, if present in excess of about 0.005 percent, formed grain-boundary films of nickel sulfide or the low-melting eutectic of nickel-nickel sulfide. Additions of manganese converted the films of nickel sulfide to globules or particles of manganese sulfide. These particles often occurred in grain boundaries; however, additions of manganese did have a moderately beneficial effect on hot and cold malleability. Additions of magnesium caused the formation of magnesium sulfide particles, which because they had a higher melting point than that of nickel, were distributed randomly throughout the microstructure and thereby caused a marked increase in hot and cold malleability. In modern practice manganese is added to nickel that has been treated with magnesium to enhance hot workability and to extend the hot-working range.

In adition to residual sulfur from the original ore, sulfur may be present in nickel because of reaction with sulfur gases, particularly sulfides and reducing compounds, in heat treatment and annealing operations.

2.5. Technology

Much of the industrial working and fabrication of nickel is closely parallel to the operations performed on steel. The information in the following paragraphs is based on articles, as indicated in the text, which should be consulted for information about nickel alloys and for more detailed information about nickel.

a. Melting and Casting

Nickel may be melted in electric, oil, or gas-fired furnaces, but coke-heated pit melting is not recommended because of possible contamination by sulfur. For small melts, the nickel is melted under a thin limestone slag, with additions of nickel oxide and carbon to cause a boil to eliminate gases. When the solidification characteristics of a small sample show that the boil has been effective, the metal is killed with silicon, the carbon content is adjusted, manganese is added, and the melt is allowed to remain quietly in the furnace to allow entrapped oxides to rise to the slag. After final deoxidation in the ladle with silicon and magnesium, the metal is poured at temperatures between 1,500 and 1,600 °C, depending upon the size of the casting and the type of mold. Pattern equipment should provide for a linear shrinkage of ¼ in/ft and gates and risers should be larger than those used for steel [386].

Large melts, in the range from 9,000 to 23,000 lb, are usually made in acid-lined open hearth or basic electric furnaces. In the open hearth, no slag is added intentionally but some is formed from the silica-alumina refractories. In basic electric furnace melting, small amounts of lime and fluorspar are added early in the heat to avoid excessive oxidation during melt-down and to minimize gas pickup from the furnace atmosphere. Carbon and nickel oxide are added to produce a degasifying boil after which the carbon content is adjusted, manganese is added, and final "deoxidation" is carried out in the ladle by additions of titanium, boron, and magnesium. The metal is then poured into cast iron molds equipped with hot tops, to produce standard ingots approximately 18 in sq by 40 in long and 4,600 lb in weight, or larger ingots up to 14,000 lb for large forgings or heavy plates. Special grades of nickel, for example, for electronic applications or for oxidized or carbon-bearing anodes for the electroplating industry, are produced by modifications of the forgoing procedure [387, 388].

b. Hot-Forming (Forging, Rolling, Extrusion)

After suitable treatment to remove surface defects, the ingots are reheated in furnaces fired by low-sulfur fuels. Natural gas, low-sulfur city gas, propane, and butane are desirable fuels; oil is generally used in the larger operations. The furnace atmosphere should be sulfur-free and always slightly reducing; fluctuation between reducing and oxidizing conditions is most harmful. The temperature range for good forging of nickel is between 870 and 1,160 °C, with heavy forging and drop forging operations carried on in the upper two-thirds of this range and light forging in the lower third [389].

Hot-rolling of nickel usually starts at about 1,150 °C. Finishing temperatures vary with the dimensions of the product, but nickel generally can be hot-worked to 650 °C, or even lower temperatures. Rolling mills of the same design as for rolling steel are suitable for rolling nickel [387].

Extrusion of nickel and high-nickel alloys requires more power than that normally used for the softer extrudable alloys because of the high strength and resistance to deformation, and the narrow range of temperature in which plastic deformation can be accomplished. Barclay [390] 20 years ago pointed out that pressures for extrusion of nickel might be 30 to 50 percent higher than for copper alloys, even when a heated container was used. Nevertheless, Betteridge and Cound [391] reported that the extrusion of bars of nickel, Monel nickel-copper alloys, and the softer alloys had been carried on for many years, and that extrusion of the harder alloys had been facilitated by the use of glass as a lubricant. ASTM Specification B161–61, Nickel Seamless Pipe and Tubing, states that hot-finished (extruded) tubing is available in some of the sizes provided for in the specification (up to 8⅝ in O. D. with wall thicknesses up to ½ in).

c. Cold-Forming (Drawing, Shearing, Punching, Spinning)

The equipment and procedures used for cold-forming nickel resemble those used for similar operations on steel.

In drawing operations, gray cast semisteel dies give good results on high-nickel materials for comparatively short runs of a few hundred pieces. However, these die materials are comparatively soft and consequently wear rapidly, which makes them unsuitable for precision work or large production runs without frequent redressing. Satisfactory die materials for steady production are hard alloy bronze, heat treated nickel chromium cast iron, chromium plated hardened steel, and tungsten carbide [392,393]. New dies or punches, when required, should be made from these materials rather than from plain carbon steel because nickel and high-nickel alloys have a strong tendency to gall against carbon steel. Dies and punches should be kept smooth at all times [392].

It requires more power to form the high-nickel materials than is required for aluminum or brass, so die components should be designed for greater strength.

Beef tallow and castor oil are satisfactory lubricants; so also are water-soluble oil or oil-soluble lubricants compounded in correct balance from these two substances. In general, pigmented type lubricants are preferred [392]. Lubricants containing lead or sulfur should generally be avoided, and should never be used if the pieces being pressed are to be annealed. For that matter, any lubricant, regardless of its nature, should be removed thoroughly before annealing.

Monel nickel-copper alloys, nickel, and Inconel nickel-chromium alloys require better lubricants than the light oils and thin soapy solutions frequently used on steel and the softer metals. The high-nickel materials do not form thin oxide films, such as are found on steel sheets, which prevent actual metal-to-metal contact, and allow the steel to flow between the die and pressure plate with relatively low frictional resistance. Copper flashing the surface of materials gives added lubrication for drawing operations but material so prepared is used only for difficult jobs. To reduce to a minimum the factors conducive to galling, lubricants with high film strength, lubricity, and wetting characteristics are required. Most of the satisfactory lubricants contain a filler of some inert material.

In drawing wire, tungsten carbide dies are used for all sizes down to 0.032-in wire and diamond dies are used for sizes smaller than 0.032-in diameter [394]. Lubricants for drawing the softer materials are flour, hard soap, and tallow; harder alloys, for example, nickel-chromium and nickel-chromium-iron alloys, may be lead coated or copper flashed prior to drawing. Mineral oil is a satisfactory lubricant for fine sizes, and water-soluble oil for superfine sizes [391].

The shearing of high-nickel alloys in sheet and plate form requires slightly more power than is needed for shearing soft steel of the same thickness. Although the additional power requirement is real, neither it nor the strength of the shear need be considered unless the job involved is close to the capacity of the equipment.

Monel alloy 400, Nickel 200, and Inconel alloy 600 sheet may be perforated to practically the same limits of hole diameters for various thicknesses of sheet as are considered commercial for soft steel, as indicated in table 23.

Table 23. *Relation between thickness of sheet and minimum permissible hole diameter for punching Monel alloy 400, Nickel 200, and Inconel alloy 600* [392]

Thickness of sheet	Approximate minimum diameter of hole
0.018 to 0.034 in, incl.	Sheet thickness x 1.5
.037 to .070 in, incl.	Sheet thickness x 1.3
.078 to .140 in, incl.	Sheet thickness x 1.2
5/32 in and heavier	Sheet thickness x 1.0

In spinning operations, the strength and work-hardening tendency of nickel require more power and more frequent annealing than are required for most of the nonferrous metals generally spun. Broad, flat, tools, preferably made of hard alloyed bronze, are recommended. Yellow soap, beeswax, or tallow lubricants should be removed prior to annealing.

d. Welding, Brazing, Soldering

Nickel and high-nickel alloys can be welded by most of the fusion and resistance welding processes. The manual metal-arc (covered electrode) and the MIG processes are most widely used for joining heavy sections and making overlays but the TIG process has nearly replaced gas welding for joining sheet thicknesses. When properly made, the as-welded joints are equal to the parent metal in strength and resistance to corrosion and only in the case of age-hardening alloys is a post-weld heat treatment needed to develop full strength. All foreign matter should be cleaned from the joint area prior to welding. Arc-welded nickel joints have an average tensile strength of 70,000 psi with minimum elongation of 30 percent, whereas gas-welded joints show an average tensile strength of 60,000 psi with 35 percent minimum elongation [395]. See also Pease [396]. The welding of nickel and nickel alloys, and welding materials, has been described in publications of the Huntington Alloy Products Division of The International Nickel Company, Inc.[397,398,399].

Spot, seam, and flash resistance-welding of nickel and high-nickel alloys is much the same as for steel, with allowance for the differences in electrical and thermal conductivities.

Nickel and its alloys may be brazed with commercially available silver brazing alloys. Fluxes are required for torch brazing and may be used in furnace brazing depending on furnace atmosphere. Special care must be exercised to prevent overheating with brazing alloys containing phosphorus and cadmium. The use of boron-containing brazing alloys is restricted to joints in heavier sections.

Soldering can be effectively used to join nickel to itself and to other alloys. A relatively high-strength solder is preferred and the joint should be so designed that the solder is not depended upon for structural strength. Solder is frequently used to seal riveted, lock-seam, or spot-welded joints. An acid-base flux yields best results. Useful booklets describing the brazing and soldering of nickel and high-nickel alloys are available [400,401].

e. Annealing

In all annealing operations of nickel, the furnace atmosphere should be free from sulfur compounds and should not fluctuate between oxidizing and reducing conditions because nickel alloys are sensitive to attack by sulfur and oxygen at elevated temperatures. Open annealing usually requires subsequent cleaning or pickling, whereas a bright surface results from box or pot annealing and from open annealing in controlled neutral or slightly reducing atmospheres.

A list of satisfactory and unsatisfactory heat sources for annealing are as follows [392]:

Satisfactory	Unsatisfactory
Electric	Coal
Acetylene	Coke
Natural gas	High sulfur oil
Butane	Unwashed producer gas
Propane	Unwashed blast furnace gas
Washed producer gas	Any fuel with sulfur over 0.5%
Washed blast furnace gas	
Oil with sulfur under 0.5%	Gas containing more than 30 grains of sulfur per 100 cu ft

The three types of annealing treatments given nickel and its alloys are (1) stress equalizing, (2) stress relieving, and (3) complete annealing.

The stress-equalizing anneal for work-hardened nickel and high-nickel alloys is carried out at low temperatures (525 to 900 °F), depending upon their composition [402]. This low-temperature treatment does not produce softness or any visible change in microstructure, but it does equalize, balance, or homogenize the principal residual stresses. The optimum temperature for such equalization depends upon the manner in which the metal or alloy has been work hardened. Cold-worked materials, possessing greater intrinsic energy than hot-worked materials, can be stress-equalized at a lower temperature. This thermal treatment effects what is known as a partial recovery. This recovery consists of a considerable increase in proportional and elastic limits, a slight increase in hardness and tensile strength, no significant change in elongation and reduction of area, balancing of internal stresses, and return of electrical conductivity towards its characteristic value for the metal or alloy in the annealed condition.

The stress-relieving anneal requires moderate temperatures, 1000 to 1300 °F, for cold-worked and hot-worked nickel and high-nickel alloys, depending upon their composition. The purpose of this treatment, sometimes referred to as temper annealing or partial annealing, is to reduce or relieve the internal macrostresses that exist in the metal as a result of cold-working, machining, casting or welding operations.

Complete annealing (sometimes termed soft annealing, or just annealing) is applied to metals and alloys that have been hardened by cold-working operations such as rolling, drawing, spinning, bending, etc., and which require softening before further cold work can be continued. The temperatures required are high (1400 to 2000 °F), depending upon the alloy. This anneal will soften the cold-worked structure by effecting recrystallization, sometimes accompanied by grain growth. In age-hardenable alloys, annealing will effect softening by dissolving the secondary precipitated phases and keeping them in a supersaturated solid solution by rapid cooling from the annealing temperature. This type of anneal is more properly called a solution heat treatment. A complete anneal is the only thermal treatment that will completely relieve both macro and micro internal stresses existing in a metal or alloy.

Figure 47 is a schematic representation of the effect of annealing temperature on cold-worked metals and alloys.

It must be recognized that time, as well as temperature, is important during annealing

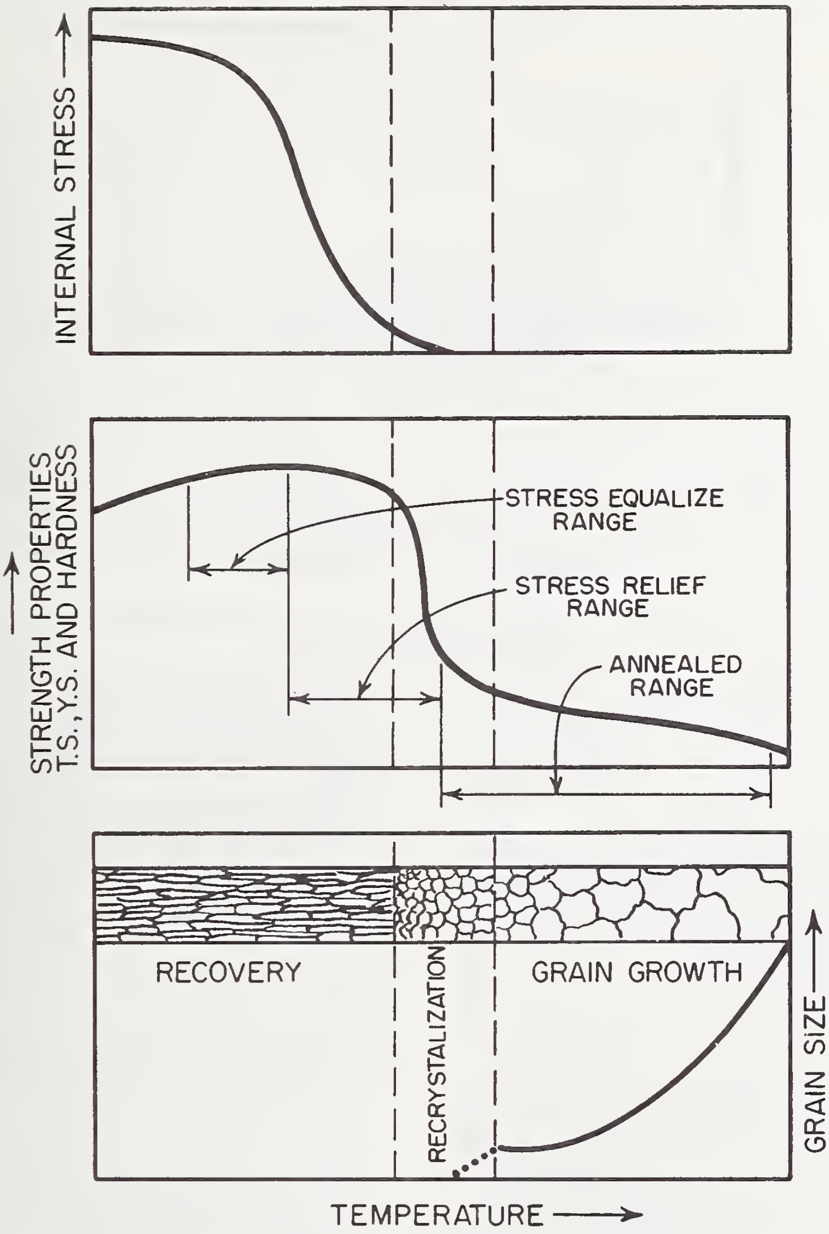

FIGURE 47. *Schematic representation of effect of temperature on cold-worked metals and alloys* [*402*].

operations. Within certain limits, the same results may be obtained at lower temperatures with longer periods of time as are obtained at higher temperatures with shorter periods of time. The relationship between time and temperature during annealing of cold-worked nickel is shown in figure 48.

f. Pickling

The resistance of nickel to corrosion makes its pickling more difficult than that of iron, carbon and low alloy steels, or copper alloys. Oil and grease must be removed by appropriate procedures prior to pickling, and discolorations from the presence of residual lubricants may be removed by proprietary chemical solutions or by soaking in a cold solution of 10 percent by volume sodium cyanide.

All the various pickling baths for nickel and its alloys contain acid [403]. After pickling, the metal should be rinsed in hot water and the acid neutralized in a 1 to 2 percent (by volume) ammonia solution.

Pretreatment baths of fused salts have been developed to aid in the pickling of many alloys. They are particularly effective in handling nickel-chromium and nickel-chromium-

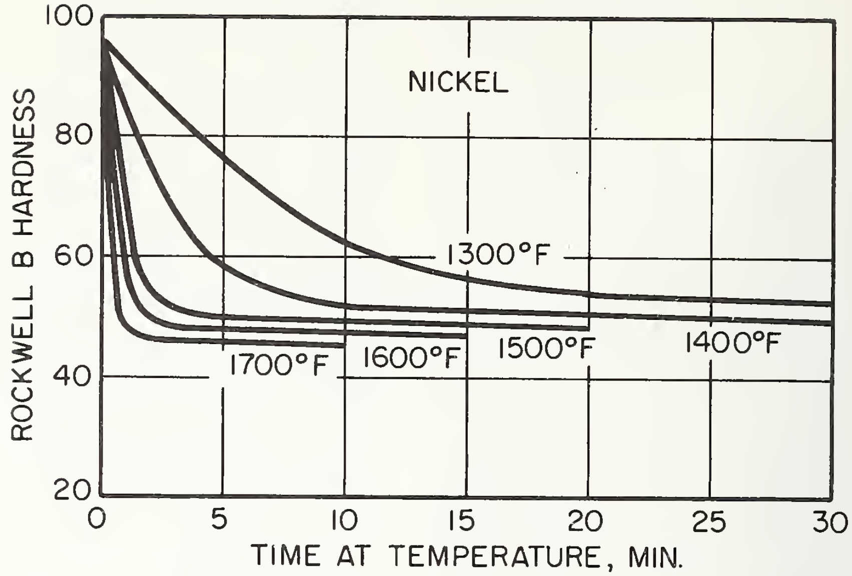

FIGURE 48. *Effect of time at various annealing temperatures on the hardness of cold-worked nickel* [*402*].

iron alloys and their use for this application is strongly recommended. These baths are patented and the manufacturer should be consulted regarding their use. There are two types, reducing and oxidizing. The sodium hydride process (E. I. duPont de Nemours and Company, Inc.) and the two Kolene processes (Kolene Corporation) are reducing processes. The Virgo process (Hooker Chemical Corpotion) is an oxidizing process.

Light oxide films may be removed by electrolytic pickling [403].

g. Machining

The tools, lubricants, etc., used in machining nickel are similar to those used for steel. Details of tool design and the procedures for various machining operations (turning, drilling, broaching, threading, reaming, planing, tapping, cutting, milling, and grinding) are described in a booklet by The International Nickel Company, Inc. [404]. This booklet also describes electrochemical machining (ECM), electrical discharge machining (or spark erosion), chemical milling, electron-beam machining, plasma-arc cutting and welding, ultrasonic machining, cold machining, and hot machining.

h. Grinding, Polishing, and Buffing

For heavy grinding, where the finish is not important, grinding wheels of No. 14 and 24 grit should be used and finer wheels, for example, No. 36 grit, may be used when better finishes are desired.

Various operations under the general heading of polishing include roughing, dry finishing, greasing, and grease coloring. Ordinarily there should be from 40 to 60 grit numbers difference between successive polishing operations.

In buffing operations, tripoli compounds are used for the removal of polishing scratches, and unfused aluminous oxide or green chromium oxide for color buffing. For the highest mirror finish, chromic oxide is used. High quality white lime compounds are very satisfactory for color buffing pure nickel and nickel plate.

Detailed information about the grinding, polishing, and buffing of nickel and its alloys was presented by Burchfield [389].

2.6. Metallography of Nickel

The primary object of metallographic examination is to reveal, by means of the microscope, the constituents and structure of metals and their alloys. The selection and preparation of the specimen is of major importance, but the preparation of metallographic specimens is essentially an art because of the diversity of available equipment, the variety of problems encountered, and the personal aptitudes, skills, and preferences of the metallographer. The ensuing discussion of the metallography of nickel and its alloys was prepared mostly by personnel of the Huntington Alloy Products Division, The International Nickel Company, Inc., and represents their normal laboratory practice.

a. Selection of Specimens

The primary requirement is that the specimen should be representative of the material being studied, but the actual selection of a

TABLE 24. *Recommended conditions for electropolishing nickel and some nickel-base alloys*

Solution	Alloy	Current density (amp/in^2)	Time	Remarks
$_3PO_4$ 37 ml	Nickel 270[a]	10–12	1 min	The water must be distilled.
lycerin 56 ml	Nickel 200[b]	9–10	1 min	Used for nickels, Monel alloys, some Inconel alloys and some Incoloy alloys; not Inconel alloy 718 and Inconel alloy 600.
$_2O$ 7 ml	Monel alloy 400	6–7	1–2 min	
	Inconel alloy 625	8–10	2–4 min	
	Incoloy alloy 800	20	2–4 min	
NO_3 33 ml	Monel alloy 400	10–15	25 sec	Used for most Monel alloys.
ethanol 66 ml	Monel alloy 404			Faster than the 37–56–7 polish. A black film is formed prior to polishing.
	Monel alloy 405			
	Monel alloy K–500			
$_3PO_4$ 25 ml	Inconel alloy 600	115	5–10 sec	Water must be distilled.
NO_3 25 ml	Inconel alloy X–750	115	5–10 sec	Used for Inconel alloys.
$_2O$ 50 ml				Use maximum cooling and stirring.

[a] High purity nickel.
[b] Commercial nickel.

pecimen depends upon the size and shape of he material, the portion or section of the maerial that is of interest, and the purpose for vhich the study is being made. For more deailed discussion of this subject, see ASTM pecification E3–62.

b. Preparation of Specimens

The degree of surface preparation to be iven to a sample is largely dependent on the ature of the examination and the type of tchant to be used. Rough grinding on an abraive wheel or on a coarse emery cloth belt is sually adequate for small specimens. Large ections, such as cross sections of ingots, looms, etc., lend themselves to preparation on surface grinder.

A suitable specimen, either unmounted or ounted in plastic with a flat surface, is preared as follows:

(1) *Grinding*. Hand or power-driven disk rinding should be carried through a series of mery papers of successively increasing fineess. The commonly used papers are No. 3, 2, , 0, 00, and 000. The papers used will depend n the starting condition of the sample. After ompletion of a grinding operation, the samle must be thoroughly rinsed to wash away ll traces of the emery before proceeding to he next finer grade. Each successive cut should e at right angles to the preceding cut, and rinding with each grit should be continued ntil all scratches left by the preceding coarser rit have been removed.

(2) *Rough polishing*. Specimens ground hrough No. 000 paper can be wet polished on broadcloth-covered wheel, using levigated lumina abrasive powder (particle size about μ) suspended in water.

A much faster method utilizes a silk- or ylon-covered wheel impregnated with diaond dust paste (particle size about 3 μ). If is method is used, preparation need consist nly of grinding through No. 1 paper, thereby liminating three grinding steps.

(3) *Final polishing*. Fine scratches remaining after the rough polishing can be removed on a microcloth- or duracloth-covered wheel using gamma aluminum abrasive powder (less that 0.1 μ size) suspended in water.

(4) *Electropolishing*. In general, better electropolishing can be obtained by starting with mechanically polished specimens. For the solutions given in table 24, most any flat, rough grind may be used as a starting point. These solutions are used as water cooled and stirred. Platinum is usually used as a cathode. All acids are concentrated.

c. Etching

In general, polished metal does not reveal the crystalline structure and etching must be used to delineate the structure and to produce optical contrast between the various constituents. Nickel is generally resistant to corrosive media and its etching involves the use of vigorous reagents which tend to form etch pits and to dissolve out the inclusions. The difficulty of etching increases with increasing purity of the metal and alternate polishing and etching frequently are required in order to obtain the desired development of the microstructure.

The etchants most frequently used for macroetching of nickel and some of the nickel-base alloys are given in table 25, and for microetch-

TABLE 25. *Macroetching of nickel and some nickel-base alloys*

Solution	Alloy	Remarks
HNO_3 50 ml $HC_2H_3O_2$ 50 ml	Nickels	
HNO_3 50 ml H_2O 50 ml	Monel alloys	The water does not have to be distilled.
HCl 40 ml H_2O_2 (30%) 40 ml H_2O 20 ml	Inconel alloys	H_2O_2 may be added as needed. Fresh solutions are required.
$(NH_4)_2S_2O_4$ 15 gm H_2O 75 ml $FeCl_3$ 250 gm HCl 100 ml HNO_3 30 ml	Weld structures of nickel-base alloys.	Time 30–120 seconds (Lepito's Reagent).

ing in table 26. For electrolytic etching, Inconel alloy 600 is used as the cathode and where water is indicated, tap water is used. Additional useful reagents are given by Smithells [405].

The microstructure of high-purity nickel is shown in figure 49.

FIGURE 49. *Microstructure of high-purity nickel (Nickel 200) as forged. Etched with NaCN — $(NH_4)_2S_2O_8$.* a. × 100. b. × 500.

2.7. Uses of Nickel

Topics discussed in this section include the production of nickel coatings by various procedures and the end uses of nickel-plated and solid-nickel objects.

a. Coatings

(1) *Electroplating.* Nickel is one of the most important metals applied by electrodeposition [406]. Nickel electrodeposits are used extensively as a foundation for a highly lustrous finish on many manufactured metallic articles. Protection of the basis metal and permanence of a stain-free surface are the primary requisites of such decorative coatings. These are obtained by an adequate thickness of nickel and a comparatively thin layer of chromium over it. Nickel coatings alone are also used industrially to protect the basis metal from corrosion or to prevent contamination of a chemical product. Although surface improvement and corrosion resistance are the principal objectives of nickel electroplating, it is also used for building up worn parts [407] and for electroforming of printing plates, tubes, and many other articles [408,409]. Williams [410] reported that steel sheet or plate up to 80 in wide and up to 20 ft long can be coated with 0.006 to 0.020 in of nickel by electroplating. Nickel electroplating was originally used on iron, steel, and copper alloys but has been extended to zinc-base die castings, aluminum, magnesium, and many other metals and plastics. An undercoat of copper is frequently employed to create a better surface for the deposition of nickel and the good appearance and tarnish resistance of the nickel coating may be further improved, for particular applications, by a final coating of other metals, including gold.

According to Gray [335], the history of electroplating goes back to the production of the first good nickel plate by Boettger in 1843, obtained from a bath containing nickel and amonium sulfates. Adams [411] in 1869 was probably the first to do nickel plating on a truly commercial basis, thereby establishing electroplating as one of the major consumers of nickel. Developments in nickel electroplating led to the installation in about 1890 of electrolytic refining in the production of nickel, and this in turn contributed to the further improvement of nickel electroplating by supplying better anode material. Developments in electroplating have been rapid since early in the present century, with improved baths that permitted plating at high speeds, with improved understanding and control of operating variables and the use of addition agents, and with the development of improved and auto-

TABLE 26. *Microetching of nickel and some nickel-base alloys*

Alloy	Solution		Voltage (volts)	Time	Remarks
Nickel and Monel alloys	H_3PO_4 H_2O	20 ml 80 ml	20	10–15 sec	General structure.
	NaCN $(NH_4)_2S_2O_3$ H_2O	10 ml 10 ml 20 ml	----------	----------	Swab: The NaCN and $(NH_4)_2S_2O_3$ additions are made from 20% stock solutions.
Inconel alloy 600 Inconel alloy X–750	HNO_3 Methanol	5 ml 95 ml	10	5–10 sec	
	HCl HNO_3 $CuCl_3$	30 ml 10 ml Saturated	----------	----------	Swab: Let stand 5 min before using, good for Inconel alloy 600 but not Inconel alloy X–750.
Inconel alloy 700	HNO_3 Methanol	20 ml 80 ml	30	15–30 sec	
	HCl HNO_3 H_2SO_4	92 ml 3 ml 5 ml	----------	----------	Swab: Add H_2SO_4 last and slowly.
Inconel alloy 625	$HC_2H_3O_2$ HCl H_2O	10 ml 3 drops 90 ml	3–4	10–20 sec	This alloy is difficult to etch but one of these two solutions should work for most conditions of heat treatment.
	H_2SO_4 HNO_3 H_3PO_4	47 ml 41 ml 12 ml	5–10	8–10 sec	
Inconel alloy 718	CrO_3 H_2O	5 gm 100 ml	10	7–10 sec	Dip in 100 ml HNO_3+4 drops of HF to remove the stain.
	CrO_3 H_2O $HC_2H_3O_2$	25 gm 7 ml 133 ml	10	5–15 sec	To dissolve the CrO_3, the solution should be heated in hot water only. Add $HC_2H_3O_2$ last. No staining.
	HCl HNO_3 Glycerin	50 ml 10 ml 10 ml	----------	----------	Swab.
Incoloy alloy 800	Glycerin HCl HNO_3	30 ml 20 ml 10 ml	----------	----------	Swab or immerse and stir.
	Oxalic H_2O	20 ml 80 ml	10	10–15 sec	Oxalic is mixed from a 20% stock solution.
Incoloy alloy 825	Oxalic H_2O	10 ml 90 ml	10	5–10 sec	Oxalic is mixed from a 20% stock solution.
Nickels and Monel alloys	HNO_3 $HC_2H_3O_2$	50 ml 50 ml	----------	2–6 sec	Good for grain size determinations, tends to pit.
High purity Nickel	HNO_3 HF	20 ml 3 ml	---------- ----------	---------- 1–3 sec	Good for grain size determination, tends to pit.
Inconel alloys	HNO_3 HF	20 ml 3 ml	---------- ----------	---------- 1–3 sec	Good for grain size determination, tends to pit. Rinse sample thoroughly.

matic equipment for conducting the operations [412,413].

Since 1915, the rate of development of nickel plating has been quite rapid. Among the highlights are high-speed plating, begun by Watts with his famous "Watts bath" [414]; control quality of deposits, first emphasized by Watts and DeVerter [415]; accurate *p*H control, introduced by Thompson [416]; low *p*H baths, suggested by Phillips [417]; commercial introduction of modern bright nickel plating begun by Schlotter [418] and the many later developments of it; design of baths for deposition of leveling, semibright and bright nickel coatings; growing appreciation of the importance of high-purity electrolytes and of high ductility and low stress in deposits; and the development of automatic plating equipment that makes possible today's high production rates and low costs.

According to Pinner, Knapp, and Diggin [406] a survey of recent information shows that the composition of the modern Watts bath can be represented reasonably well by the following:

Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	240–340 g/l
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	30– 60 g/l
Boric acid (H_3BO_3)	30– 40 g/l

An all-chloride bath was developed by Blum and Kasper [419]. The better-buffered half-chloride, half-sulfate bath of Pinner and Kinnaman [420] has advantages of both the Watts and the high-chloride baths and has been found to be especially suitable for high-speed plating.

Information of value on the electroplating of nickel is contained in several publications of The International Nickel Company, Inc., [421,422,423,424,425].

Improvements in the nickel anode material have kept pace with improvements in the bath and in the operating procedure. Nickel con-

Table 27. *Examples of industrial nickel-plating baths and operating conditions*

	Watts bath		All chloride bath	Intermediate bath	Hard plating bath	Special purpose bath	Nickel sulfamate bath	Sulfate bath
	(High *p*H)	(Low *p*H)						
Nickel sulfate oz/gal	32	44		26	24	16		38.5
Sodium sulfate oz/gal								3.2
Nickel sulfamate oz/gal							60	
Nickel chloride oz/gal	6	6	40	23			1.0	
Ammonium chloride oz/gal					3.3	2		
Boric acid oz/gal	4	5	4	5.3	4.0	2	5	4.8
*p*H	4.5 to 6.0	1.5 to 4.5	2.0	1.5	5.6 to 5.9	5.0 to 5.5	4	2.5
Temperature °F	115 to 160	115 to 140	140	115	110 to 140	Room	110	95
Current density Amp/ft²	20 to 100	25 to 100	25 to 100	100	25 to 50	5 to 10	50	20 to 30

taining up to 10 percent of impurities was acceptable as an anode material in the early baths. The development of the Watts bath, containing chlorides, permitted the use of the 99-percent, chill-cast nickel anode, and later, of the 99-percent, rolled anode that contained small amounts of nickel oxide for depolarizing purposes. A later development, for particular applications, was the cast or rolled carbon-silicon-nickel anode, which under some conditions forms an adherent, porous, carbon-silica film that acts as a bag. Anodes cut from electrolytic nickel sheet have been used to a limited extent, and several patents have been issued for introducing sulfur into nickel anodes to promote corrosion of the anodes.

Several special baths are cited by Gray [335]. In addition, references to the use of sulfamate [425a], fluoborate [426,427], and pyrophosphate [428] baths, and to the electrodeposition of nickel from molten salt baths [429] have been noted. The brightening action of cadmium salts has long been known, and a great number of organic addition agents have been proposed and used to control the surface appearance (brightness) of the deposit, and sometimes for other reasons [335,430,431]. A black nickel deposit, containing nickel sulfide, can be obtained [432]. Indira et al. [433] described a solution for black nickel plating and showed that a high sulfur content was a prerequisite for achievement of jet-black coatings. Wesley and Knapp [434] patented a method of black nickel plating. McCarthy [435] described the production of various colors on several basis metals using a black nickel plating electrolyte. Wesley [436] reported the production of malleable sheets up to 6 mm thick of nickel that contained only 34 ppm of detectible impurities, by electrodeposition from a purified nickel chloride-boric acid solution, using iridium-platinum electrodes.

Electroplating on aluminum requires special treatment because of interference by the surface oxide film, but procedures have been developed for plating nickel directly on aluminum [437,438,439,440,441,442,443,444]. Likewise, special treatments have been developed so that nickel can be plated on beryllium [445], on magnesium [446,447], on molybdenum [448,449], on titanium [450], on uranium [451], on zinc [452], and on zirconium [453]. Numerous processes have been developed for the plating of nickel alloys. A review of recent developments in nickel plating was written by Castell [454].

Examples of industrial nickel-plating baths and operating conditions are shown in table 27, without reference to brightening agents and other possible additions. In many industrial operations, the nickel plating may be applied over an undercoat of copper and may be followed by a final thin coating of chromium. Recommended practice for the preparation of nickel for electroplating with nickel is discussed in ASTM Specification B 343–60T. The requirements of ASTM Specifications for minimum thickness of coatings for service conditions of varying severity are summarized in table 28. More recent ASTM specifications are being issued; however these specifications will adhere to the same standards.

The physical and mechanical properties of electroplated nickel are affected by the composition of the bath, by all the variables in bath operation, and by the presence of metallic and gaseous impurities. These effects have been reviewed in many articles [455,456,457, 458]. The mechanical properties of nickel deposits for engineering uses are summarized in table 29.

Table 28. *ASTM standards for nickel coatings*

	Thickness of coating, in (min)			
	Type D	Type F	Type K	Type Q
On steel (ASTM A 166–61T)				
Copper plus nickel	0.0020	0.0012	0.00075	0.00040
Nickel (if copper is used)	.00100	.00060	.00040	.00020
Chromium (if required)	.000010	.000010	.000010	.000010
On copper and its alloys (ASTM B 141–58)				
Nickel		.00050	.00030	.00010
Chromium (if required)		.000010	.000010	.000010
On zinc and its alloys (ASTM B 142–61)				
Copper plus nickel	.0020	.0012	.00075	.00050
Copper	.00020	.00020	.00020	.00020
Final nickel	.0010	.00050	.00030	.00030
Chromium (if required)	.000010	.000010	.000010	.000010

ABLE 29. *Mechanical properties of nickel deposits for engineering uses [459]*

Type of bath	Watts, low *p*H		Chloride		Hard, as plated	Sulfamate, as plated
	As plated	Annealed	As plated	Annealed		
nsile strength, psi	63,000	50,000	100,000	58,000	156,000	90,000
ongation, % in 1 in	31	50	21	48	6	10
ckers hardness numbers	137	63	240	81	400	200
ockwell hardness	75 B	17 B	99 B	36 B	42 B	------

Hammond [458] noted that nickel plating nay involve risk of hydrogen embrittlement in teels of 180,000 psi or higher, but that this nay be obviated by low-temperature baking fter plating. Beck and Jankowsky [460] reorted that hydrogen embrittlement of 4340 teel induced by chromium plating was subtantially reduced by an undercoat of Watts-ype nickel.

In addition to electroplates of nickel alone, aths and operating conditions have been deeloped for the deposition of nickel alloys. ome of these are nickel-aluminum [461], ickel-boron [462], nickel-chromium [463], ickel-cobalt [464], nickel-iron [465], nickel-olybdenum [466], nickel-phosphorus [467], ickel-rhenium [468], nickel-tin [469], and ickel-zinc [470]. Some ternary alloys that ave been plated are nickel-iron-chromium 471] and nickel-cobalt-copper [472]. Couch t al. [473] patented the production of nickel-luminide coatings.

The various processes used for plating nickel re described in a booklet by The International ickel Company, Inc.[474].

(2) *Electroless plating.* Brenner and Riddell [475] decribed a process developed at the ational Bureau of Standards in 1946 for the eposition of nickel from an ammoniacal soluon containing hypophosphite by chemical reuction. The following year the process was xpanded to include deposition of nickel from cid solutions and the deposition of cobalt from oth alkaline and acid solutions. Reduction of ickel salts by hypophosphite had been long nown as a chemical reaction, but Brenner and iddell were the first to develop a controlled utocatalytic reaction to produce a sound, coerent metallic coating that could be built up appreciable thicknesses. The coatings conain up to 6 or 7 percent of phosphorus, probbly in the form of finely dispersed phosphides. s deposited, the coatings have a Vickers hardess number as high as 700, but heating at levated temperatures reduces the hardness, nd heating for at least 4 hr at 725 to 800 °C onverts the plated coating into an iron-nickel lloy [476]. The deposits are somewhat less agnetic, but are similar to electrodeposited ickel in resistance to rusting as indicated by the salt spray test. The electroless process has three advantages over electroplating:

1. Coatings deposit with uniform thickness in recesses as well as on exposed surfaces.
2. There is no buildup of coating on points or edges.
3. No electrical equipment is required.

Electroless nickel plating can be deposited directly upon surfaces that catalyze the reaction, for example, on aluminum, cobalt, copper, gold, iron, nickel, palladium, platinum, and silver. A method of electroless nickel plating of magnesium and thorium was patented by Puls and Vincent [477] and electroless nickel plating of beryllium was described by Roberts [478]. Titanium, zirconium, and hafnium have also been chemically plated with nickel [479]. Semiconductors, such as graphite and silicon carbide, may be electroless plated by touching the semiconductor with a piece of aluminum or steel to start the reaction, and nonconductors, such as glass, plastics, and ceramics, may be electroless plated after dipping in palladium solution or being otherwise treated to form an absorbed film of palladium or a palladium compound. However, cadmium, manganese bronze, lead and its alloys, and silicon cannot be electroless plated, according to Panchenko and Krokhina [480].

The compositions of various baths for electroless nickel plating and the operating procedures have been described by Krieg [481] and by Aitken [482].

Patents for the electroless deposition of nickel-boron [483] and nickel-vanadium [484] alloys have been issued.

The history of the electroless plating process was reviewed by Brenner [485]. MacLean and Karten [486] reported that small fuse parts with deep blind holes could be plated with 0.1 mil of nickel. Rich [487] reported that the use of ultrasonic vibrations from stainless steel transducers increased the rate of electroless nickel plating. Gutzeit and Landon [488] described operations of a large-scale, electroless, custom plating shop. Chinn [489] reviewed the subject of electroless plating and cited numerous examples of its practical use.

(3) *Electroforming.* Nickel electroforming, accomplished by the use of electroplating processes, is defined as the production or the reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit. It is a low-cost production method for forming complex assemblies or intricate internal contoured shapes which require high dimensional accuracy and smooth surface finish. The process is sometimes referred to as "cold casting." Inasmuch as the electrodeposit that constitutes an electroformed article is used as a separate structure, its mechanical properties are a matter of major importance.

Nickel ordinarily is electroformed in a Watts-type solution or a nickel sulfamate bath, such as shown in table 30. The *p*H of all nickel solutions should be maintained within a relatively narrow range of about 0.5 unit for good control of physical and mechanical properties, but a relatively low *p*H of about 3 is preferred for some applications, whereas a *p*H of 4 to 4.5 is preferred for others.

TABLE 30. *Composition and operating conditions for two nickel electroforming baths* [490]

	Watts bath	Sulfamate bath
Nickel sulfate or sulfamate	30 to 50 oz/gal [a] 44	30 to 60 oz/gal [a] 50
Nickel chloride	4 to 8 [a] 6	0.4 to 0.8 [a] 0.6
Nickel	10 to 12 [a] 11	8 to 14 [a] 10
Boric acid	4 to 5 [a] 5	4 to 6 [a] 4
*p*H	2.0 to 4.5	3.5 to 4.2
Temperature	115 to 140 °F	80 to 140 °F
Current density	25 to 50 A/ft^2	20 to 150 A/ft^2

[a] Typical or average operating condition.

The structure and properties of electroformed nickel (or alloy) depend on electrodeposition conditions as follows: kind and concentration of the nickel salts, concentration of chloride or other anion employed for assisting the dissolution of anodes, *p*H of the solution, impurity concentrations, solution temperature, cathode current density, kind and amount of solution agitation, and interrelation of these factors. The kind and concentration of organic chemical agents added to the electrodeposition solution for avoiding pitting, reducing stress, or refining the grain structure frequently have profound effects on properties.

Kura et al.[491], in a review of the literature, gave the following ranges for the physical and mechanical properties of electroformed nickel:

Density	0.321 to 0.327 $lb/in.^3$
Modulus of elasticity	23,000,000 to 28,000,000 psi
Coefficient of linear expansion near room temperature.	3.1 to 6.3 microinch/°F
Ultimate tensile strength	55,000 to 215,000 psi
Yield strength	32,000 to 128,000 psi
Elongation in 2 in	2 to 27 percent

These authors noted that as a rule, an increase was observed in the tensile and yield strengths for electroformed nickel, and a decrease in ductility was evident when the temperature for the electrodeposition bath was lowered. They note further that, of the various baths used for electroforming, stronger nickel with a higher yield strength was obtained with the nickel chloride and nickel sulfamate solution than with any other. Modern electroforming solutions were discussed by Diggin [492] and the physical and mechanical properties of electroformed nickel at both elevate and subzero temperatures were reported b Sample and Knapp [493].

Electroforming is particularly applicabl to the manufacture of phonograph recor stampers [494], printing plates [495], screen [496], etc. Even pressure vessels have bee electroformed [497].

(4) *Nickel cladding.* Nickel cladding, lik electroplating, supplies corrosion resistan nickel-surfaced material that is cheaper tha solid metal. In this process the cladding meta is pressure welded to one or both sides of a open-hearth steel slab in a rolling mill at abou 2,200 °F. If the bonding surfaces have bee properly cleaned and protected during heating, excellent bonding through the formatio of an iron-nickel solid solution is accomplishe during hot reduction to between one-eight and one-sixteenth of the original thickness.

The ratio of cladding material to the bas plate is usually expressed as a percentage o the total thickness of the plate. For exampl a ½-in plate clad 10 percent on one side onl consists of about 0.45 in of steel and 0.05 in o nickel; clad 10 percent on both sides, it woul be 0.40 in of steel and 0.05 in of nickel on eac side. When both sides are clad, the same thickness of nickel usually is applied to each side but different thicknesses on the two sides ma be developed if desired. Nickel-clad steels ar regularly supplied with 5-, 10-, 15-, or 20-percent cladding on a 55,000-psi minimum tensil strength steel as base material. According t Theisinger and Huston [498], nickel cladding does not affect the mechanical properties of the clad material, as illustrated by the following data of ½-in steel with and without 10-percen nickel cladding.

	Tensile strength	Yield point	Elongation in 8 in	Reduction in area
	psi	*psi*	%	%
Clad	60,600	40,400	30.0	57.2
Plate	60,800	40,200	30.5	59.0

A relatively new process for metallurgically bonding a pore-free coating onto mild stee consists of applying carbonyl nickel powder in slurry form directly to the surface of a moving strip of hot rolled steel [498a]. The slurry is then dried and sintered to a porous nickel layer which is densified to a nonporous coat by passing between the rolls of a hot compaction mill. Nominal nickel coating thicknesses on the order of 0.0005 to 0.0025 in have been achieved after cold rolling.

Metals have also been clad with nickel by explosive bonding techniques.

Cladding is not restricted to the use of nickel only. Steel may be clad with Monel alloy 400, Inconel alloy 600, stainless steel, etc. In welding the clad surface of a plate, a covered electrode of approximately the same composition as the cladding is used. ASTM Specification A265–62 covers nickel and nickel-base alloy clad steel plate.

(5) *Sprayed and vapor-deposited coatings.* Protective coatings of nickel or of nickel alloys may be applied by metal-spray processes, which are particularly adapted for coating large objects of irregular shape [499]. Pure nickel can be sprayed with either a wire or powder gun. Nickel alloys are usually sprayed in a powder gun because they are more readily available in powder form. After spraying, the material is fused to form a metallurgical bond with the base material, which may be steels, irons, nickel and nickel alloys, copper and copper alloys, and refractory alloys. A self-bonding material that does not have to be fused after spraying is nickel aluminide, which has been decribed by Sheppard [500]. Kura et al. [491] summarized the process of metal spraying of nickel and its alloys. A patent for obtaining a smooth uniform coating of nickel by spraying with an aqueous solution was issued to Carlson and Prymula [501].

Chemical vapor deposition (CVD) is accomplished by causing gaseous molecules to react chemically at, or near, a heated surface under conditions such that one, and only one, of the reaction products is a solid and is deposited on the heated surface. As the reaction continues, atoms (or molecules) are added to the growing metal lattice one at a time. Such a procedure has been called a "molecular forming" process. Considerable detail concerning the mechanism of deposition at low pressures and the properties of nickel coatings was given by Owen [502]. Nickel can also be vapor deposited by electron beam β rays.

Nickel can be deposited by the thermal decomposition of nickel carbonyl, of nickel acetyl acetonate, or by the hydrogen reduction of nickel chloride. According to Owen [503], nickel carbonyl is used because it is highly volatile. The plating temperature is under 250 °C and rates of deposition as fast as 0.030 in/hr are achieved without difficulty.

Tewes et al. [504] studied four potential catalytic agents and found that the use of the hydrogen sulfide/oxygen catalytic mixture achieved the same plating rate at 100 °C as was obtained at 150 °C without a catalyst.

The strength of vapor-deposited nickel films of 700 to 4360 Å thickness was studied by D'Antonio et al.[505], who concluded that a significant contribution to the high strength of thin metal films can be attributed to the vapor-deposition process which, owing to its severe quenching effect, is believed to promote the formation of many point defects which inhibit the motion of dislocations.

Recent developments in the technique of nickel plating from the vapor of nickel carbonyl have been reviewed by Owen [506].

Gas plating of nickel has been used to coat synthetic fibers such as nylon, rayon, glass, etc.[507,508,509]. The protection afforded uranium by the thermal decomposition of nickel-carbonyl vapor was reported by Owen [510] to be considerably superior to electrodeposited coatings of the same thickness.

According to Cummins [511], the addition of ammonia gas to nickel carbonyl plating gas results in the production of nickel-containing films of relatively high electrical resistance. These coatings are applied to the preparation of electrical resistance units.

Breining [512] obtained a patent on the deposition of nickel-phosphorus alloys by gas plating.

b. Nickel Powders

By varying the conditions of electrodeposition, nickel may be deposited as a powder rather than as a continuous plate [513,514, 515,516]. Nickel powder has been produced by electrolysis of fused salts [517], grinding of sulfurized nickel shot, hydrogen reduction of nickel oxide, and in the ammonia-leach process for the recovery of nickel from its ores [518], but the principal production of nickel powder for powder metallurgy uses is by decomposition of nickel carbonyl or by the ammonia-leach process. Various types of carbonyl-nickel powders are also available [519]. The properties of sintered carbonyl nickel powder compacts were reported by Prill and Upthegrove [520].

Nickel powder may be used by itself to form all-nickel parts, or in combination with other metal powders to produce alloys or compounds [45,521,522,523,524]. Pure nickel strip can be produced from powder [525,526,527, 527a].

Carbonyl nickel powders of irregular particle shape and low bulk density are used in the production of porous nickel electrodes for nickel-cadmium storage batteries and hydrogen-oxygen fuel cells employing alkaline electrolytes [528,529,530,530a,530b].

Nickel powder parts are particularly valuable in the field of electronics, and controlled-expansion and magnetic alloys formed by powder-metallurgy techniques have advantages over melted metal [531]. Cathode-base materials for the electron tube industry have been made by the powder rolling of nickel powder with controlled alloy additions to achieve unusual combinations of properties, such as electrical passivity and mechanical strength at high temperature [531a]. Nickel-silver contact materials have been made by powder metallurgy [532], as have nickel-base alloy turbine blades [533]. Nickel alloyed with up to 40 percent of tungsten is useful for thermionic valve construction [182].

Sintered nickel steel engineering components have been made by the pressing and sintering of mixtures of iron and nickel powders [533a]. Nickel-chromium alloy powders added to iron powder produce compacted parts with tensile strengths between 80,000 and 120,000 psi [533a,534].

Nickel or nickel-alloy objects infiltrated with silver or a silver alloy have effective resistance to wear at elevated temperatures [535]. The compound NiAl, formed by powder metallurgy technique, has refractory properties which make it useful in the temperature range from 850 to 1,150 °C [536]. Forming of stainless-steel powders by slip casting instead of the more conventional pressing has been reported [537], and this technique should be applicable to other alloys and to nickel itself, particularly for the production of thin-walled and special shapes.

Tungsten-nickel-copper compositions, commonly called "heavy alloys," have found commercial applications requiring high specific gravities. Nickel powder mixed with copper powder is used to bond the tungsten particles.

Nickel powder may be used to bond carbides of titanium, tantalum, and columbium in the formation of sintered carbide objects. Nickel, like cobalt, wets the carbide particles and forms extensive interlocking bonds [538,539].

Nickel-chromium-boron powders have been used as a hard-facing overlay [540].

c. End Uses of Nickel and Nickel-Surfaced Materials

The tarnish resistance and corrosion resistance of nickel make nickel and nickel plate useful in many industries, including the paper and pulp industry, food, dairy and beverage industries, and the petroleum, textile, and plastic and automotive industries [541,542]. These properties plus electrical and magnetic properties make nickel useful in the electrical and electronic industries. The following list of ASTM Specifications indicate the form and shapes of nickel that are available for the construction of equipment or parts for these conditions of use:

B 39–22	Nickel.
B160–61	Nickel rod and bar.
B161–61	Nickel pipe and tube, seamless.
B162–61	Nickel plate, sheet, and strip.
B163–61T	Nickel and nickel alloy, seamless, condenser and heat-exchanger tubes.
B295–54T	Nickel and nickel-base alloy covered welding electrodes.
B141–58	Electrodeposited coatings of nickel and chromium on copper and copper-base alloys.
B142–61	Electrodeposited coatings of nickel and chromium on zinc and zinc-base alloys.
B355–60T	Nickel-coated soft or annealed copper wire.
A166–61T	Electrodeposited coatings of nickel and chromium on steel.

Nickel finds a variety of uses in the electrical industry [543], including the use of very thin films sputtered or vapor deposited, as resistance thermometers at very low temperatures [150]. A thin film of nickel, which transmits 30 percent of the incident light to the germanium semiconductor, improves the performance of a photoelectric cell [544].

In the field of electronics, nickel forms the base of the cathodes in practically all small and moderate size radio and television tubes, and in the deep-sea portion of the Trans-Atlantic telephone cable. The use of nickel and its alloys with aluminum, tungsten, and rhodium in cathodes, grids, and other parts of electronic tubes, has been the subject of numerous articles and patents [295,545,546,547].

In the chemical industry, nickel is widely used for handling caustic soda and other alkalies, even at elevated temperatures.

The use of nickel in nuclear power plants was discussed by Convey [62], Koenig [548], and Dalzell [549]. Fuller [550] reported that more than 1,200 miles of piping internally plated with 0.003 to 0.005 in of nickel would be used in the Atomic Energy Commission's gaseous diffusion plant at Portsmouth, Ohio.

Heavy electrodeposits of nickel, for resistance to wear and corrosion or to build up worn ports, have some advantages over chromium plating [551] and are used in transportation equipment, in paper and textile mills, in equipment and tools for oil drilling, in food processing, and in the printing industry.

Nickel combustion boats and crucibles for laboratory use may be made from sheet metal [552]. Nickel tubes with walls 0.1 mm thick were used for diffusion purification of hydrogen [553] and tubes of pure nickel 0.015 in thick are used as a protective material for beryllium rod during drawing to wire of 0.005 in diam [554]. Nickel is an activator of phosphors [555]. Nickel powder is pyrophoric under some conditions and finds use in incendiaries, tracer ammunition, igniters, primers, etc.[556]. Nickel-plated silk was used in England as a wartime substitute for fine copper gauze for straining gasoline [557], and nickel-plated wires produced a superior Fourdriner cloth [558]. Nickel was recommended as a container for bromine [559], and for use as a spinneret in the production of acetate and cuproammonium fibers [560]. According to Atkinson [561], about 500,000 lb of nickel is used annually in precious metal jewelry, including gold-filled and rolled-gold plate and the white and colored golds.

About 1 percent of the world consumption of nickel represents uses of nonmetallic forms, i.e., compounds such as sulfates, chlorides, carbonates, oxides, and hydroxides. These compounds are used in the electroplating industry, in the production of alkali storage batteries, and in the production of nickel catalysts other that Raney catalysts. Nickel compounds are used, as a dip bath and in ground coats, for applying vitreous enamel to steel [562,563, 564].

3. Nonferrous Alloys

3.1. General

The nonferrous alloys of which nickel constitutes either a major or minor percentage are so numerous that it is impossible to present a comprehensive coverage in this circular. An attempt has been made to group these alloys into certain classes and attention will be directed to the more representative materials. There are many general reviews of the properties and uses of high nickel alloys that are of interest [565,566,567,568,569,570].

3.2. High Nickel Alloys

a. Nickels

Table 31 gives the nominal chemical composition of a group of nickels containing a minimum of 94 percent nickel. Except for four alloys, the minimum nickel content is 99 percent. Each of these alloys is manufactured for particular usage because of certain inherent properties.

Nickel 200 (99.00% Ni min, 0.15% C max, 0.35% Mn max, 0.40% Fe max, 0.010% S max, 0.35% Si max), is commercially pure wrought nickel and has been discussed in a previous section. It has good mechanical properties and excellent resistance to many corrosive environments. Much of its strength is retained at high temperatures and it is tough and ductile at subzero temperatures. Its corrosion resistance makes it particularly useful for manufacturing product purity in the handling of foods, synthetic fibers and caustic alkalies.

Nickel 201 is similar to Nickel 200 except that the carbon content is held to a maximum

TABLE 31. *Commercial nickel alloys* [*43*]

Designation		Nominal chemical composition—percent											Previous designation
		Ni	C	Mn	Fe	S	Si	Cu	Cr	Al	Ti	Others	
Nickel	200	99.5	0.06	0.25	0.15	0.005	0.05	0.05	--------	--------	--------	--------	"A" Nickel.
Nickel	201	99.5	.01	.20	.15	.005	.05	.05	--------	--------	--------	--------	Low Carbon Nickel.
Nickel	204	95.2	.06	.20	.05	.005	.02	.02	--------	--------	--------	Co 4.50	Nickel 204.
Nickel	205	99.5	.06	.20	.10	.005	.05	.05	--------	--------	0.02	Mg 0.04	"A" Nickel (electronic grade).
Nickel	211	95.0	.10	4.75	.05	.005	.05	.03	--------	--------	--------	--------	"D" Nickel.
Nickel	220	99.5	.06	0.12	.05	.005	.03	.03	--------	--------	.02	Mg 0.04	"220" Nickel.
Nickel	230	99.5	.09	.10	.05	.005	.03	.01	--------	--------	.003	Mg 0.06	"230" Nickel.
Nickel	233	99.5	.09	.18	.05	.005	.03	.03	--------	--------	.003	Mg 0.07	"330" Nickel.
Nickel	270	99.98	.01	<.001	<.001	<.001	<.001	<.001	<.001	--------	<.001	Co <0.001 Mg <0.001	
Permanickel alloy	300	98.6	.25	.10	.10	.005	.06	.02	--------	--------	.50	Mg 0.35	Permanickel alloy.
Duranickel alloy	301	94.0	.15	.25	.15	.005	.55	.05	--------	4.50	.50	--------	Duranickel alloy.
Monel alloy	400	66.0	.12	.90	1.35	.005	.15	31.5	--------	--------	--------	--------	Monel alloy.
Monel alloy	401	44.5	.03	1.70	0.20	.005	.01	53.0	--------	--------	--------	Co 0.50	Monel "401" alloy.
Monel alloy	402	58.0	.12	0.90	1.20	.005	.10	40.0	--------	--------	--------	--------	Monel "402" alloy.
Monel alloy	403	57.5	.12	1.80	.50	.005	.25	40.0	--------	--------	--------	--------	Monel "403" alloy.
Monel alloy	404	55.0	.06	.01	.05	.005	.02	44.0	--------	0.02	--------	--------	
Monel alloy	R–405	66.0	.18	.90	1.35	.050	.15	31.5	--------	--------	--------	--------	"R" Monel alloy.
Monel alloy	406	84.0	.12	.90	1.35	.005	.15	13.0	--------	--------	--------	--------	LC Monel alloy.
Monel alloy	474	54.0	.01	trace	0.01	.001	<.01	46.0	--------	trace	--------	--------	
Monel alloy	K–500	65.0	.15	.60	1.00	.005	.15	29.5	--------	2.80	.50	--------	"K" Monel alloy.
Monel alloy	501	65.0	.23	.60	1.00	.005	.15	29.5	--------	2.80	.50	--------	"KR" Monel alloy.
Inconel alloy	600	76.0	.04	.20	7.20	.007	.20	0.10	15.8	--------	--------	--------	Inconel alloy.
Inconel alloy	604	74.0	.04	.20	7.20	.007	.20	.10	15.8	--------	--------	Nb 2.0	Inconel "600" alloy.
Inconel alloy	625	61.0	.05	.15	3.00	.007	.30	.10	22.0	--------	--------	Nb 4.0 Mo 9.0	
Inconel alloy	700	46.0	.12	.10	0.70	.007	.30	.05	15.0	3.00	2.20	Co 28.5 Mo 3.75	Inconel "700" alloy.
Inconel alloy	702	79.5	.04	.05	.35	.007	.20	.10	15.6	3.40	0.70	--------	Inconel "702" alloy.
Inconel alloy	718	52.5	.04	.20	18.5	.007	.30	.07	18.6	0.40	.90	Nb 5.0 Mo 3.1	Inconel "718" alloy.
Inconel alloy	721	71.0	.04	2.25	7.20	.007	.12	.10	16.0	-----	3.00	--------	Inconel "M" alloy.
Inconel alloy	722	75.0	.04	0.55	6.50	.007	.20	.05	15.0	.60	2.40	--------	Inconel "W" alloy.
Inconel alloy	X–750	73.0	.04	.70	6.75	.007	.30	.05	15.0	.80	2.50	Nb 0.85	Inconel "X" alloy.
Inconel alloy	751	72.5	.04	.70	6.75	.007	.30	.05	15.0	1.20	2.50	Nb 1.00	Inconel "X–550" alloy.
Incoloy alloy	800	32.0	.04	.75	46.0	.007	.35	.30	20.5	0.30	.30	--------	Incoloy alloy.
Incoloy alloy	801	32.0	.04	.75	44.5	.007	.35	.15	20.5	-----	1.00	--------	Incoloy "T" alloy.
Incoloy alloy	804	42.6	.06	.85	25.4	.007	.50	.40	29.3	.25	.40	--------	Incoloy "804" alloy.
Incoloy alloy	825	41.8	.03	.65	30.0	.007	.35	1.80	21.5	.15	.90	Mo 0.30	Ni-O-Nel alloy.
Hi-Span-C alloy	902	42.0	.02	.40	48.5	.008	.50	.05	5.4	.65	2.40	--------	Ni-Span-C alloy.

of 0.02 percent. It is particularly suited for spinning and cold forming operations because of its low base hardness and low work-hardening rate. It is also preferred to Nickel 200 for applications involving exposure to temperatures above 600 °F.

Nickel 204 (0.20% C max, 0.35% Mn max, 0.30% Fe max, 0.008% S max, 0.20% Si max, 0.20% Cu max, 0.05% Ti max, 4.00/4.60% Co, remainder Ni) is characterized by its excellent magnetostrictive properties. At optimum bias, its electromechanical coefficient is 0.5/0.6; saturation magnetostriction is about min 38 ppm. Transducers utilizing this alloy exhibit high efficiency, are rugged, and have excellent corrosion resistance.

Nickel 205 (99.00% Ni min, 0.15% C max, 0.35% Mn max, 0.20% Fe max, 0.008% S max, 0.15% Si max, 0.15% Cu max, 0.01/0.05% Ti, 0.01/0.08% Mg) is designed especially for electrical and electronic components. Its modulus of elasticity and damping factor are sufficiently high to minimize vibrational and microphonic effects. Sufficient strength is maintained at normal bombardment temperatures to prevent deformation during outgassing. In addition, it has a high Curie temperature and a high magnetostrictive coefficient.

Nickel 211 (93.70% Ni min, 0.20% C max, 4.25/5.25% Mn, 0.75% Fe max, 0.015% S max, 0.15% Si max, 0.25% Cu max) is designed to resist sulfur compounds at elevated temperatures. This alloy maintains much of its strength when exposed to degassing temperatures. It is useful for supports sealed into glass where embrittlement from sulfur in the heating flame is a factor. Electron emission is low enough to make it useful for grid wires in electron tubes even when the wire becomes contaminated with barium.

Nickel 220 (99.00% Ni min, 0.08% C max, 0.20% Mn max, 0.10% Fe max, 0.008% S max, 0.01/0.05% Si, 0.10% Cu max, 0.01/0.05% Ti, 0.01/0.08% Mg) is widely used for cathodes in electronic receiving tubes. It is effective where fairly easy activation is required without liberating excessive amounts of barium.

Nickel 230 (99.00% Ni min, 0.10% C max, 0.15% Mn max, 0.10% Fe max, 0.008% S max, 0.010/0.035% Si, 0.10 % Cu max, 0.005% Ti max, 0.04/0.08% Mg) is designed for use in active cathodes. Its closely controlled composition makes it useful for certain special electron-tube applications.

Nickel 233 (99.00% Ni min, 0.10% C max, 0.30% Mn max, 0.10% Fe max, 0.008% S max, 0.10% Si max, 0.10% Cu max, 0.005% Ti max, 0.01/0.10% Mg) is used for plates (anodes) in vacuum tubes, and oxide-coated and cold cathodes and structural parts of tubes.

Nickel 270 (99.97% Ni min, 0.02% C max, 0.001% Mn max, 0.005% Fe max, 0.001% S max, 0.001% Si max, 0.001% Cu max, 0.001% Ti max, 0.001% Co max, 0.001% Mg max) is a high-purity product exceptionally free from nonmetallic inclusions. Its low base hardness and good ductility permit heavy cold deformation without reannealing.

Duranickel alloy 301 (93.00% Ni plus Co min, 0.30% C max, 0.50% Mn max, 0.60% Fe max, 0.01% S max, 1.00% Si max, 0.25% Cu max, 4.00/4.75% Al, 0.25/1.00% Ti) is an age-hardenable alloy employing aluminum and titanium as the age-hardening elements. It combines the excellent corrosion resistance characteristic of nickel with the additional advantages of greater strength and hardness. Alloy 301 is age hardened by heating in the temperature range of 800 to 1300 °F; the time and temperature depend upon the properties desired. Tensile strengths in excess of 200,000 psi can be obtained in this material [565].

Permanickel alloy 300 (97.00% Ni plus Co min, 0.40% C max, 0.50% Mn max, 0.60% Fe max, 0.01% S max, 0.35% Si max, 0.25% Cu max, 0.20/0.60% Ti, 0.20/0.50% Mg) is an age-hardenable alloy similar to Duranickel alloy 301 in its strength and corrosion resistance, but has higher thermal and electrical conductivity. It is somewhat difficult to heat treat and Duranickel alloy 301 is recommended in preference to Permanickel alloy 300 except for applications requiring Permanickel's superior conductivity or magnetic properties [571].

Data on the physical properties of these and other high-nickel alloys are given in table 32.

b. Nickel-Chromium Alloys

Nickel-chromium alloys (and Ni-Cr-Fe alloys) have many applications ranging from thermocouples to structural units, depending upon their electrical and mechanical properties and their resistance to heat, oxidation, and corrosion. Perhaps their most outstanding characteristic is their heat resistance, although they do not qualify as superalloys, which are treated in a subsequent section. However, many nickel-chromium base alloys, even though treated in this section, are actually superalloys.

According to the nickel-chromium constitution diagram (fig. 50) [572], nickel is capable of forming a solid solution with up to about 30 percent of chromium. The two most important nickel-chromium alloys contain 10 and 20 percent of chromium.

The 90 percent Ni–10 percent Cr alloy, known as Chromel alloy P, is used as a heating element up to 2400 °F. However, its most important use is as the positive wire of a base-metal thermocouple with the 95 percent Ni, balance Si, Mn, Al alloy known as Alumel. Roeser, Dahl, and Gowens [573] reported the values shown in table 33 for the thermal emf of this thermo-

TABLE 32. *Physical constants of nickel alloys* [43]

Alloy Designation		Density lb/in³	Modulus of elasticity 10^6 psi		Melting range °F	Specific heat. Btu/lb/°F 70 °F	Coefficient of thermal expansion in/in/°F×10^{-6} from 70 °F to					Thermal conductivity Btu/ft ²/hr/in/ °F				Electrical Resistivity ohms/cmil/ft					Curie temperature, °F		Permeability, (*H*=200)		Poisson's Ratio
			Tension	Torsion			200 °F	500 °F	1000 °F	1500 °F	2000 °F	70 °F	500 °F	1000 °F	1500 °F	70 °F	500 °F	1000 °F	1500 °F	2000 °F	annealed	Age hardened	Annealed	Age hardened	
Nickel	200	0.321	30.0	11.0	2615/2635	0.109	7.4	7.9	8.5	9.0	9.5		374	370		57	126	228	276		680				0.31
Nickel	201	.321																							
Nickel	204	.321	29.2				7.4	7.8	8.6	9.2						65					770				
Nickel	205	.321														57									
Nickel	211	.315					7.4	7.9	8.5	9.1	9.6	306	296	326	365	102	195	267	312	354					
Nickel	220	.321																							
Nickel	230	.321																							
Nickel	233	.321																							
Nickel	270	.321	30.0		2650	.11	7.4	7.8	8.6	9.1		655				43	125	218	263		667				
Permanickel alloy	300	.316	30.0	11.0		.106	6.8	7.9	8.4	8.9	9.1	[a]400				94.5					600	563			
Duranickel alloy	301	.298	30.0	11.0	2550/2620	.104	7.2	7.7	8.2	9.0		165	211	265	316	255	310	349	373	403	60/120	200			.31
Monel alloy	400	.319	26.0	9.5	2370/2640	.102	7.7	8.7	9.1	9.7	10.3	151	204	264	323	307	342	367	397	427	20/50				.32
Monel alloy	401	.321					7.6	8.5	9.2	9.8	10.6					310									
Monel alloy	402	.320																							
Monel alloy	403	.320	25.0			.100	7.8	8.5	9.0	9.6						319							1.01		
Monel alloy	404	.321	25.0	9.4		.099	7.4	8.5	9.2	9.8						300					−110		1.02		.295
Monel alloy	R–405	.319	26.0	9.5	2370/2460	.102	7.7	8.7	9.1	9.7	10.3	151	204	264	323	307	342	367	397	427	20/50				.32
Monel alloy	406																								
Monel alloy	474	.322	25.0			.097						146				300					< −110		[b]1.01		
Monel alloy	K–500	.306	26.0	9.5	2400/2460	.100	7.6	8.2	8.7	9.5		121	167	220	272	370	382	393	404		< −210	< −150	1.001	1.002	.32
Monel alloy	501	.306	26.0	9.5	2400/2460	.100	7.6	8.2	8.7	9.5		121	167	220	272	370	382	393	404		< −210	< −150	1.001	1.002	.32
Inconel alloy	600	.304	31.0	11.0	2500/2600	.106	7.4	7.8	8.4	9.0		103	127	158	193	620	639	680	683	704	−192		1.010		.29
Inconel alloy	604	.305					6.8	7.6	8.2	9.0		101	126	160	192	666	687	715	709	728	< −320		1.004		
Inconel alloy	625	.305	29.8	11.4		.098	7.1	7.4	7.8	8.7		68	93	121	151	776	809	830	821	806					.31
Inconel alloy	700	.295	32.0		2375/2480	.11	6.9	7.5	8.1	9.2							717				< −320	< −320	1.001	1.004	
Inconel alloy	702	.302	32.0				6.7	7.7	8.3	9.2		81	106	144		738	765	787	757	716		< −320		1.003	
Inconel alloy	718	.296	29.0	11.2			7.2	7.9	8.2	9.3	10.0	78	104	135	167	751	770	799	799	810	< −320	−170	1.001	1.001	.29
Inconel alloy	721	.298					7.3	8.0	8.4	9.3		79													
Inconel alloy	722	.298	31.0	11.0	2540/2600	.105	6.7	7.9	8.4	9.4	10.5	102				750						−125		1.002	
Inconel alloy	X–750	.298	31.0	11.0	2540/2600	.103	7.0	7.4	8.1	9.1		83	104	131	159	731	754	783	768		−225	−193	1.002	1.0035	
Inconel alloy	751	.298	31.0	11.0	2540/2600																				
Incoloy alloy	800	.290	28.0	11.0	2475/2525	.12	7.9	9.0	9.4	10.1		80	109	139	174	595	662	722	764	788	−175		1.009		.30
Incoloy alloy	801	.287	29.0				8.1	9.0	9.3	10.1															
Incoloy alloy	804	.286	28.0				8.0									638					< −320		1.003		
Incoloy alloy	825	.294	28.0		2500/2550		7.8	8.4	8.8	9.6		77	103	131	164	678	719	761	770	793	< −320		1.005		
Ni-Span-C alloy	902	.293	24/29	9/10	2650/2700	.12	4.2	6.0				84	114	141		611					340	380			

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[a] 32—212 °F

[b] 27 °F.

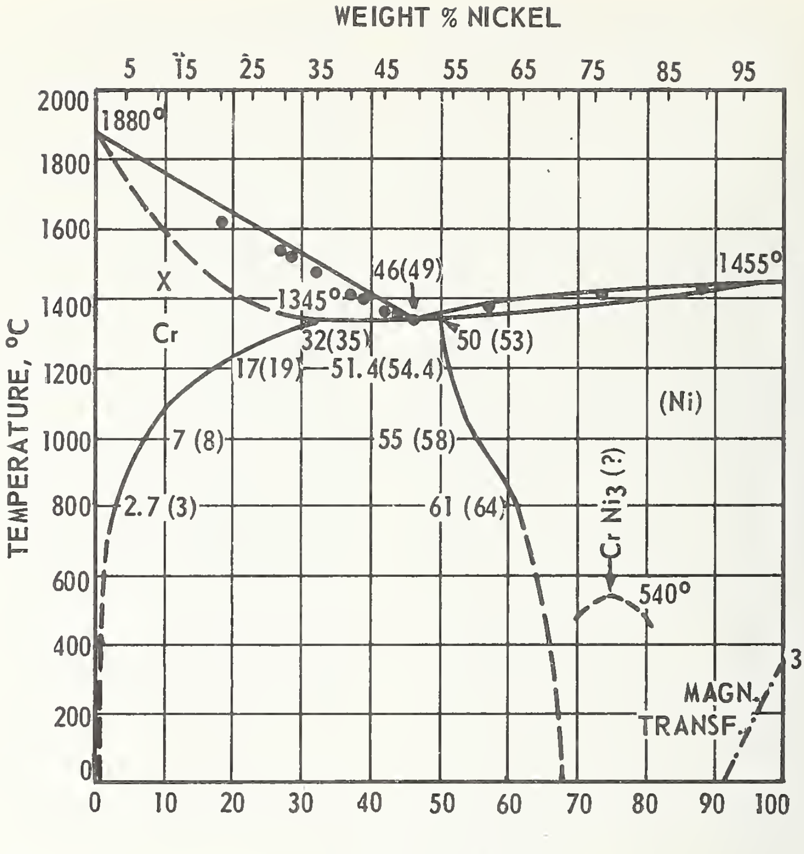

FIGURE 50. *Nickel-chromium constitution diagram* [*572*].
Numbers refer to atomic (weight) percent at the temperatures indicated.

couple at temperatures up to 1,400 °C. The life of the thermocouple is short in oxidizing atmospheres above about 1,100 °C, and the emf is subject to change in an alternately oxidizing and reducing atmosphere.

The 80 percent Ni–20 percent Cr alloy, known as Chromel alloy A, was developed in 1906 by A. L. Marsh for use as an electrical resistance alloy [574]. The use of the drawn or rolled alloy for electrical heating elements is discussed in ASTM Specification B344–65. Properties of interest of the nickel-chromium and related alloys are summarized in tables 34 and 35 [575 and 576]. The effect of increasing temperature on the resistivity of 80–20 alloy is shown in figure 51 [577]. Values for the specific heat of 80 Ni–20 Cr, as reported by Douglas and Dever [578] and shown in figure 52, show a discontinuity in the vicinity of 600 °C that has not yet been fully explained.

TABLE 33. *Thermal electromotive force of chromel-alumel thermocouple with cold junction at 0 °C* [*573*] [a]

Temperature	Electromotive force	Temperature	Electromotive force
°C	mV	°C	mV
−200	−5.75	700	29.14
−100	−3.49	800	33.31
0	0	900	37.36
100	4.10	1,000	41.31
200	8.13	1,100	45.14
300	12.21	1,200	48.85
400	16.39	1,300	52.41
500	20.64	1,400	55.81
600	24.90		

[a] More detailed tables are presented in NBS Circular 561, published in 1955.

The maximum temperature to which a heating alloy is subjected is one of the most important factors governing service life. Whether the temperature is constant or intermittent also has a marked effect. Data from accelerated laboratory tests (fig. 53) [575] illustrate the effects of temperature on heating elements made from 80–20 alloy.

Resistance to oxidation is important in heating units. Zima [579] reported that the rate of oxidation of 80–20 alloy at 2000 °F, in oxygen at atmospheric pressure, was only a little more than 1 percent of the oxidation rate of pure nickel under the same conditions. Rates of oxidation of 80 Ni–20 Cr and of nickel are appreciably less in air than in oxygen. Gulbransen and Andrew [233] reported that pure chrom-

TABLE 34. *Physical properties of electric resistance heating elements* [575]

Typical composition, %	Resistivity at 68 °F, ohm per cir mil-ft	Specific gravity	Density, lb/in³	Average percent change in resistance from 68 °F to				Thermal expansion, micro in/in/ °F from 68 °F to			Tensile strength at 68 °F, 1000 psi	Approximate melting point, °F	Maximum furnace operating temperature in air, °F
				500 °F	1000 °F	1500 °F	2000 °F	212 °F	1060 °F	1485 °F			
78.5 Ni, 20 Cr, 1.5 Si, (80–20)	650	8.41	0.3039	+4.2	+ 7.0	+ 6.3	+ 7.7	7.5	8.4	9.8	100/200	2550	2100
73.5 Ni, 20 Cr, 5 Al, 1.5 Si	830	7.90	.2854	+2.5	+ 2.8	− 1.6	− 3.7	7.0	-------	-------	130/180	2540	2200
68 Ni, 20 Cr, 8.5 Fe, 2 Si	700	8.33	.3010	+3.9	+ 6.7	+ 6.0	+ 7.1	-------	7.0	-------	130/180	2540	2100
60 Ni, 16 Cr, 22.5 Fe, 1.5 Si	675	8.25	.2979	+5.9	+10.9	+12.4	+16.2	7.5	8.4	9.8	95/175	2462	1850
35 Ni, 20 Cr, 43.5 Fe, 1.5 Si	610	7.95	.2870	+8.4	+16.7	+21.8	+24.8	8.7	8.7	-------	70/150	2515	1700

TABLE 35. *Physical properties of electrical resistance alloys* [576]

Typical composition, %	Resistivity at 68 °F, ohms per cir mil-ft	Temperature coefficient of resistance, microhm/ohm/°C	Thermal emf vs copper, microvolts/°C	Thermal expansion, micro-in/°C	Tensile strength at 20 °C, 1000 psi	Specific gravity at 20 °C	Density, lb/in³
99.8 Ni	48	+6000 (20 to 35 °C)	−22 (0 to 75 °C)	15	50/110	8.9	0.32
71 Ni, 29 Fe	120	+4500 (20 to 100 °C)	−39 (0 to 100 °C)	15	70/150	8.5	.31
80 Ni, 20 Cr	675	+ 85 (−55 to 100 °C)	+ 5 (0 to 100 °C)	13	100/200	8.4	.31
75 Ni, 20 Cr, 3 Al+Cu or Fe	800	± 20 (−55 to 100 °C)	+ 1 (0 to 100 °C)	13	130/180	8.1	.29
76 Ni, 17 Cr, 4 Si, 3 Mn	800	± 20 (−55 to 100 °C)	− 1 (0 to 100 °C)	15	175/200	7.8	.28
60 Ni, 16 Cr, 24 Fe	675	+ 150 (20 to 100 °C)	+ 0.8 (0 to 75 °C)	13	95/175	8.3	.30
35 Ni, 20 Cr, 45 Fe	610	+ 350 (20 to 100 °C)	− 3 (0 to 100 °C)	14	80/160	7.9	.29

ium oxidized 4 times as fast, and pure nickel 12 times as fast, as the 80–20 alloy at temperatures from 500 to 950 °C under an oxygen pressure of 7.6 cm. In another publication [580], these authors reported that the rates of oxidation at about 900 °C were lower for continuous exposure than for hot-cold cycling. The mechanism of oxidation of nickel-chromium alloys (up to 80% Cr) has been studied by Birks and Rickert [581] at temperatures up to 1100 °C. Hopkinson and Copson [582] evaluated the effect of additions of niobium, titanium, and silicon on the internal oxidation of several nickel-chromium and nickel-chromium-iron alloys. Carburization and oxidation in industrial gases at 900 to 1,000 °C is avoided if 2 percent of silicon is added to the 80 Ni–20 Cr alloy [583].

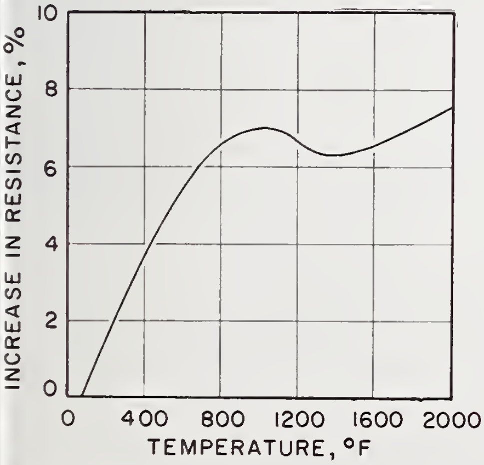

FIGURE 51. *Effect of temperature on the electrical resistance of Chromel A (80 Ni–20 Cr)* [577].

Osipov and Miroshkina [584] reported that the highest resistance to short-time plastic deformation of nickel-chromium alloys at temperatures up to 1,000 °C was obtained with the highest chromium content tested (23.82%), but that the creep rate in long-time tests at high temperatures was increased. The effect of minor elements and of atmosphere on the creep-rupture properties of 80 Ni–20 Cr alloys was reported by Widmer and Grant [585,586]. Haynes [587] found that the addition of niobium to low-

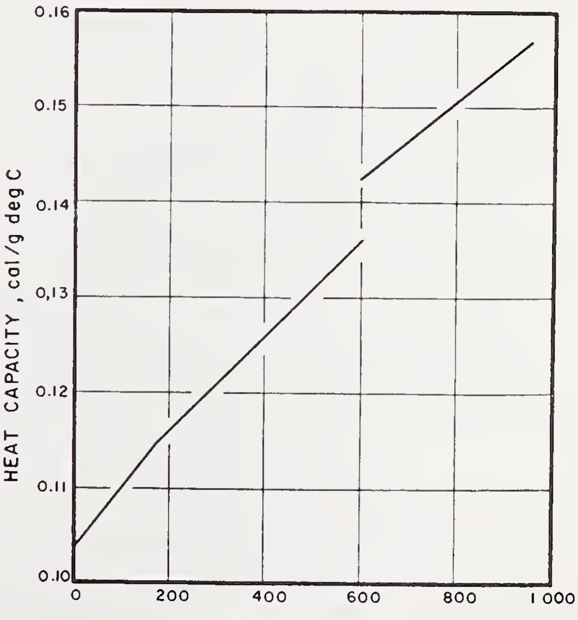

FIGURE 52. *Specific heat of Chromel A (80 Ni–20 Cr)* [578].

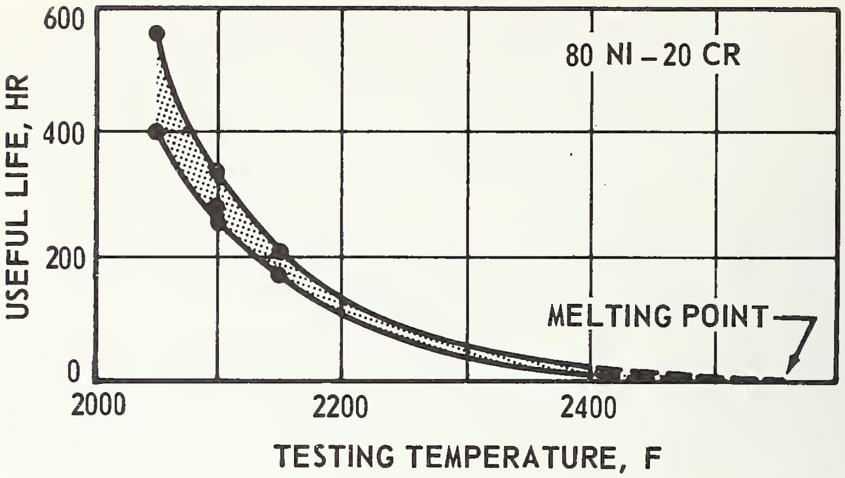

FIGURE 53. *Effect of temperature on the useful life of 80 Ni-20 Cr alloy* [575].

carbon nickel-chromium alloys can confer marked precipitation-hardening capacity. The room-temperature yield strength was raised and creep resistance at elevated temperatures was improved. Further improvement resulted from additions of molybdenum and/or tungsten. Koster and Christ [588] conducted a systematic study of the effect of varying additions of cobalt, aluminum, and titanium on the mechanical and physical properties of 80 Ni–20 Cr and 60 Ni–20 Cr–20 Co alloys.

The properties enumerated for the nickel-chromium alloys, plus their resistance to various corrosive media, make wrought 80 Ni–20 Cr suitable for engineering construction, particularly for use at temperatures higher than those that the less expensive nickel-chromium-iron alloys can withstand. However, the 80–20 alloy is subject to plastic flow under relatively light loads at high temperatures and, therefore, does not appear in lists of superalloys.

According to Bagger [589], 80 Ni–20 Cr forgings have good corrosion resistance, moderate strength characteristics, and are used for high-temperature applications. The alloy forges readily at 2,200 °F and is annealed at 1,600 to 1,900 °F.

The series of alloys known as Nimonic alloys are nickel-chromium and nickel-chromium-cobalt base alloys specifically developed to meet strict limitations on permissible creep of vital components under given conditions of stress and temperature. There are also available complementary casting alloys, known as Nimocast alloys, for high-temperature service. Detailed data on these alloys are given in publications by Henry Wiggin and Co.[590,591] and additional data are given by Forrest and Armstrong [592], Forrest and Smith [593], and Franklin et al.[594]. The forgeability of the Nimonics was studied by Yoda et al.[595], and spot-welding techniques were reported by Waller and Knowlson [596]. Compositions of the Nimonic alloys are given in table 36.

Nimonic alloy 75 is basically an 80–20 nickel-chromium alloy, stiffened by a small addition of titanium. The alloy combines the inherent oxidation resistance of the nickel-chromium alloys with improved mechanical properties at elevated temperatures. It is comparatively ductile at room temperature, permitting forming by spinning, pressing, or rolling, and is weldable by all conventional methods.

Nimonic alloy 80A is an 80–20 nickel-chromium alloy hardened by closely controlled additions of titanium and aluminum. In addition to its good creep properties, its resistance to high-temperature fatigue is noteworthy. These properties, combined with the oxidation resistance inherent in the nickel-chromium alloys, make it an ideal material for gas-turbine blades and other highly stressed components operating

TABLE 36. *Chemical composition of the Nimonic alloys* [590]

Alloy	Percent											
	C	Si	Cu	Fe	Mn	Cr	Ti	Al	Co	Mo	B	Ni
Nimonic alloy 75	0.08/0.15	1.0 max	0.5 max	5.0 max	1.0 max	18 /21	0.2/0.6	----------	----------	----------	----------	bal
Nimonic alloy 80A	.1 max	1.0 max	.2 max	3.0 max	1.0 max	18 /21	1.8/2.7	1.0/1.8	2.0 max	----------	0.008 max	bal
Nimonic alloy 90	.13 max	1.5 max	----------	3.0 max	1.0 max	18 /21	1.8/3.0	.8/2.0	15 /21	----------	----------	bal
Nimonic alloy 105	.2 max	1.0 max	.5 max	2.0 max	1.0 max	13.5/15.75	0.9/1.5	4.5/4.9	18 /22	4.5/5.5	----------	bal
Nimonic alloy 115	.20 max	1.0 max	.2 max	1.0 max	1.0 max	14 /16	3.5/4.5	4.5/5.5	13.5/16.5	3 /5	----------	bal

within the recommended limits of temperature and stress.

Nimonic alloy 90 has a nickel-chromium-cobalt base resulting in a material which has generally superior properties to Nimonic 80A, enabling it to be used successfully at temperatures up to 900 °C.

Nimonic alloy 105 is a nickel-chromium-cobalt alloy with an addition of molybdenum together with modified titanium and aluminum contents. It has outstanding resistance to creep at temperatures higher than those at which Nimonic alloy 90 can be used.

Nimonic alloy 115 was developed to have even better high-temperature properties than Nimonic alloy 105. When melted in vacuum, it has a temperature advantage of about 40 °C over Nimonic 105.

The physical and mechanical properties of cast 40 Ni–60 Cr alloy were investigated by McDowell and Mihalisin [597] and the superior resistance of this alloy to residual oil-ash corrosion has been described [598].

c. Nickel-Chromium-Iron Alloys

The nickel-chromium alloys, modified by the addition of iron and other elements, form a large group of materials characterized generally by excellent heat and corrosion resistance and good strength at moderately elevated temperatures. The Huntington Alloy Products Division of The International Nickel Company, Inc. markets a family of nickel-chromium-iron alloys under the trademarks "Inconel" and "Incoloy." Nominal compositions of these alloys are given in table 31 and physical constants are given in table 32. Additional alloys, analyses of which have been standardized by the Alloy Casting Institute, are discussed in the section dealing with cast heat-resisting steels. The constitution of the ternary system nickel-chromium-iron at 650 °C (1200 °F) is shown in figure 54.

The 80 Ni–14 Cr–6 Fe alloy, made by adding ferrochromium to nickel and originally designated as Inconel, was first offered in 1932 to the dairy industry for its resistance to corrosion by milk [600]. It is now designated as Inconel alloy 600 with a slightly different composition. Nickel contributes in high degree to its resistance to corrosion by many inorganic and organic compounds throughout wide ranges of acidity and alkalinity. Chromium confers resistance to sulfur compounds in the atmosphere or in many other corrosives; it also provides resistance to oxidizing atmospheres at elevated temperatures, and to oxidizing conditions in corrosive solutions. Its chromium content makes it superior to pure nickel under oxidizing

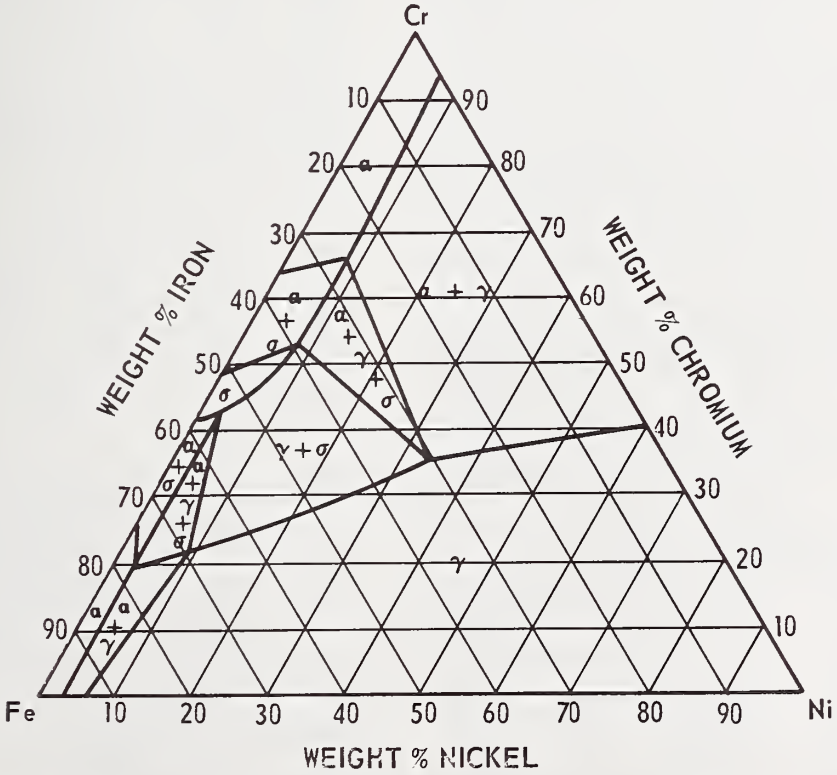

FIGURE 54. *Constitution of the terary system nickel-chromium-iron at 650 °C [599].*

conditions, while at the same time its high nickel content enables it to retain a considerable corrosion resistance under reducing conditions. Inconel alloy 600 has been used for the alkaline digesters in paper making [601], in petroleum refineries [602], and in the soap and fatty acids industry [220], as well as many other applications. It shows excellent resistance to sulfur dioxide but is corroded by hydrogen sulfide [603]. Moore and Mason [604] reported that Inconel alloy 600 was more resistant than stainless steel to lead bromide vapor at 1,350 to 1,650 °F, and Farber et al. [605] found that it was the most resistant, of all the metals tested, to nitric acid at temperatures up to 1,700 °F. According to Johnson et al. [606], the wear and sliding fraction properties of cast Inconel alloy 610 against ball-bearing steel (SAE 52100) compared favorably with the performance of nodular iron. Weldments made in inert gas with Inconel filler metal 62 welding rod were better than those made with a metal-arc coated electrode when the weldments were tested at 1,800 °F, but both procedures were equally good when the weldments were tested at 1,400 and 1,600 °F [607].

Some of the room-temperature mechanical properties of Inconel alloy 600 are tensile strengths ranging from 80,000 to 100,000 psi for annealed rod and bar to 165,000 to 185,000 psi for spring-temper wire. Corresponding yield strengths are 25,000 to 50,000 psi and 150,000 to 175,000 psi, with elongations in 2 in of 50 to 35 percent and 10 to 2 percent, respectively [608]. The strength properties at elevated temperatures are summarized in tables 37, 38 and 39.

Inconel alloy 600 has excellent properties at subzero temperatures. The strength factors increase considerably without appreciable change in ductility factors and toughness. Some low temperature properties are summarized in table 40.

The addition of aluminum and titanium to Inconel alloy 600 confers the ability to age harden, and additions of niobium further stiffen the matrix and stabilize the carbides. Inconel alloy X–750, formerly designated Inconel X alloy, is the age-hardening variety of Inconel alloy 600. This alloy was developed to have a

TABLE 37. *Tensile properties of hot-rolled Inconel alloy 600 at elevated temperatures [608]*

Temperature	Tensile strength	Yield strength (0.2%)	Elongation in 2 in	Modulus of elasticity
°F	*psi*	*psi*	*%*	10⁶ *psi*
70	90,500	36,500	47	31.0
600	90,500	31,000	46	29.5
800	88,500	29,500	49	28.0
1000	84,000	28,500	47	26.8
1200	65,000	26,500	39	25.5
1400	27,500	17,000	46	24.0
1600	15,000	9,000	80	22.5
1800	7,500	4,000	118	21.0

TABLE 38. *Creep properties of Inconel alloy 600 [608]*

Temperature, °F	Stress (psi) for secondary creep rate of					
	0.01% per 1000 hr			0.1% per 1000 hr		
	Cold drawn, annealed	Hot rolled	Coarse grained[a]	Cold drawn, annealed	Hot rolled	Coarse grained[a]
800	30,000	47,000	--------	40,000	54,000	--------
900	18,000	29,000	--------	28,000	40,000	--------
1000	6,000	13,000	--------	12,500	25,000	--------
1100	3,400	7,800	--------	6,800	12,000	--------
1200	2,200	8,000	--------	--------	9,500	--------
1300	1,400	4,700	4,000	--------	6,200	5,000
1400	970	2,300	3,500	--------	3,600	--------
1500	660	770	2,800	--------	1,500	3,200
1600	450	460	1,700	880	750	2,000
1700	--------	260	810	--------	420	1,100
1800	340	340	350	560	560	560
1900	--------	--------	--------	--------	--------	--------
2000	160	160	160	270	270	270
2100	100	100	100	170	170	170

[a] 2 hr at 2050 °F, air cooled.

TABLE 39. *Stress rupture properties of Inconel alloy 600 bar [608]*

Temperature, °F	Stress (psi) to produce rupture in				
	10 hr	100 hr	1,000 hr	10,000 hr	100,000 hr
	Cold-drawn, annealed				
1000	74,000	50,000	34,000	[a] 23,000	[a] 16,000
1200	34,000	23,000	14,500	[a] 9,400	[a] 6,000
1400	13,000	8,400	5,600	[a] 3,600	[a] 2,400
1600	7,500	4,800	3,000	[a] 1,900	[a] 1,200
1800	4,400	2,800	1,800	1,150	[a] 730
2000	2,100	1,400	[a] 920	[a] 620	[a] 400
	Hot rolled, annealed (2 hr at 1650 °F)				
1350	20,000	13,500	9,200	[a] 6,400	[a] 4,400
1600	8,100	5,300	[a] 3,500	[a] 2,200	[a] 1,500
1800	4,400	2,800	1,800	1,150	[a] 730
2000	2,100	1,400	[a] 920	[a] 620	[a] 400
	Coarse grained (2 hr at 2050 °F, air cooled)				
1350	19,000	14,800	9,800	[a] 7,000	[a] 5,000
1500	11,500	8,000	5,600	[a] 4,000	[a] 2,800
1600	8,000	5,300	[a] 3,500	[a] 2,300	[a] 1,500
1800	4,400	2,800	1,800	1,150	[a] 730
2000	2,100	1,400	[a] 920	[a] 620	[a] 400
2100	1,600	1,100	--------	--------	--------

[a] Extrapolated

TABLE 40. *Mechanical properties of Inconel alloy 600 bar at low temperatures [608]*

Condition	Temperature	Tensile strength	Yield strength, (0.2%)	Elongation in 2 in	Reduction of area	Charpy impact, (V-notch)
	°F	*psi*	*psi*	*%*	*%*	*ft-lb*
Annealed	70	93,800	36,800	37.3	64.1	236
	−110	106,400	42,400	39.8	64.0	206
Hot rolled	70	87,000	--------	42.5	71.9	213
	−315	116,800	--------	51.0	72.7	169
Cold drawn 50%	70	145,000	--------	10.0	35.1	69
	−315	182,000	--------	10.0	49.5	61

TABLE 41. *Some properties of age-hardened*[a] *Inconel alloy X–750 bar stock [608]*

Temperature	Tensile properties				Creep strength, stress (psi) to produce an elongation of		Stress-rupture strength, stress (psi) for rupture in		Modulus of elasticity	Endurance limit (10⁸ cycles)
	Tensile strength	Yield strength (0.2%)	Elongation in 2 in	Reduction in area	0.1% per 1,000 hr	0.01% per 1,000 hr	100 hr	1,000 hr		
°F	*psi*	*psi*	*%*	*%*					*10⁶ psi*	*psi*
70	162,000	92,000	24	30	----------	----------	----------	----------	31.0	----------
600	154,000	88,000	28	34	----------	----------	----------	----------	28.7	----------
1000	140,000	84,000	22	30	----------	----------	115,000	110,000	26.7	----------
1200	120,000	82,000	9	11	63,000	54,000	80,000	68,000	25.5	55.0
1350	92,000	74,000	7	12	38,000	30,000	50,000	40,000	24.4	48.5
1500	52,000	44,000	22	34	18,000	14,000	28,000	18,000	23.1	36.0

[a] Solution treated 2100 °F for 4 hr, aged 1550 °F for 24 hr, and re-aged 1300 °F for 20 hr, air cooled.

low creep rate under high stresses at 1200 to 1500 °F after suitable thermal treatment and a considerable portion of its high-temperature strength is retained at temperatures up to 1500 °F. It may be used as spring material at moderately elevated temperatures. Above 1500 °F the creep strength falls off rapidly and the resistance to oxidation is inferior to that of alloy 600. Some properties of alloy X–750 are summarized in table 41.

Inconel alloy 625 is a high strength corrosion resistant material in which the nickel-chromium matrix is solid-solution strengthened by additions of molybdenum and columbium [608a]. Figures 55 and 56 show the tensile and stress-rupture properties, respectively, of this alloy.

Inconel alloy 700 has excellent high-temperature strength characteristics and good oxidation and corrosion resistance. Its major use is for blades in aircraft jet engines, but the material is useful in many additional applications because of its unusual high-temperature properties [609].

Inconel alloy 702 is a nickel-chromium base alloy that contains relatively high aluminum content for excellent resistance to oxidation at elevated temperatures. At high temperatures the surface of a nickel-rich, nickel-chromium alloy becomes covered with a compact layer of uniformly thick oxide; the presence of aluminum improves the protective action of the oxide.

Inconel alloy 718 is a nickel-chromium-iron-molybdenum alloy made age-hardenable by the addition of niobium. It has a number of unique characteristics which distinguish it from the family of nickel-chromium-iron alloys hardened by aluminum and titanium. These are exceptionally high yield, tensile, creep, and rupture strengths at temperatures up to 1300 °F; good ductility in the temperature range of 1200 to 1400 °F, and sluggish response to age hardening, which permits annealing and welding without spontaneous hardening during heating and cooling. It may be pickled in the age-hardened condition without intergranular attack and can be repair welded in the age-hardened condition. Inconel alloy 718 is annealed at about 1750 °F and aged 1325 °F. The ageing time is quite long—16 hr. Some of the mechanical properties are summarized in figure 57.

IN–102 is essentially a nickel-chromium-iron base alloy (15% Cr, 7% Fe) solid-solution strengthened with 3 percent columbium, 3 percent molybdenum, and 3 percent tungsten. It

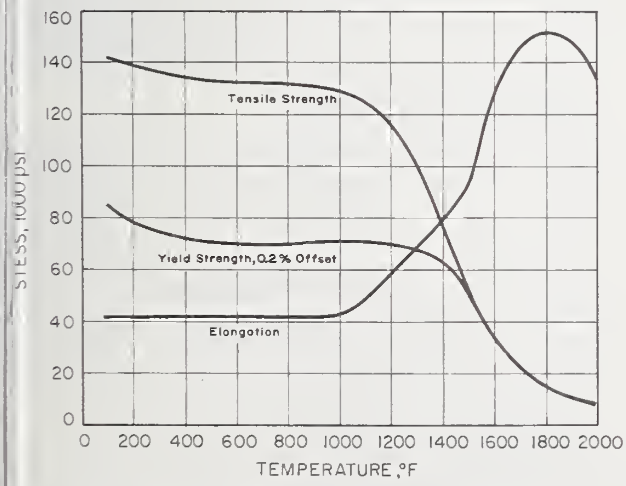

FIGURE 55. *Tensile properties of Inconel alloy 625 [609].*
(Hot rolled 9/16 in rod, annealed 1 hr at 1600 °F.)

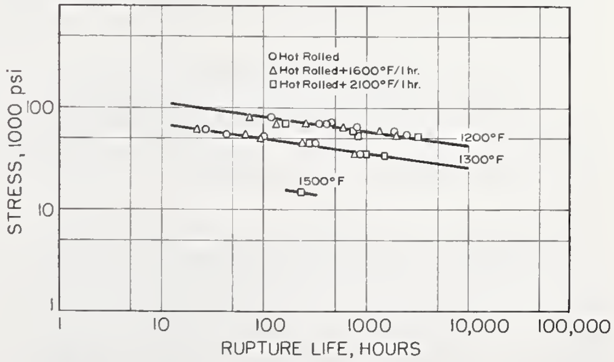

FIGURE 56. *Stress-rupture strength of Inconel alloy 625 [609].*
(Hot rolled 9/16 in rod, annealed 1 hr at 1600 °F.)

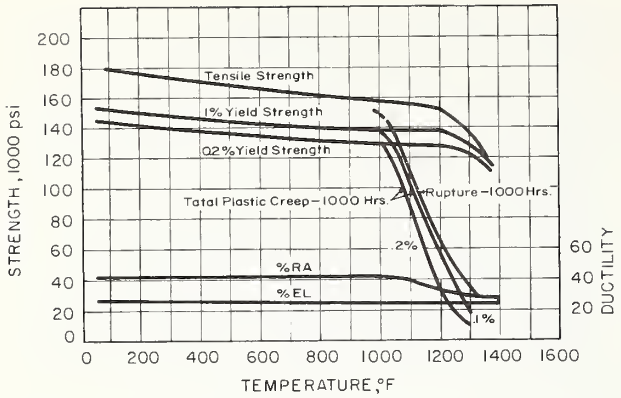

FIGURE 57. *Tensile, creep, and rupture properties of Inconel alloy 718 [610].*
(Bar stock annealed 1 hr at 1700 °F and aged 16 hr at 1325 °F.)

was developed to meet the need for stronger materials for steam turbine applications at 1200 °F. At this temperature, its 10,000-hr rupture strength is 40,000 psi.

As may be seen from table 31, the Incoloy nickel-iron-chromium alloys are characterized by a much lower nickel content than the Inconel alloys, but the chromium contents are higher. Incoloy alloy 800 is an austenitic solid solution alloy and was developed to provide a material of good strength and resistance to oxidation and carburization at elevated temperatures. Some of its more important uses are in the industrial heating field for furnace equipment, baskets, trays, muffles, radiant tubes, etc.; in the petrochemical field for reformer and cracker tubes; in the domestic appliance field as a sheath material for electrical resistance heating elements; and in the food industry for process equipment. Its corrosion resistance has led to its use in a variety of corrosive environments. Incoloy alloy 825 (formerly designated Ni-O-Nel alloy) was developed to handle a wide variety of corrosive solutions, some of unusual severity. Many of the successful applications of Incoloy alloy 825 are in the handling of sulfuric acid solutions in a variety of processes where few other materials have adequate corrosion resistance.

The various Inconel alloys and Incoloy alloys are amenable to fabrication by forging, machining, and welding. Typical stress-rupture values are shown in figure 58. A condensed review of nickel-base alloys was written by Kihlgren [611].

Wick [612] patented an alloy suitable for valve-seat-insert castings containing 0.85-3.5 percent total carbon, 0.5-3.0 percent Mn, 1.5-3.5 percent Si, 5-20 percent Cr, 4-12 percent Mo, 4-12 percent Co, 4-12 percent W, 0.2-6.0 percent Cu, 0.2-4.0 percent Al, 5-35 percent Fe, remainder Ni. The alloy is stated to be resistant to thermal cracking at temperatures in the region of 1500 °F, to have good hot-hardness properties and high-temperature impact resistance, and to be stable at high temperatures. Its expansion characteristics are compatible with those of the engine block in which the valve seat is inserted, it retains a good seal, is resistant to corrosion by the hot exhaust gases of an internal combustion engine, and it can be used for heavy-duty applications if required.

d. Other High-Nickel Alloys

The first of the high nickel corrosion-resistant alloys known as Hastelloy alloys were nickel-molybdenum-iron alloys, but in subsequent alloys the composition was considerably changed. The nominal compositions of some of the Hastelloys as given by Fritzlen [613] are shown in table 42.

TABLE 42. *Nominal compositions of Hastelloy alloys [613, 613a]*

Alloy	Percent							
	Ni	Mo	Fe	Cr	W	Si	Cu	Others
Hastelloy alloy B	62	28	5	----	-------	----	-----	
Hastelloy alloy C	54	17	5	15	4	----	-----	
Hastelloy alloy D	85	----	----	----	-------	10	3	
Hastelloy alloy F	47	7	17	22	-------	----	-----	
Hastelloy alloy G	44	6.5	20	22.2	1.0 max	----	2.0	Co 2.5 max. 2.1 Cb+Ta
Hastelloy alloy N	70	17	5	7	-------	----	-----	
Hastelloy alloy W	62	24.5	5.5	5	-------	----	-----	
Hastelloy alloy X	47	9	18	22	-------	----	-----	

The Hastelloy alloys are not high-strength alloys, although many of them retain such a high percentage of their room-temperature strength at very high temperatures that structural applications at high temperatures are not unusual. Their strengths vary, depending on composition and form, but generally these alloys have tensile strengths in the neighborhood of 100,000 psi and yield strengths of approximately 50,000 psi. They are used, however, primarily for applications requiring exceptional corrosion resistance. The Hastelloy alloys are amenable to fabrication by forming and welding.

Hastelloy alloy B is notable for its unusually high resistance to all concentrations of hydrochloric acid at temperatures up to the boiling point. It is also resistant to other nonoxiding acids and salts, and has valuable high-temperature properties in that it retains over two-thirds of its room temperature strength at 1600 °F in oxidizing atmospheres (not oxidizing solutions). It may be used at high temperatures in reducing atmospheres. It should not be used for strongly oxidizing acids or salts.

Hastelloy alloy C possesses an unusual degree of resistance to oxidizing solutions, especially those containing chlorides, and to hypochlorite solutions and moist chlorine. It resists nitric, hydrochloric, and sulfuric acids at moderate

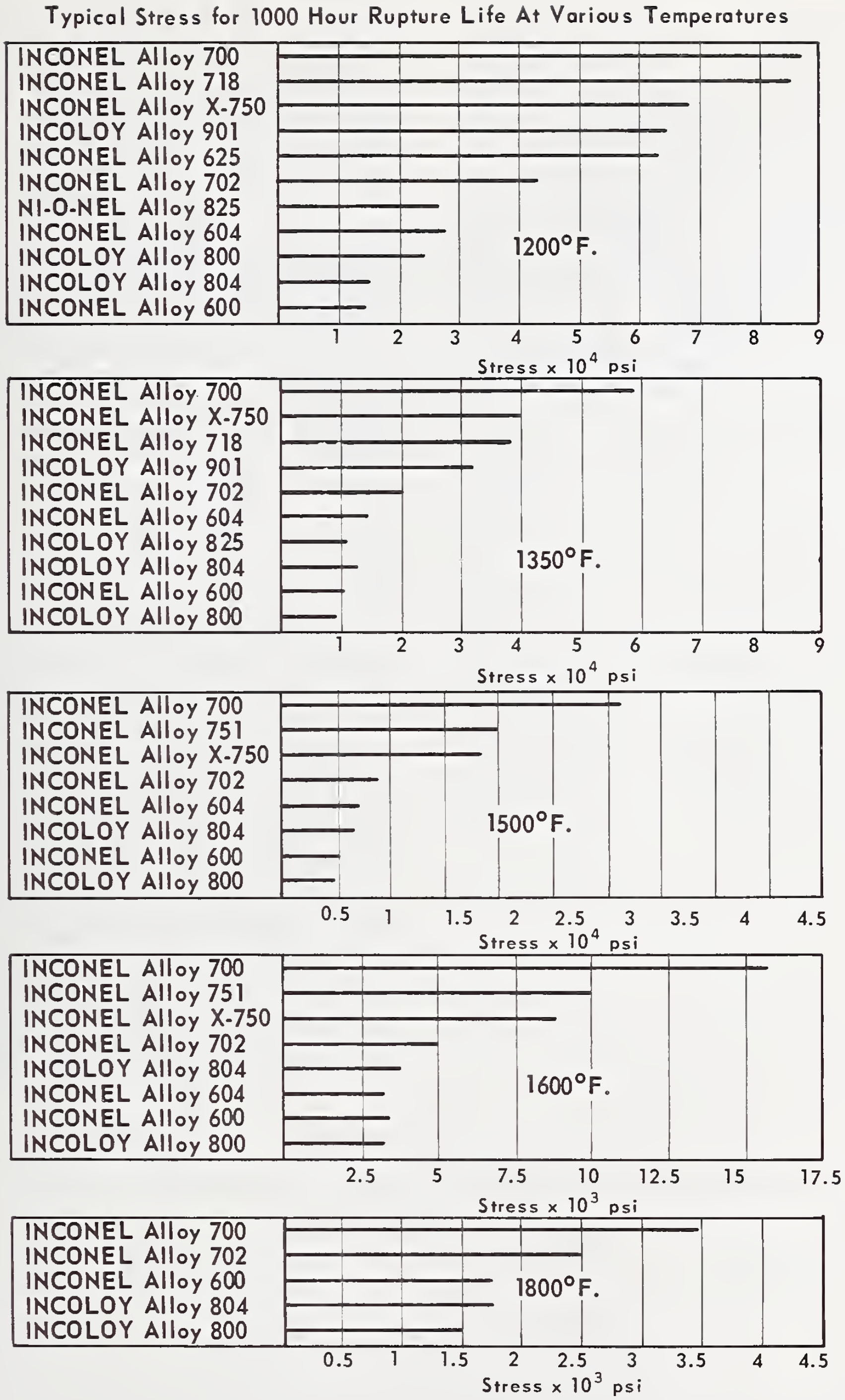

FIGURE 58. *Typical stress for 1000-hr rupture life of nickel alloys at various temperatures* [*43*].

temperatures, has excellent resistance to many corrosive organic acids and salts, and is resistant to oxidizing and reducing atmospheres up to 2000 °F. It should not be used above 120 °F in nitric and hydrochloric acid and salt combinations. An extensive study of the effect of heat treatment on the corrosion resistance of this alloy was reported by Streicher [614].

The most important property of Hastelloy alloy D is its resistance to all concentrations of hot sulfuric acid. It is also resistant to hydrochloric acid under mild conditions and to other nonoxidizing acids and salts. It should not be used under oxidizing conditions at elevated temperatures.

Hastelloy alloy F withstands the corrosive effect of acid and alkaline, and oxidizing and reducing conditions. It is especially resistant to stress-corrosion cracking in chloride solutions. A major use has been for lining sulfite pulp digesters and in semichemical pulping processes.

Hastelloy alloy G is used primarily for nuclear fuel applications [613a].

Hastelloy alloy N (also designated INOR-8) was developed for use as a container material for molten fluoride salts. It has good oxidation resistance in air up to 1800 °F. It is not recommended for nitric acid service.

Hastelloy alloy W is primarily a high-temperature alloy for extended structural applications up to 1400 °F. It also has excellent short-time strength at temperatures as high as 75 to 90 percent of its melting temperature.

Hastelloy alloy X has exceptional strength and oxidation resistance up to 2200 °F and is useful for many industrial furnace applications because of its resistance to oxidizing, neutral, and carburizing atmospheres. It has had wide use for aircraft parts such as jet engine tailpipes, after-burners, turbine blades and vanes. Donachie and Shepheard [615] studied the creep-rupture behavior of this alloy; their stress-rupture curves are shown in figure 59.

Another group of high-nickel corrosion-resisting alloys are the Illium alloys [615a]. The nominal compositions of some of these alloys as given by Johnson [616] are shown in table 43.

TABLE 43. *Nominal compositions of some Illium alloys [616]*

Alloy	Percent			
	Ni	Cr	Mo	Cu
Illium B	50	28	8.5	5.5
Illium G	56	22.5	6.5	6.5
Illium R	68	21	5	3
Illium 98	55	28	8.5	5.5

Illium R alloy is a wrought alloy, but the others are cast. All may be machined and welded.

The Illium alloys are characterized by high resistance to sea water and to many fluorine compounds. They should never be used for halogens, halogen acids, or halogen salt solutions.

e. Superalloys

The line of demarcation between heat-resistant (or high-temperature) alloys and superalloys is rather tenuous; as indefinite, indeed, as the dividing line between ferrous and nonferrous. Many of the superalloys are modifications of the heat-resistant, corrosion-resistant alloys and many of the nickel alloys already discussed fall into the general category of superalloys. Although attention will be directed mainly to those superalloys having nickel as a major, or at least a significant, part of their composition, it must be emphasized that the number of superalloys is legion, that most of them contain nickel, and that a systematic approach to their classification has never been developed.

Grant [617] pointed out that single-phase alloys such as Nichrome and Inconel alloy 600 are weak above about 1250 °F, but that their high-temperature strength and resistance to creep are materially improved by the introduction of a stable, hard phase or phases, i.e., precipitated carbides or intermetallic compounds. Most of the high-nickel superalloys are of the Al-Ti age-hardenable type. In these alloys, chromium is present to provide oxidation resistance along with some auxiliary strengthening. Columbium, molybdenum, tungsten, and tantalum are often present, separately or together, to provide solid solution strengthening of the matrix. The major part of the strengthening at high temperatures, however, is due to the precipitation of the $Ni_3(Al,Ti)$ compound, generally designated the

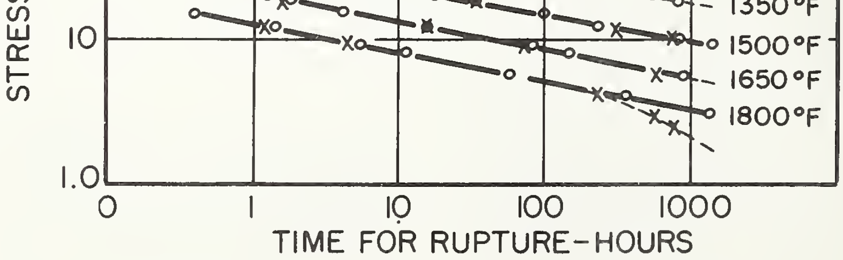

FIGURE 59. *Stress-rupture curves for Hastelloy alloy X [615].*

TABLE 44. *Compositions and treatments of high-temperature alloys* [621]

Alloy Designation	Nominal chemical composition, percent															Form			Treatment
	C	Mn	Si	Cr	Ni	Co	Mo	W	Cb	Fe	Ti	Al	B	Zr	Other	Cast	Bar	Sheet	
Alloy 713C	0.12			12.5	Bal		4.2		2.0		0.8	6.1	0.012	0.10		x			None.
Alloy 713LC	.05			12.0	Bal		4.5		2.0		.6	5.9	.010	.10		x			None.
Alloy 901	.05	0.10	0.10	12.5	42.5		5.7			Bal	2.8	.2	.015				x		2000/2/WQ+1450/2/AC +1325/24/AC.
Alloy 901																		x	1950/½/RAC+1400/2/AC.
A-286	.05	1.35	.50	15.0	26.0		1.3			Bal	2.0	.2	.015				x		1800/1/OQ+1325/16/AC.
B-1900	.10			8.0	Bal	10.0	6.0				1.0	6.0	.015	.10	4.0 Ta	x			None.
D-979	.05	.25	.20	15.0	Bal		4.0	4.0		27.0	3.0	1.0	.010				x		1900/1/OQ+1550/6/AC +1300/16/AC.
Discaloy	.04	.90	.80	13.5	26.0		2.7			Bal	1.7	0.1	.005				x		1850/2/OQ+1350/20/AC +1200/20/AC.
GMR 235-D	.15			15.5	Bal		5.0			4.5	2.5	3.5	.050			x			None.
Hastelloy alloy R-235	.15			15.5	Bal		5.5			10.0	2.5	2.0						x	1975/1/WQ+1975/½/AC +1400/16/AC.
Hastelloy alloy X	.10	.50	.50	22.0	Bal	1.5	9.0	.6		18.5								x	2150/1/RAC.
Inconel alloy 625	.05	.15	.30	22.0	Bal		9.0		4.0	3.0	.2	.2					x		2100/1/WQ.
Inconel alloy 700	.12	.10	.30	15.0	Bal	28.5	3.7			.7	2.2	3.0					x		2160/2/AC+1600/4/AC.
Inconel alloy 702	.04	.05	.20	15.6	Bal					.4	.7	3.4						x	2000/1/AC+1350/4/AC.
Inconel alloy 718	.04	.20	.30	18.6	Bal		3.1		5.0	18.5	.9	.4					x		1800/1/AC+1325/8/FC 20 °/hr to 1150/AC.
Inconel alloy 718																		x	1700/1/AC+1325/8/FC 100 °/hr to 1150/AC.
Inconel alloy 722	.04	.55	.20	15.0	Bal					6.5	2.4	.6						x	1975/4/AC+1300/20/AC.
Inconel alloy 750	.04	.70	.30	15.0	Bal				.9	6.8	2.5	.8					x		2100/2/AC+1550/24/AC +1300/20/AC.
Inconel alloy 750																		x	1950/½/AC+1300/20/AC.
IN 100	.18			10.0	Bal	15.0	3.0				4.7	5.5	.014	.06	1.0 V	x			None.
IN 102	.06			15.0	Bal		3.0	3.0	3.0	7.0	.6	.4	.005	.03	.02 Mg		x		1800/1/AC.
L-605	.10	1.50	.50	20.0	10.0	Bal		15.0										x	2250/1/RAC.
M-22	.13			5.7	Bal		2.0	11.0				6.3		.60	3.0 Ta	x			None.
MAR-M 200	.15			9.0	Bal	10.0		12.5	1.0		2.0	5.0	.015	.05		x			1600/50/AC.
MAR-M 246	.15			9.0	Bal	10.0	2.5	10.0			1.5	5.5	.015	.05	1.5 Ta	x			1550/50/AC.
M-252	.15	.50	.50	20.0	Bal	10.0	10.0				2.6	1.0	.005				x		1900/4/AC+1400/16/AC.
Nicrotung	.10			12.0	Bal	10.0		8.0			4.0	4.0	.050	.05		x			None.
Nimonic alloy 80A	.06	.10	.70	19.5	Bal	1.1					2.5	1.3					x		1975/8/AC+1300/16/AC.
Nimonic alloy 90	.07	.50	.70	19.5	Bal	18.0					2.4	1.4					x		1975/8/AC+1300/16/AC.
Nimonic alloy 115	.15			15.0	Bal	15.0	3.5				4.0	5.0					x		2175/1½/AC+2010/6/AC.
N-155	.15	1.50	.50	21.0	20.0	20.0	3.0	2.5	1.0	Bal					.15 N		x		2150/1/WQ+1500/4/AC.
PDRL 162	.12			10.0	Bal		4.0	2.0	1.0	Bal	1.0	6.5	.020	.10	2.0 Ta	x			None.
Refractaloy 26	.03	.80	1.00	18.0	Bal	20.0	3.2			16.0	2.6	.2					x		2100/1/OQ+1500/20/AC +1350/20/AC.
Rene 41	.09			19.0	Bal	11.0	10.0				3.1	1.5	.005				x		1950/4/AC+1400/16/AC.
Rene 41																		x	1950/½/AC+1400/16/AC.
S-816	.38	1.20	.40	20.0	20.0	Bal	4.0	4.0	4.0	4.0							x		2150/1/WQ+1400/16/AC.
TD-Nickel	.01	<.01	<.01	<.01	Bal	.03	<.01			<.01		<0.1			2.2 ThO_2		x		S.R. 1800/1 Argon/AC.
TD-Nickel																		x	S.R. 1800/15 min Argon/AC.
TRW 1900	.11			10.3	Bal	10.0		9.0	1.5		1.0	6.3	.030	.10		x			None.
Udimet 500	.08			18.0	Bal	18.5	4.0				2.9	2.9	.006	.05			x		1975/4/AC+1550/24/AC +1400/16/AC.
Udimet 500	.07			19.0	Bal	19.0	4.2				3.0	3.0	.007	.05		x			2100/4/AC+1975/4/AC +1400/16/AC.
Udimet 520	.05			19.0	Bal	12.0	6.0	1.0			3.0	2.0	.005				x		2025/4/AC+1550/24/AC +1400/16/AC.
Udimet 630	.03			18.0	Bal		3.0	3.0	6.5	18.0	1.0	.5					x		1875/4/AC+1400/8/AC +1200/10/AC.
Udimet 700	.08			15.0	Bal	18.5	5.2				3.5	4.3	.030				x		2150/4/AC+1975/4/AC+1550/24/AC +1400/16/AC.
Unitemp AF 1753	.24			16.3	Bal	7.2	1.6	8.4		9.5	3.2	1.9	.008	.06			x		2150/4/AC+1650/6/AC.
Waspaloy	.08			19.5	Bal	13.5	4.3				3.0	1.3	.006	.06			x		1975/4/AC+1550/24/AC +1400/16/AC.
X-40	.50	.75	.75	25.5	10.5	Bal		7.5								x			None.
16-25-6	.06	1.35	.70	16.0	25.0		6.0			Bal					.15 N	x			2150/1/WQ

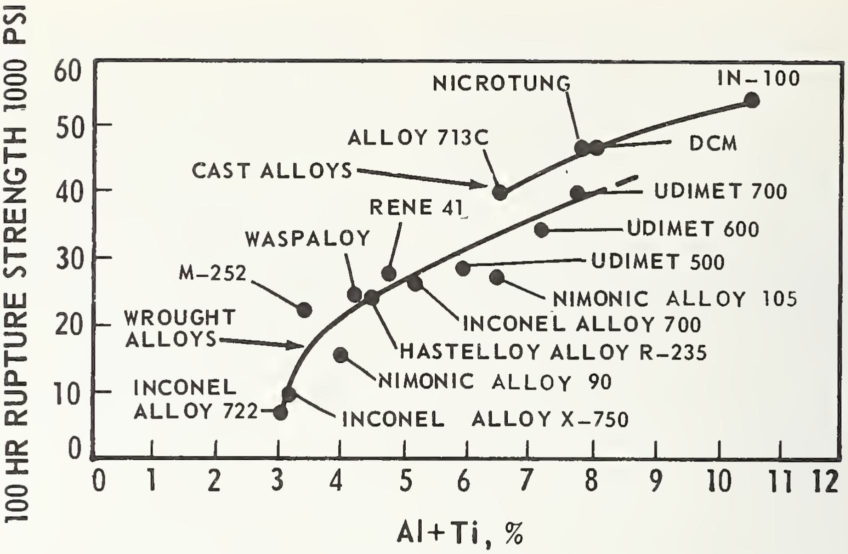

FIGURE 60. *The effect of aluminum plus titanium content on the 100-hr rupture life at 1600 °F of several high-temperature nickel alloys* [*618*].

gamma prime phase. The remarkable strengthening effect of this compound on commercial high-strength nickel alloys is indicated in figure 60. The improvement in the stress-rupture properties of some nickel-base alloys modified by precipitation-hardening and alloying additions, according to Ver Synder [574], is shown in figure 61. In some of the alloys cobalt is often present, replacing substantial amounts of nickel (or iron). In many alloys boron and zirconium are purposeful addition elements, importing improvements in high temperature creep properties and/or increased malleability. The status of the cobalt- and nickel-base high-temperature alloys was discussed by Sharp [618].

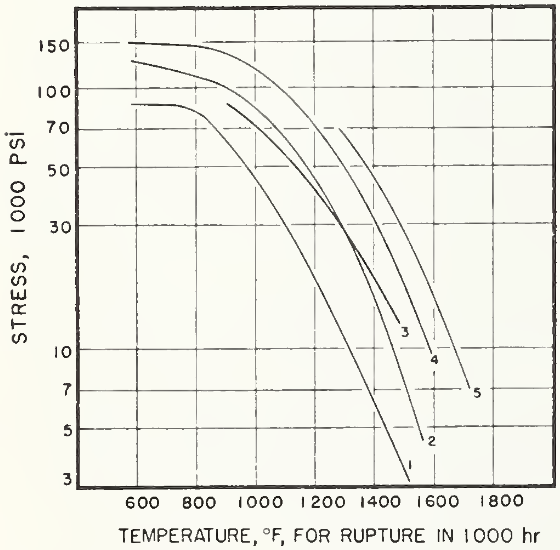

FIGURE 61. *Effect of modified compositions on the stress-rupture properties of some nickel-base alloys* [*574*].

Curve	Additional elements	Typical alloys
1	None	Inconel alloy 600; 80 Ni-20 Cr
2	2.5 Ti, 0.6 Al	Inconel alloy 722 W; Nimonic alloy 80.
3	19 Mo, 5 W	Hastelloy alloy C
4	2.5 Ti, 1 Al, 10 Co, 3 to 10 Mo	M252, Waspalloy
5	2.5 Ti, 3 Al, 13.3 Co, 3 Mo	Inconel alloy 700; Udimet alloy 500.

The high-temperature strengths of the superalloys increase the difficulty of hot working, and alloys with extra-special properties require extra-special care in forging. The selection of tools, cutting fluids, and machinability data for machining superalloys was discussed by Halverstadt [619]. Because of forming difficulties, some of the nonferrous superalloys, especially those high in aluminum, titanium, cobalt, tungsten, and molybdenum, are used in cast or investment-cast forms [620].

Table 44 gives a listing of the names and compositions of many nickel-bearing superalloys as listed by the International Nickel Company [621] and their strengths at elevated temperatures are summarized in figure 62. This reference contains considerable additional information on both the physical and mechanical properties of the alloys noted in table 44.

An extensive compilation of the compositions and strengths of superalloys was prepared by Simmons and Metzger [622] and a review of the properties and treatments of nickel-chromium high-temperature alloys was written by Young [623].

Maxson [624] described a general purpose alloy (45% Ni, 25% Cr, 3% W, 3% Mo, 3% Co, 1.25% Si, 0.08 % C max, bal Fe) for use in a

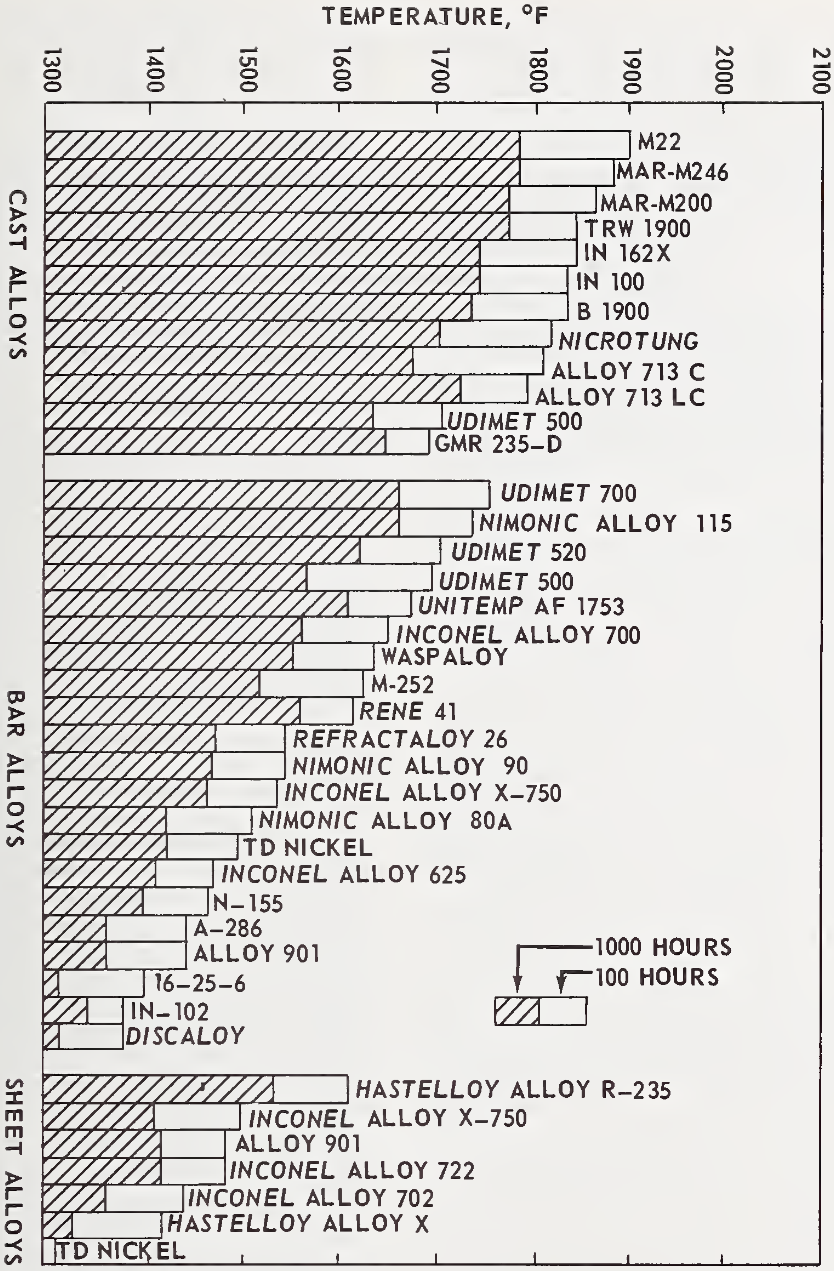

FIGURE 62. *Temperature to produce rupture in various high temperature alloys in 100 and 1000 hr at a stress of 20,000 psi* [*621*].

broad high-temperature range. He gives the following 100-hr stress rupture values:

1350 °F	23,000 psi
1400	18,500
1450	14,500
1500	10,500
1550	9,050
1600	7,200.

Freche et al. [625] reported that the strongest alloy obtained in their investigation (8% Ta, 6% Cr, 6% Al, 4% W, 4% Mo, 2.5% V, 1% Zr, 0.125% C, bal Ni) had as-cast rupture lives at a stress of 15,000 psi as follows:

1800 °F	1,200 hr
1850	560
1900	185.

Ultimate tensile strengths of 80,000, 54,300, and 49,200 psi were obtained at 1800, 1900, and 2000 °F, respectively. This alloy also exhibited extremely limited workability.

TD nickel is pure nickel strengthened by a dispersion of 2 percent thorium oxide. Anders et al. [626] describe its characteristics as follows:

> "Stress-rupture and creep strength better than superalloys from 1900 to 2400 °F.
> "Properties insensitive to overheating.
> "Easily fabricated.
> "Notch insensitive, good impact and fatigue properties.
> "Physical properties similar to wrought nickel; high thermal conductivity.
> "Lack of intergranular attack in oxidizing and corrosive media.
> "Resistant to oxidation and corrosion."

Stress-rupture data for TD nickel are shown in figure 63. The metallurgy and properties of thoria-strengthened nickel were reviewed by Rice [627].

Mechanical properties at high temperatures are the principal basis for evaluating superalloys, but physical properties such as coefficient of expansion, thermal conductivity, and emissivity are important in many high-temperature applications. Thermal stresses due to differential expansion of single parts subject to different temperatures, or of different parts at a joint, may comprise 50 percent of the total load and have been responsible for many cases of failure [628]. In general, a low coefficient of expansion is desired; in the case of dissimilar metal joints, the two coefficients may be high or low as long as they are equal. Thermal conductivity becomes critical in applications such as combustion chambers, especially when uneven combustion produces hot spots. Since most high-temperature alloys have comparatively low thermal conductivity, differential heating and hot spots can easily lead to severe distortion and actual burning through of the metal [628]. The International Nickel Company, Inc. has tabulated data on the physical properties of interest of the various nickel superalloys [621].

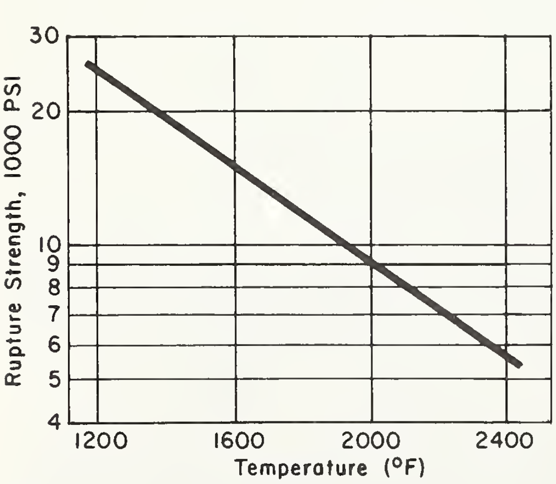

Figure 63. *100-hr stress-rupture strength of TD nickel [626].*

f. Nickel-Copper Alloys

Nickel and copper form a continuous series of solid solutions, as indicated by the phase diagram established by Guertler and Tammann [629] in 1907 and subsequently confirmed by other investigators; Pilling and Kihlgren [630] presented the diagram shown in figure 64. The solid solution alloys have a face-centered cubic structure and the lattice constant varies linearly with atomic concentration from 3.60 Å for copper to 3.54 Å for nickel. The only transition in the solid alloys is the magnetic transition, which varies with the weight percent of nickel from 353 °C for nickel to 25 °C for 70/30 Ni-Cu to about −170 °C for 50/50 Ni-Cu.

Impurities affect the physical and mechanical properties of the high-nickel alloys in much the same manner is they affect nickel. The carbon content must be kept low to avoid precipitation of free graphite with consequent intercrystalline brittleness. Additions of carbide-forming elements, such as manganese or titanium, reduce the amount of graphite precipitation. Sulfur is extremely harmful in these alloys and must be kept low. Lead in the presence of silicon coarsens the structure and causes cracking, particularly in sand-cast materials. Controlled additions of silicon, manganese, magnesium, and zinc are beneficial in most of the alloys.

The corrosion resistance of the nickel-copper alloys that contain more than 50 percent nickel are benefited by the high degree of nobility of copper and by the ability of nickel to protect itself, frequently through the development of passive oxide films. Such alloys are, in general, more resistant than nickel under reducing conditions and more resistant than copper under oxidizing conditions.

(1) *Monel alloys.* The most important of the high nickel-copper alloys are the Monel alloys. According to Mudge [631], in the early days of the nickel industry attempts were made to produce alloys from the Sudbury ores directly, without separating the copper and nickel. R. C. Stanley in 1905 perfected a process of oxidizing

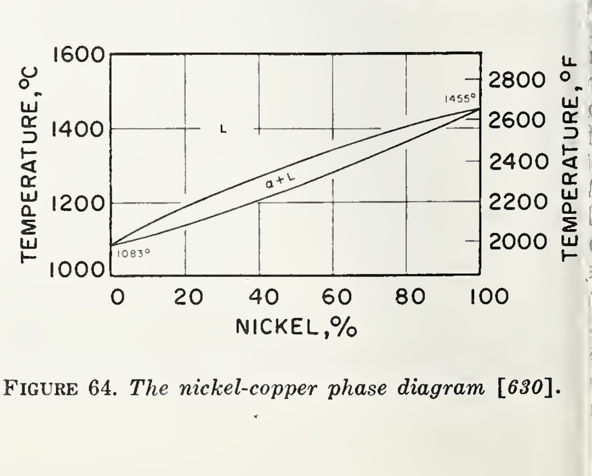

Figure 64. *The nickel-copper phase diagram [630].*

ne matte, which contained roughly twice as nuch nickel as copper, reducing the oxidized natte with charcoal, and adding magnesium to roduce a wrought alloy that was silvery white nd brighter than nickel, stronger than mild teel, and notably resistant to sulfuric acid and o sea water. The new alloy was named Monel n honor of Ambrose Monell, then president of he International Nickel Company.

The first large order for this alloy was for heet which was installed in 1909 as roofing for ne Pennsylvania Railroad station in New York ity and was still free from trouble in 1955 631]. Intensive research developed ever-idening use of this engineering material and y 1955, according to Mudge, there were 800 ecorded uses of Monel alloys, with corrosion esistance responsible for the majority of them. hroughout the development of the family of Ionel nickel-copper alloys, additions of chro-nium, manganese, aluminum, iron, molyb-enum, tungsten, titanium, and other metals ere tried for increased strength and for other easons. In the 1920's it was found that additions of about 4 percent of aluminum made the asic alloy age hardenable [632]. It is now nown that 16 different elements confer age-ardening characteristics on nickel and high-ickel alloys, the most important being alumi-um, titanium, columbium, and silicon, with nagnesium, molybdenum, tungsten, and beryl-um used to a lesser extent. The age-hardened Ionel alloys are readily fabricated in the soft ondition and can be hardened to strength levels omparable to those of quenched and tempered lloy steels and still retain their resistance to orrosion. Nominal compositions of the various Ionel alloys that are currently available from nternational Nickel are shown in table 31 and neir physical properties are shown in table 32.

The Monel nickel-copper alloy metals have seful resistance to neutral and alkaline salts, xidizing alkaline salts (except hypochlorites), ulfuric, hydrochloric, hydrofluoric and phos-horic acids (the alloys have useful resistance o corrosion by all acids except those that are ighly oxidizing), organic acids and compounds, nd alkalies. The alloys are not resistant to xidizing acid salts, nitric and nitrous acids, nd sulfurous acid. They are resistant to corro-ion by all common dry gases at room tempera-ure. They are not resistant to such gases as romine, chlorine, nitric oxides, ammonia, and ulfur dioxide in the presence of appreciable mounts of water.

Monel alloy 400 is available in all commer-ial forms and tempers. It is characterized by ood strength and ductility combined with xcellent resistance to many corrosive environ-nents. The alloy is notable for its toughness naintained over a wide temperature range. osenberg [323] reported a Charpy V-notch npact value of 180 ft lb at −78 °C. Sixty years of experience has established this alloy as a standard engineering material. It is a general purpose alloy used in many industries. Some typical applications are crude petroleum stills, process vessels, piping, pump and propeller shafts, gasoline and fresh water tanks, boiler feed water heaters, heat exchangers, deaerating heaters, valves and pumps, chemical processing equipment, marine fixtures, and electrical and electronic components.

Monel alloy 400 gives excellent service in sea or brackish water under high-velocity conditions, as in propellers, impellers, and condenser tubes, where resistance to the effects of cavitation and erosion are important. Corrosion rates in strongly agitated and aerated sea water usually do not exceed 1 mpy. Another important consideration in the use of the alloy in corrosive environments is its general freedom from stress-corrosion cracking. The limiting temperatures for use of alloy 400 in various environments are given in table 45.

TABLE 45. *Limiting temperatures for Monel alloy 400* [633]

Service or environment	Temperature, °F
Air	[a] 1000
Carbon monoxide	[a] 1500
Hydrogen	[a] 2000
Chlorine	800
Fluorine	900
Hydrogen chloride	450
Hydrogen fluoride	1200
Sodium, potassium, sodium-potassium (static)	1100
Steam	800

[a] Sulfur free. Do not exceed 500 to 600 °F if appreciable amounts of sulfur are present.

The results of the ASTM 20-year atmospheric exposure tests of Monel alloy 400 as reported by Copson [223], are shown in figure 65. Comparison with the results reported for nickel in figure 30 shows that alloy 400 is equally excellent in resisting the less corrosive atmospheres and is markedly superior to nickel in resistance to the industrial atmospheres of Altoona and New York City. In the ASTM 20-year tests, specimens of the alloy exposed at Altoona decreased 16 percent from the preexposure tensile strength of 80,000 psi, those at New York 11 percent, those at Sandy Hook 5.5 percent, and the changes in tensile strength at the other four stations were of the order of ±1 percent. According to Grant and Bucklin [634], Monel alloy 400 has very good resistance to oxidation at temperatures up to about 900 °F. From 900 to 1300 °F the surface scale is still thin and very adherent, but grain boundary penetration of oxide is evident. Above 1500 °F the bulk oxide grows rapidly, remains adherent and apparently quite dense, but is poorly protective.

According to Jenkins and associates [315], the 70/30 Ni/Cu alloy has the best high-temperature strength of the straight nickel-copper alloys, as shown in figure 66. This alloy also has

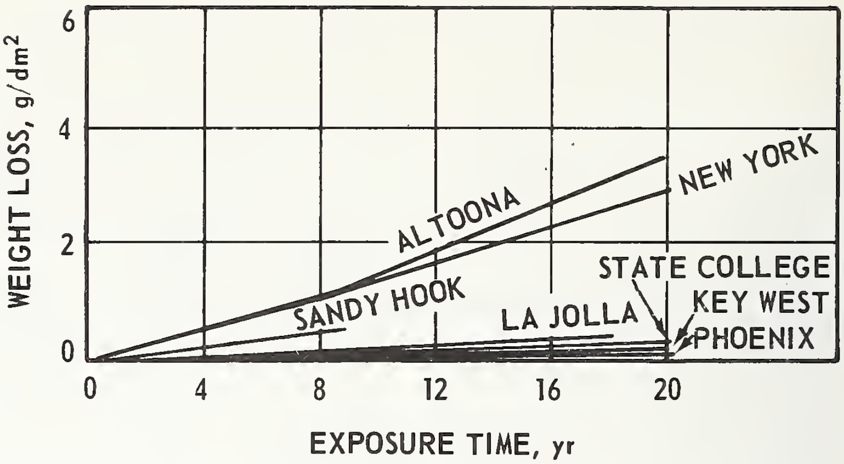

Figure 65. *ASTM 20-year atmospheric exposure tests of Monel Alloy 400* [*223*].

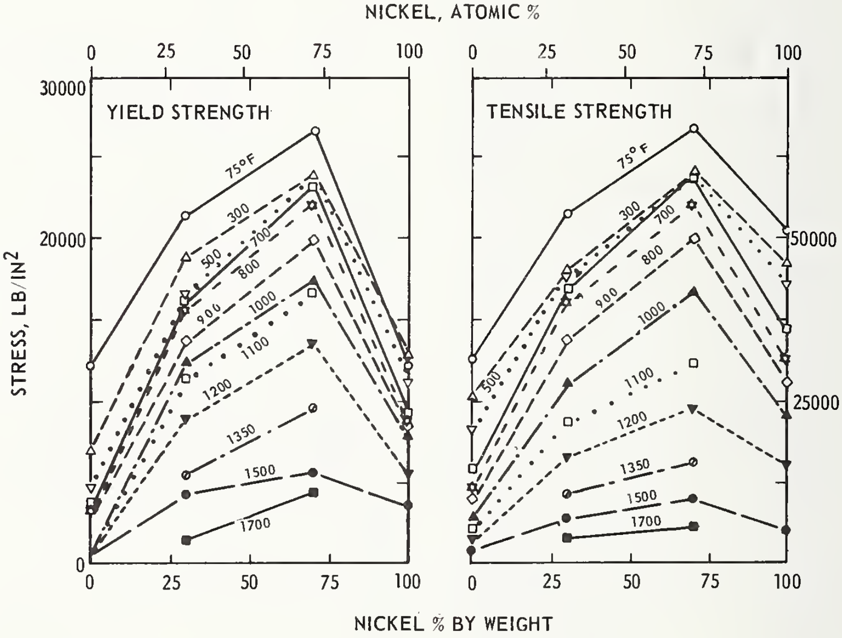

Figure 66. *Effect of nickel content and test temperature on the yield and tensile strengths of initially annealed specimens of the copper-nickel system* [*315*].

the greatest resistance to creep [346,348]. The stress required to produce equal second-stage creep rates at different temperatures is significantly higher for the 70/30 Ni/Cu alloys as annealed (fig. 67) or as cold drawn 40 percent (fig. 68) than for any other of the nickel-copper alloys. Creep rupture curves for Monel, from data by Grant and Bucklin [634], are shown in figure 69.

The effect of temperature on the elastic constants of Monel alloys 400 and K–500 is shown in figure 70.

Monel alloy 401 has a low temperature coefficient of electrical resistivity. It is used in the manufacture of wire-wound resistors.

Monel alloy 402 is used for fixtures in operations for pickling steel and copper alloys. It is resistant to hot sulfuric acid pickling solutions and to hydrogen embrittlement when it is galvanically coupled to steel.

In Monel alloy 403, the nickel, iron, and manganese contents are so adjusted that the alloy remains nonmagnetic at the freezing point of

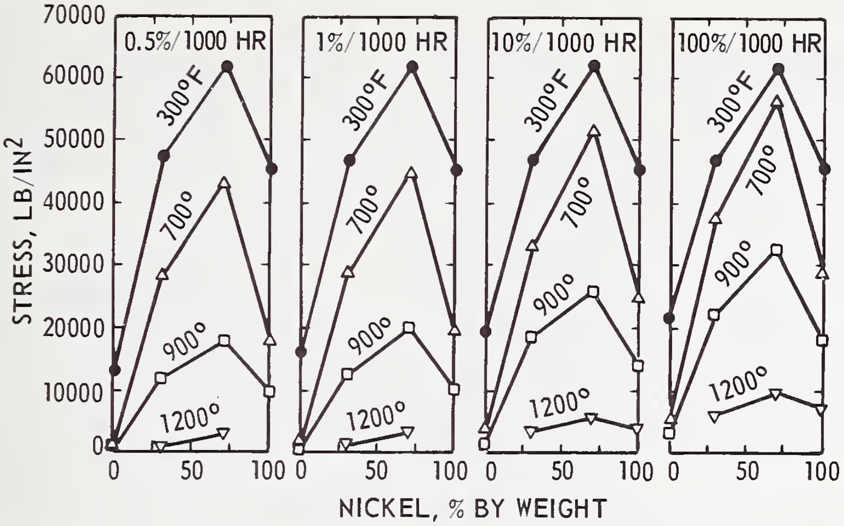

FIGURE 67. *Variation of stress with nickel content in Ni-Cu alloys to produce equal second-stage creep rates at different temperatures of the annealed metals [346].*

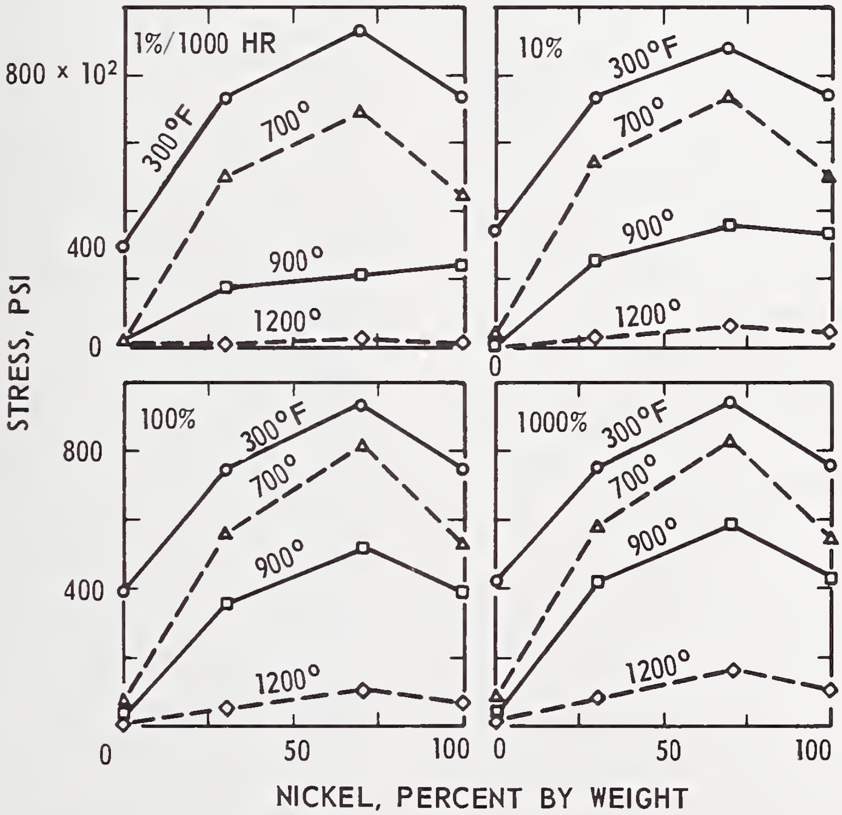

FIGURE 68. *Variations of stress with nickel content in Ni-Cu alloys to produce equal second-stage creep rates at different temperatures of the cold-drawn (40%) metals [348].*

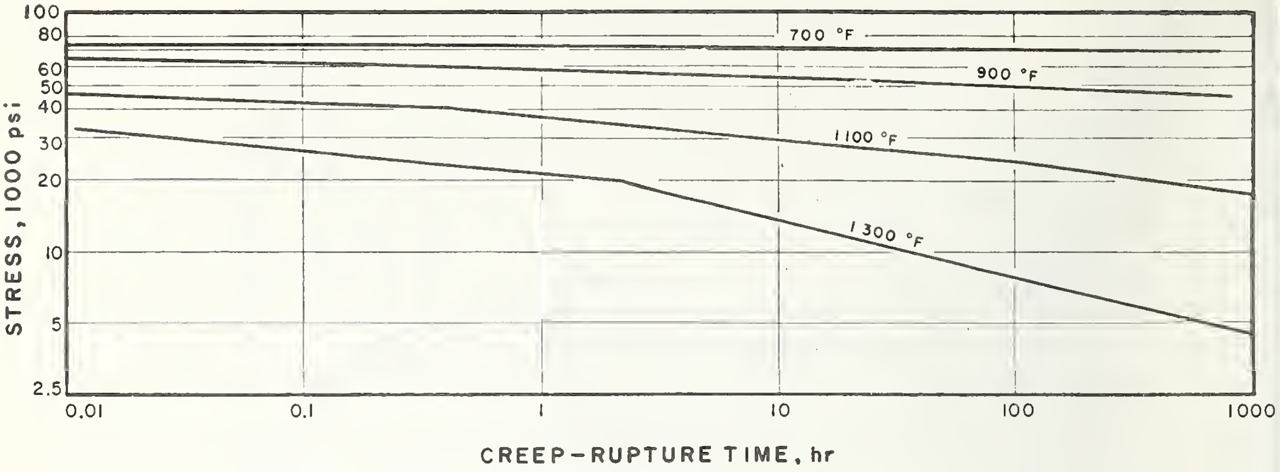

Figure 69. *Stress versus creep-rupture life for annealed Monel alloy 400 at 700 to 1300 °F* [*634*].

sea water (27 °F). It was developed for use in mine-sweepers.

Monel alloy 404 is characterized by low magnetic permeability and excellent brazing characteristics. Residual elements are controlled at low levels to provide a clean wettable surface even after prolonged firing in wet hydrogen. Its permeability (typically 1.004 at room temperature, 200–Oe field strength) is not significantly affected by processing and fabrication. This property makes it particularly suitable for electronic applications. The alloy has low vapor pressure, thermal expansion characteristics compatible with other metals, and strengths at outgassing temperatures. It finds use as wave guides, transitor capsules, metal-to-ceramic seals, and power tubes.

Monel alloy R–405 is similar to Monel alloy 400 in all respects except that a controlled amount of sulfur is added to improve machining characteristics. It is designed particularly for use with automatic screw machines. Typical applications are for water meter parts, valve seat inserts, screw machine products, and fasteners for nuclear applications.

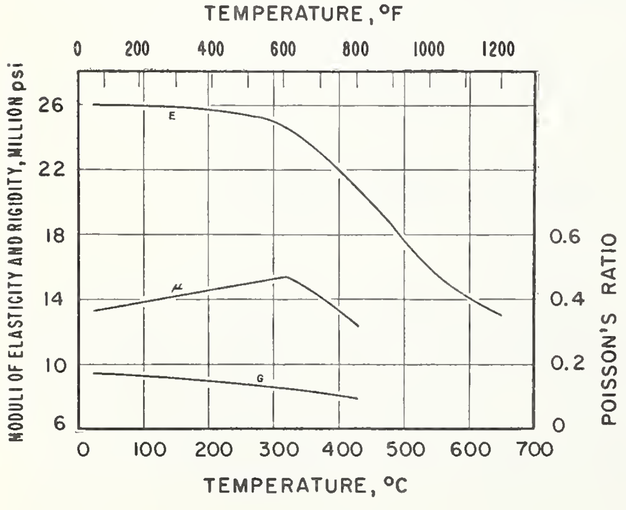

Figure 70. *Effect of temperature on the modulus of elasticity (E), the modulus of rigidity (G), and Poisson's ratio (μ) of Monel alloy 400 and Monel alloy K–500* [*635*].

Monel alloy 406 is used particularly for its resistance to corrosion from some mineral waters. It finds application in hot-water tanks.

Monel alloy 474 is a relatively new high-purity nickel-copper alloy. It is essentially free from nonmetallic inclusions. It is nonmagnetic and its low permeability is not substantially affected by processing and fabrication. The alloy has good formability and superior brazing characteristics even in a wet hydrogen (high dew point) atmosphere. Its typical applications are the same as those for Monel alloy 404.

Monel alloy K–500 is an age-hardenable nickel-copper alloy with a long history of successful industrial use. Heating the solution-treated alloy at 1080 °F precipitates small particles of $Ni_3(Al, Ti)$, which increase strength and hardness. Higher properties are achieved when the alloy is cold worked prior to age hardening. This alloy has good mechanical properties over a wide temperature range. Strength, toughness, and ductility are retained at —423 °F as indicated in table 46, and it is nonmagnetic to temperatures below —210 °F.

Monel alloy 501 is similar to alloy K–500 in all respects except that it has improved machin-

Table 46. *Tensile properties of Monel alloy K-500 (aged sheet)* [*43*]

	Room temp.	−100 °F	−320 °F	−423 °F
Tensile strength psi	154,000	166,000	183,000	200,000
Yield strength psi	97,000	107,000	120,000	136,000
Elongation %	22	24	30	28

ing characteristics. This is achieved through use of a higher carbon content and controlled heating which results in precipitation of graphite particles in the material. It is designed particularly for use at high production rates with automatic screw machines.

The nominal range of mechanical properties for some of the Monel nickel-copper alloys is given in table 47.

TABLE 47. *Nominal range of mechanical properties of Monel alloys (wrought rods and bars)* [43]

Monel alloy	Temper	1000 psi		Elongation in 2 in, %	Brinell hardness number, 3,000 kg
		Tensile strength	0.2% yield strength		
400	Hot finished	80– 95	40– 65	45–30	140–185
	Cold drawn, stress relieved	84–120	55–110	35–22	160–225
	Annealed	70– 85	25– 40	50–35	110–140
402 and 403	Hot finished	70– 95	25– 65	45–30	130–185
	Cold drawn, stress relieved	75–120	45–100	35–15	150–225
	Annealed	65– 85	23– 40	50–35	100–140
R-405	Hot finished	75– 90	35– 60	45–30	130–170
	Cold drawn	85–115	50–100	35–15	160–240
	Annealed	70– 85	25– 40	50–35	110–140
K-500	Hot finished	90–135	40–110	45–20	140–160
	Hot finished, age hardened	140–170	100–125	30–17	265–330
	Annealed	90–110	40– 60	45–25	140–185
	Annealed, age hardened	130–160	85–110	30–20	250–300
	Cold drawn	100–135	70–100	35–13	175–260
	Cold drawn, age hardened	135–180	95–130	30–15	255–325

3.3. Low-Nickel Alloys

a. Copper-Nickel Alloys [4]

The copper-nickel alloys find a variety of uses because of their combinations of physical and mechanical properties and their excellent resistance to saline water corrosion. The oldest use was for coinage, the largest use today is in marine applications, particularly heat-exchange equipment. Some other uses depend upon the nonmagnetic characteristics of the alloys, their electrical resistance, and their thermal electromotive force in relation to other metals or alloys. A comprehensive review of the properties, fabrication, and applications of copper-nickel alloys was written by Nothing [636]. In a general fashion, the strength properties decrease as the nickel content decreases [637,713]. Electrical resistivity follows the same pattern. The properties of cupronickels at temperatures from —300 to +1500 °F were surveyed by Pritchard [638].

(1) *Coinage alloys.* Feely [639] reported that the total use of nickel in coinage from 1850 to 1955 was 65,646 tons. The alloy that accounted for the great bulk of the nickel consumed was the traditional coinage alloy of 75 percent copper and 25 percent nickel. The 1954 uses of this alloy included the United States 5-cent piece, the French 100-franc coin, and the United Kingdom's half-crown, florin, shilling, and sixpence. Commercially pure nickel was used for some coins in India and the Netherlands, and nickel-clad steel was used in Israel. Low-nickel alloys also were used, for example, 95 percent copper-5 percent nickel in some of the coins of Columbia; silver-copper-zinc-5 percent nickel alloys in Sweden and Australia; copper-aluminum-2 percent nickel in Finland and Denmark; and a copper-zinc-1 percent nickel alloy was used in Pakistan, Paraguay, and the United Kingdom. Because of the shortage of silver, the dimes and quarters of the United States are now copper sandwiched between a 75/25 Cu/Ni alloy—the overall nickel content of the coins is 8.33 percent.

(2) *Corrosion-resistant and engineering alloys.* All of the cupronickels have desirable physical and mechanical properties and are resistant to corrosion in many media. Consequently, almost every possible composition from 1 to 50 percent nickel has been marketed under one or more trade names, but the most widely used alloys are classed, for specification purposes, in three groups:—the 70/30 (CA 715), the 80/20 (CA 710), and the 90/10 (CA 706) copper-nickel groups.

Cupronickels containing 10 to 30 percent of nickel have long been noted for their resistance to sea water, which led to many marine applications, particularly in the field of heat exchanger tubes, condensers, etc. For use in marine and heat exchanger environments, the beneficial effects of small amounts of iron on the erosion-corrosion behavior have been well established [640,641]. The iron contents for 70/30 and 90/10 copper-nickel have been standardized at 0.4-0.7 percent and 1.0-1.8 percent, respectively. Addition of slightly less than 1 percent of manganese is useful for deoxidation and desulfurization during casting. Improvement in the resistance of the cupronickels to sea water, through additions of iron, also was evident as improved resistance to a variety of fresh and industrial waters, well waters high in carbon dioxide, boiler feed waters, etc. This led to improved performance in powder plant applications, such as steam condensation from turbines, and to extended use in heat exchangers in the chemical and petroleum industries. As LaQue [641] pointed out, when alloys are used in heat exchanger tubes with one side exposed to corrosives at high temperatures, reaction on the side in contact with the corrosive is fully as significant as the attack on the water side. LaQue's review of the resistance of the cupronickels to a variety of corrosive media included the following: they resist sulfuric acid very well; they are resistant to brines in salt-plant operations and to sodium hydroxide solutions but are attacked by fused sodium hydroxide at 750 °F;

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[4] The copper industry has recently adopted a standard numbering system for all copper-base alloys. In line with this arrangement, 90/10 Cu-Ni is CA (copper alloy) 706; 80/20 is CA 710, 75/25 is CA 713, and 70/30 is CA 715.

they are superior to other copper-base alloys in resisting ammonia and its compounds. The presence of sulfides in high temperature hydrocarbon strains has limited use of copper nickels to the 70–30 copper nickel grade in refinery condensers. The presence of sulphides (from decay of organic wastes in sea water) has led to wider use of both the 90–10 and the 70–30 grades in coastal power plant condensers in preference to other less resistant copper base condenser tube alloys. In certain locations the concentration of organic wastes is so great as to limit the service life of copper nickel though they are often continued in service under even these most adverse conditions. Data were presented on their resistance to halogens and halogen compounds other than brines. Ordinarily the cupronickels have good resistance to chlorinated solvents, and the 90:10 alloy is better than the 70:30 in resistance to miscellaneous organic compositions. Their resistance to pulp and paper stock suspensions is superior to that of phosphor bronze; in miscellaneous uses in petroleum refineries their performance is generally good at ordinary and moderate temperatures, but the presence of hydrogen sulfide at elevated temperatures results in severe attack.

Tice and Venizelos [642] reported that the 70:30 alloy showed the highest corrosion resistance of all the alloys they tested for use in condenser tubes and Donachie [643] found that the 70:30 alloy offered usable strength above the normal service range of 300 to 500 °F. Hopkinson [644] found that the addition of several other metals increased the resistance of 70:30 to scale exfoliation, but that only silicon, beryllium, and columbium produced significant improvement. Simmons et al. [645] concluded that the combination of strength, ductility, and corrosion resistance of Cufenloy 30 (30% Ni, 0.5% Fe, 0.6% Mn, bal Cu) rendered it suitable for use in unfired pressure vessel applications at temperatures up to about 850 to 900 °F. Cufenloy 40 (56% Cu, 41% Ni, 2% Fe, 1% Mn) was described as having properties sufficiently improved over those of Cufenloy 30 so that design factors could be significantly increased [646]. An evaluation of the resistance to stress corrosion of 28 common copper-base alloys led Thompson [647] to the conclusion that the highest resistance to stress corrosion was offered by tough pitch copper and 70:30 cupronickel. Szabo [648] showed that the 80/20 Cu/Ni alloy was superior to aluminum brass, Admiralty brass, and 70/30 brass in resistance to stress corrosion. The characteristics, properties, and applications of the cupronickels have been discussed by Everhart [649] and by Shepherd [650], and the physical and mechanical properties of the 70/30 alloy have been described by The International Nickel Company, Inc. [651]. The compositions and mechanical properties as outlined in ASTM Specification B111–66a for copper and copper alloy seamless condenser tubes and ferrule stock are given in table 48. Copper-nickel tubing has been commonly supplied and used in the as drawn condition, taking advantage of its superior resistance to stress cracking to gain practical advantages in dent resistance and handling.

Mechanical properties of the cupronickels, as was the case for the Monel alloys, improve at low temperature. For example, Geil and Carwile [314] reported that the tensile strength of annealed, high-purity 70/30 Cu/Ni increased in almost linear fashion from 54,000 psi at room temperature to 83,000 psi at —196 °C. The mechanical properties of the cupronickels fall off at moderately elevated temperatures. Port and Blank [652] discussed the creep characteristics at 300, 400, and 500 °F of the 70:30, 80:20, and 90:10 alloys. They reported that the 90:10 alloy was affected more than the others by increasing temperature within this range, and that the creep strength of the 90:10 alloy containing 1.08 percent iron was double that of the 90:10 alloy containing 0.68 percent iron. Jenkins and co-workers [315,346,348] studied the tensile and creep properties of high-purity 70/30 Cu/Ni alloys and some of their results have already been presented in the discussion of the Monel nickel-copper alloys. Fig-

TABLE 48. *Compositions and mechanical properties of copper alloy condenser tubes as listed in ASTM specification B111-66a*

Alloy	Composition, percent						Minimum tensile requirements			
	Cu (min)	Ni	Pb max	Fe	Zn max	Mn max	Temper	Tensile strength, psi	Yield strength, psi[a]	Elongation in 2 in., percent
60–40	52.5	40.0/43.0	0.05	1.5 /2.5	0.3	0.5 /1.7	Drawn, stress relieved	85,000	65,000	[b]12 or 15
65–35–5	60	29.0/33.0	.05	4.75/5.75	1.0	1.0	Annealed	74,000	36,000	30
70–30	65.0	29.0/33.0	.05	0.40/0.70	1.0	1.0	Annealed	52,000	18,000	
70–30	65.0	29.0/33.0	.05	.40/0.70	1.0	1.0	Drawn, stress relieved	72,000	50,000	[b]12 or 15
80–20	74.0	19.0/23.0	.05	.5 /1.0	1.0	1.0	Annealed	45,000	16,000	
90–10	86.5	9.0/11.0	.05	1.0 /1.8	1.0	1.0	Annealed	40,000	15,000	
90–10	86.5	9.0/11.0	.05	1.0 /1.8	1.0	1.0	Light drawn	(c)	(c)	(c)
95–5	91.2	4.8/ 6.2	.05	1.3 /1.7	1.0	0.30/0.80	Light drawn	40,000	30,000	

[a] At 0.5 percent extension under load.
[b] The lower value is for wall thickness up to 0.048 in., inclusive; the higher value is for wall thickness over 0.048 in.
[c] No minimum properties established.

ure 71, from the work of Jenkins, Digges, and Johnson [315], shows that the strengthening effect of cold work upon the yield and tensile trengths of the 70/30 Cu/Ni alloy is completely liminated at 1200 °F and above.

In Powell and Blanpied's review [123] of hermal conductivities at low temperatures, the values cited for the cupronickels are: for the 0/10 alloy, 470 mW/cm deg K at room temperature, 380 at 80 °K, and 12 at 4.2 °K; for he 80/20 alloy, 4.5 mW/cm deg K at 9 °K and .9 at 1.9 °K; for the 70/30 alloy, 290 mW/cm leg K at room temperature.

Hawthorne and Borth [653] describe a spe- ialized type of welding applicable to CA 715 70/30 Cu/Ni) and The International Nickel ompany, Inc. publishes a more general bulle- in on welding and brazing [653a].

Bouillon and Stevens [654] observed that the xidation resistance of copper was improved by he addition of 5 and 10 percent nickel. A high- trength 70/30 copper-nickel contains 5 percent ron [655]. Higher strength copper-nickel al- oys for military service have been described by orkin [655a]. Precipitation-hardening 70/30 u/Ni containing beryllium is available in cast r wrought form [655b].

The advantages offered by the 90/10 Cu/Ni s a material of construction for seawater pipe- ines have been described [656,657]. Its use as sheathing material for wood piling in seawater has been advocated by Hunt and Schillmoller [658].

The 70/30, 80/20, and 90/10 alloys are used as castings, as well as in the wrought form. Vanick [659] and Shepherd [650] discussed the production, processing, and use of castings.

The alloys that are called cupronickels in the United States are called Kunifers in England, with numbers to indicate the nickel content, for example, Kunifer 30, Kunifer 10, Kunifer 5. Mechanical properties of the low-nickel cupronickels make them suitable for some ordnance uses, for example, alloys containing 2.5 to 5 percent of nickel are used as driving bands and the 15-percent alloy as bullet jackets.

(3) *Thermocouple and electrical resistance alloys; alloys for electrical use.* The cupronickel that contains 45 percent of nickel and generally known as constantan, but marketed under a number of trade names, is useful as a thermocouple element. It has the highest thermal emf against platinum of any of the copper-nickel alloys [660]. It is used with copper and especially with iron [661]. According to Roeser and Dahl [662], the emf of the platinum-constantan thermocouple increases regularly with increasing temperature to about 43 mV at 1800 °F (although the maximum temperature for this thermocouple use is 1650 °F); the iron-constantan thermocouple produces higher emf values at any particular temperature, for example, 57 mV at

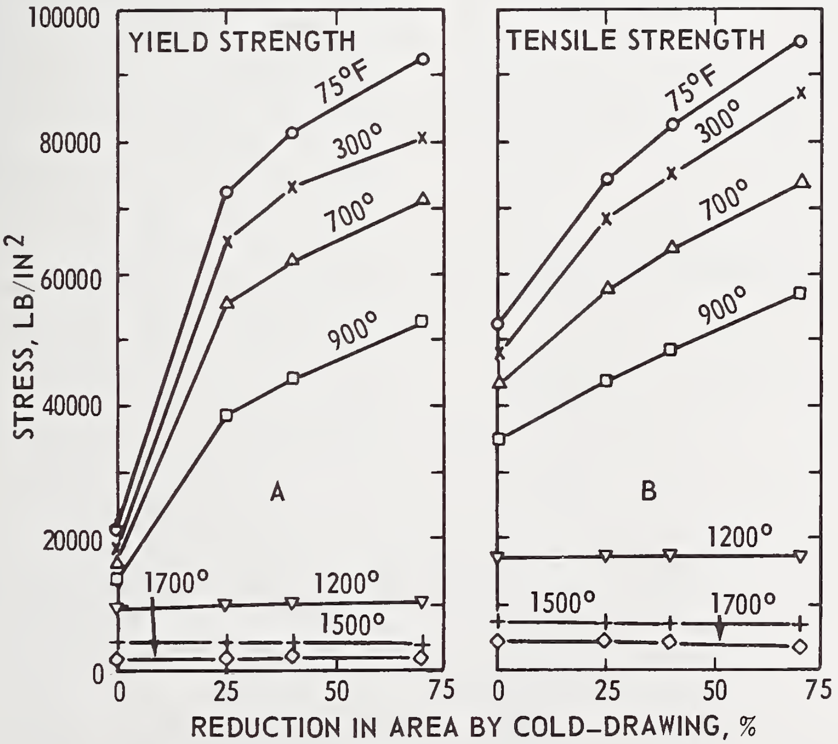

FIGURE 71. *Effect of cold drawing and test temperature on the yield and tensile strength of 30:70 Ni:Cu alloy* [315].

1800 °F; the copper-constantan thermocouple up to 750 °F produces emfs only slightly lower than those of iron-constantan.

The curve of electrical resistivity versus composition reaches a maximum at 50 to 55 percent of nickel, according to Shibuya [663]. Constantan has about the maximum resistivity of the cupronickels and has been used as a heating element and as a resistance unit in rheostats and electrical instruments. According to Guettel [660], constantan has the highest electrical resistivity (50 microhm-cm) and the lowest temperature coefficient of resistance (±0.00002 from 68 to 300 °F) of any of the copper-nickel alloys. The change in resistance may be either positive or negative, depending on small variations in composition and on variations in the amount of cold work. The maximum temperature for use as a resistor is 930 °F. Cupronickels with lower nickel contents and correspondingly lower resistivities are used for heating applications such as radiant heating panels, electric blankets, etc., but the 45-percent nickel alloy is the outstanding cupronickel for this use.

The nickel-base electrical resistance alloys have been considered previously, but there are several copper-nickel and copper-manganese-nickel alloys that should be noted in this section. The Metals Handbook [576] lists the alloys shown in table 49 for use in electrical resistors. Of these, manganin has been almost universally adopted for use in the construction of precision resistors, slide wires, and other components for electrical measuring and control instruments. Manganin is a stable solid solution. Its electrical stability, verified by several decades of experience, is such that there is no more than 1 ppm change per year when the alloy is properly heat treated and protected.

Recently announced very pure 70/30 cupronickel [663a] is used for special electronic applications where residual metallic impurities could interfere with the proper functioning of the alloy.

b. Copper-Nickel-Zinc Alloys (Nickel Brasses)

The copper-nickel-zinc alloys are of very old origin, dating back to the paktong of ancient China. Early in the 19th century two alloys, "Neusilber" and "Argentan," which resembled silver in appearance and were suitable for tableware and culinary purposes, were developed in Germany and the name German silver was in general use until after World War I, when it was supplanted in the trade by the name nickel silver. The alloys also have been known as nickelene. Inasmuch as the alloys do not contain any silver whatever, the use of such designations as German silver or nickel silver is misleading, particularly to the layman, but the term nickel silver has been firmly established in industry. The alloys are properly and accurately designated as copper-nickel-zinc alloys or as nickel brasses and are covered by the Copper Development Association numbers CA 730–790, inclusive.

The addition of nickel to brass gradually changes the normally yellow color to white so that at about 12 percent of nickel the typically brass appearance is practically gone. According to Grosvenor [664], the alloys contain the three major elements in the approximate ranges of 45 to 75 percent copper, 5 to 30 percent nickel, and 5 to 45 percent zinc. The principal functions of nickel are to whiten the alloys, to increase the strength properties for given zinc contents, to improve the resistance to corrosion, and to decrease the susceptibility of copper-zinc brasses to stress corrosion. The single (alpha) phase alloys have excellent ductility at room temperature but only fair hot-working properties, whereas the two-phase (alpha-beta) alloys are hot workable over a wide temperature range but are not sufficiently ductile at room temperature to be cold worked extensively. Lead is often added to improve the machinability.

The compositions and properties of selected nickel silvers, according to The International Nickel Co., Inc. [665], are given in table 50. The density of the alloys is about 0.31 lb/in^3, the coefficient of thermal expansion is about 9.1×10^{-6}/°F, thermal conductivity varies between 17 and 27 Btu/sq ft/ft/hr/°F, electrical conductivity varies between 5.5 and 10 percent IACS, the modulus of elasticity is about 18,000,000 psi and the modulus of rigidity is about 6,800,000 psi.

TABLE 49. *Physical properties of copper-nickel electrical resistance alloys [576]*

Composition	Resistivity, ohms per cir mil-ft at 20 °C	Temperature coefficient of resistance, microhm/ohm/°C	Thermal emf versus copper, microvolts per °C	Thermal expansion, micro-in/°C	Tensile strength at 20 °C, 1000 psi	Specific gravity at 20 °C	Density, lb per cu in
98 Cu-2 Ni	30	+1500 (0 to 100 °C)	−14 (0 to 75 °C)	17	30 to 60	8.9	0.32
94 Cu-6 Ni	60	+ 800 (0 to 100 °C)	−12 (0 to 75° C)	17	40 to 85	8.9	.32
89 Cu-11 Ni	90	+ 400 (0 to 100 °C)	−24 (0 to 75 °C)	17	35 to 75	8.9	.32
78 Cu-22 Ni	180	+ 300 (0 to 100 °C)	−36 (0 to 75 °C)	17	50 to 100	8.9	.32
55 Cu-45 Ni (constantan)	300	± 40 (20 to 100 °C)	−42 (0 to 75 °C)	15	66 to 125	8.9	.32
87 Cu-13 Mn (manganin)	290	± 15 (15 to 35 °C)	+ 1 (0 to 50 °C)	19	40 to 90	8.2	.30
83 Cu-13 Mn-4 Ni (manganin)	290	± 10 (20 to 35 °C)	− 1 (0 to 50 °C)	19	40 to 90	8.4	.31
85 Cu-10 Mn-4 Ni (shunt manganin)	230	± 10 (20 to 45 °C)	− 1.5 (0 to 50 °C)	19	50 to 100	8.4	.31
70 Cu-10 Mn-20 Ni	294	± 20 (20 to 35 °C)	−10 (0 to 50 °C)	16	70 to 120	8.2	.30
67 Cu-27 Mn-5 Ni	600	± 20 (20 to 35 °C)	+ 2 (0 to 50 °C)	20	67 to 110	8.5	.31

TABLE 50. *Composition and mechanical properties of some nickel silvers (nickel brasses) [665]*

Copper alloy No.	Composition, percent			Condition	Yield strength (0.5% extension under load), 1,000 psi	Tensile strength, 1,000 psi	Elongation in 2 in, percent	Rockwell hardness, B scale
	Cu	Ni	Zn					
CA 735	72	18	10	Annealed	23 to 28	50 to 58	40 to 50	38 to 52
				Hard	72	79	4	85
CA 752	65	18	17	Annealed	25 to 30	58 to 60	32 to 40	40 to 55
				Half-hard	62	74	8	83
				Hard	74	85	3	87
CA 754	65	15	20	Annealed	18 to 28	53 to 61	34 to 43	22 to 55
				Half-hard	62	74	10	80
				Hard	75	85	3	87
CA 766	56.7	12	31.5	Annealed	24 to 29	56 to 63	32 to 43	40 to 55
				Hard	82	98	3	88
CA 770	55	18	27	Annealed	27	60	40	55
				Hard	85	100	3	91
CA 774	45	10	45	Forged	36	83	25	73

Kihlgren et al. [666] studied the physical properties of cast nickel silvers and Vanick [667] reviewed the compositions, properties, and uses of leaded casting alloys. He reported that tin strengthens and hardens the alloys, lead promotes machinability, zinc is a useful deoxidizer, and that nickel is progressively beneficial to the corrosion resistance, color, and mechanical properties.

The three most common copper-nickel-zinc alloys contain 72, 65, and 55 percent copper, 18 percent nickel and the remainder zinc. These alloys have good resistance to corrosion by both fresh and salt waters. The resistance to corrosion by saline solutions is usually much better than that of brasses of the same copper content because the relatively large amount of nickel inhibits dezincification.

The mechanical properties, corrosion resistance, and attractive appearance of these alloys have led to a variety of engineering, decorative, and architectural uses. They are used in spring applications, in food-handling equipment, gift and tableware usually silver plated, marine fittings, in the chemical industry, in musical, dental, and drafting instruments, slide fasteners, and as the base metal for moderate priced jewelry with or without plated coatings. The improved machinability and performance in blanking operations of the leaded alloys results in uses as parts of fishing reels, in cigarette lighters, and in grills and keys. According to Dume [668], the electrical resistivity of the alloys containing 5 to 30 percent of nickel increases with increasing percentage of nickel, leading to their use in rheostats.

The cast alloys have many uses, including ornamental plaques, architectural parts, fittings, plumbing fixtures, valves, hardware, dairy and soda fountain equipment, etc.

3.4 Miscellaneous Alloys

There are any number of nickel alloys that do not fall into any of the categories discussed in this report. Many of these were developed for specific applications.

An alloy intended to satisfy the demand for a corrosion-resistant nongalling, nonseizing alloy suitable for use at room temperature or at high temperatures in bearing and seal applications, even if lubrication is temporarily deficient, was patented by Parana [669]. Composition was given as 3 to 8 percent Ag, 3 to 9 percent Zn, 6 to 9 percent Sn, 3 percent Mn max, 0.3 percent C max, remainder Ni.

Teasel and Hoffman [670] patented a nickel-base alloy for spark-plug electrodes. The alloy displays high resistance to erosion by electrical discharge and to inter- and intragranular attack when exposed to the temperatures and corrosive conditions involved in operation or fabrication of spark-plug electrodes. The range of composition is 90 percent Ni min, 0.5-3 percent Mn, 0.1-2 percent Zr, 0.5-3 percent Cr, 0.2 to 1.5 percent Si, 0.5 percent Fe max, 0.5 percent C max, 0.25 percent impurities max.

Foerster and Kopituk [671] described a series of brazing and coating alloys with compositions as follows:

Alloy 50—93% Ni, 3.5% Si, 2.25% B, 1% other.
Alloy 52—91% Ni, 4.5% Si, 3.25% B, 1% other.
Alloy 53—82% Ni, 4.5% Si, 2.9% B, 7% Cr, 3% Fe, 0.5% other.
Alloy 56—71% Ni, 4% Si, 3.75% B, 16% Cr, 4% Fe, 1% other.

The alloys are intended for use in steam and other valves, high-temperature jet and rocket parts, roller parts, honeycomb mats, etc.

Long [672] reported an investigation to develop nickel-base brazing alloys having good ductility. The most promising alloys are shown in table 51.

TABLE 51. *Nickel-base ductile brazing alloys [672]*

Composition—percent							Liquidus temperature	Braze flow temperature	Hardness, Rc
Ni	Mo	Si	Mn	Cr	Sn	Fe			
							°F	°F	
61.0[a]	10.7	4.76	18.2	4.5	-----	0.8	2080	2150	30–33
66.0[a]	16.2	7.65	5.9	-----	3.5	.7	2050	2150	40
54.7[a]	14.0	5.8	25.0	-----	-----	-----	------	1925	44
69.7[b]	13.7	6.9	8.3	-----	-----	1.3	------	2100	44
82.0[b]	8.7	4.2	5.0	-----	-----	.5	------	2200	33
82.3[a]	8.7	1.7	5.0	-----	-----	2.3	2350	2400	R_b 72

[a] Produced in powder form by atomization.
[b] Produced in shot-cast form.

Table 52. *Nickel-base wide-gap brazing alloys [673]*

Designation	Composition, percent						Temperature, °F			Remarks
	Ni	Cr	Si	Cu	Mn	B	Solidus	Liquidus	Brazing	
J8100	Bal	20.0	10.0	--------	--------	--------	2030	2075	2125–2175	Capillary brazing alloy.
J8590	28.0	--------	2.0	Bal	10.0	--------	1850	2000	2050–2100	Capillary brazing alloy.
NSB	Bal	--------	2.0	--------	--------	0.8	1980	>2300	>2300	Used for filler alloy for wide-gap brazing.
J8101	60% J8100+40% nickel powder						--------	--------	2240	Wide-gap brazing material.
J8105	70% J8100+30% NSB powder						--------	--------	2125–2175	Wide-gap brazing material.
J8591	80% J8590+20% iron powder						--------	--------	2050–2100	Wide-gap brazing material.

The application of furnace brazing to the fabrication of large sheet-metal structures has been inhibited in the past by the joint clearances required to insure the necessary capillary attraction (0.002–0.006 in). Mobley and Hoppin [673] developed a series of capillary and wide-gap brazing alloys, the compositions of which are given in table 52. Two high temperature brazing alloys for joining materials such as high-alloy steels, stainless steels, and nickel-chromium alloys were patented by Evans and Pattee [674,675]. Compositions were given as 30-60 percent Ni, 20-45 percent Sn, 10-30 percent Pd, 4-8 percent Si, and 58-68 percent Ni, 25-40 percent Sn, 3-10 percent Co. Hoppin [676] also patented a high-temperature brazing alloy (10–30% Cr, 8–12% Si, 7–15% Mn, remainder Ni), and Cape [677] patented a low-melting (1700-1750 °F) alloy having the preferred composition of 65 percent Ni, 25 percent Fe, 3.5 percent B, 4.5 percent Si, 1.25 percent P. Witherell [678] described an all-position welding electrode for producing sound nonporous crack-free welds on copper-containing alloys by means of a welding electrode, the core wire of which contains 25 to 35 percent Ni, up to 1 percent Fe, up to 1 percent Si, up to 3 percent Mn, up to 1 percent Ti, <0.15 percent C, remainder Cu.

Nickel-tungsten alloys, containing 60 to 95 percent of nickel, produced by powder metallurgy techniques, exhibit several of the desirable qualities of cathode core metal for radio tube construction [182]. Tungsten-nickel and ternary alloys were suggested as heavy alloys for use as high-inertia masses or for x-ray protection [679]. Nickel-chromium-gold-cobalt alloys were suggested as platinum-colored alloys for dentures [680] and nickel-chrominum-molybdenum-cobalt alloys were recommended for pen nibs [681].

Beryllium-nickel alloys containing 2-3 percent of beryllium exhibit good castability, a hardness similar to that of steel, resistance to heat checking, crazing, and corrosion, and good wear resistance [682].

Buehler and Wiley [683] described the unique properties of Nitinol, a 55-percent nickel-titanium alloy.

Uranium-nickel alloys approximating the formula U_6Ni have better resistance than uranium metal to corrosion in reactors [684].

Grala [685] reported that the intermetallic compound Ni_3Al homogenized at 1,800 °F, had tensile strengths of 32,100 psi at room temperature and 19,600 psi at 1,500 °F. Heat treatment at 2,200 °F increased the grain size and reduced the strength.

The presence of 1 percent of nickel produces hard particles of Ni_3Ti which are responsible for the superior wear resistance of titanium-bearing zinc-alloy forming dies [686].

4. Ferrous Alloys

4.1. General

As indicated in figure 3, more than half of the nickel consumed in the United States in 1964 was used in steel and cast irons, thus bearing evidence to its importance as an alloying element.

Nickel is unique among elements added to steel in that it forms a continuous series of solid solutions with iron (fig. 72). A peritectic reaction occurs at 1512 °C (2754 °F) and 4.3 a/o Ni. The solidification interval of the entire system is very narrow. The temperature of the minimum in the liquidus curve, which occurs at about 67 a/o nickel, has been reported as high as 1436 °C (2616 °F) [687] and as low as 1420 °C (2606 °F) [688]. Both the alpha and delta solid solutions have a body-centered cubic lattice, whereas the gamma phase is face-centered cubic.

Nickel is one of the two common alloying elements (manganese is the other) that lowers the A_3 transformation temperature of iron. When carbon is present, nickel also lowers the A_1 temperature and reduces the carbon content of the eutectoid. Because of the effectiveness of nickel in depressing the gamma- to-alpha transformation in iron, the austenitic solid solutions existing at elevated temperatures are stable at room temperature under any condition of cooling when the nickel content exceeds about 30 percent. Many of these austenitic alloys possess

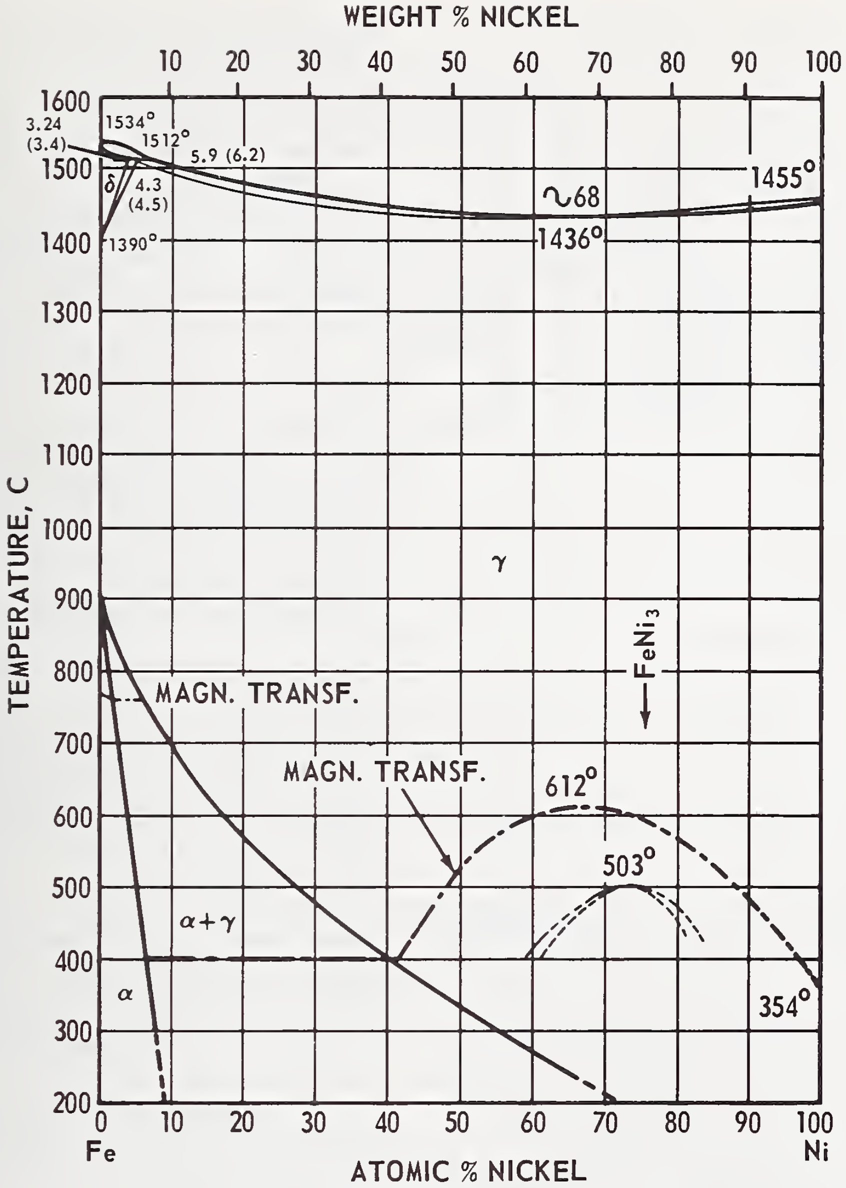

FIGURE 72. *Iron-nickel equilibrium diagram* [*572*].
Numbers refer to the atomic (weight) percent at the temperatures indicated.

nusual magnetic, expansion, and thermoelastic roperties that make them of great value to ndustry. Although frequently referred to as igh-nickel steels, they are more properly decribed as iron-nickel alloys.

Because of the formation of metastable strucural states which vary widely according to comosition and heat treatment, and the extreme luggishness of diffusion at temperatures below bout 500 °C (932 °F), the exact location of he equilibrium phase boundaries has met with reat experimental difficulties. The boundaries f the alpha and gamma phases shown in figure 2 are those reported by Owen and Liu [689].

The Curie temperatures of the iron-nickel alloys decrease steadily up to about 42 percent nickel. With higher nickel, the magnetic transformation of the gamma phase increases to a maximum of 612 °C (1134 °F) at about 64 to 68 a/o of nickel.

Hansen [572] notes that with the exception of the ordered $FeNi_3$ structure, which is of the Cu_3Au (Ll_2) type, only the body-centered-cubic alpha structure (A2 type) and the face-centered cubic gamma structure (Al) type have been found in the iron-nickel system. He notes further that this disproves the existence of compounds such as Fe_2Ni, Fe_3Ni_2, $FeNi_2$, and $FeNi_4$ which had been previously suggested on the basis of curves of physical properties versus

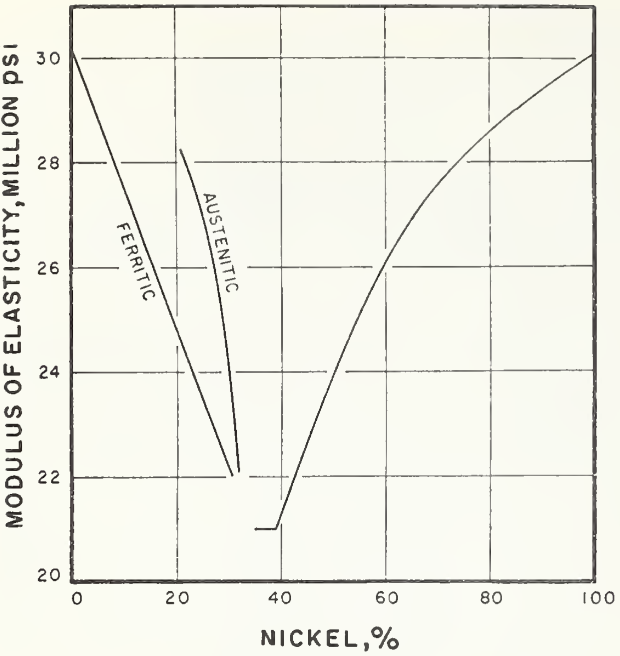

FIGURE 73. *Modulus of elasticity of iron-nickel alloys [696].*

composition. According to neutron-diffraction work [690], ordered $FeNi_3$ possesses a magnetic superstructure.

The addition of nickel to iron, and of iron to nickel, expands the lattice. The parameter of the gamma phase was found to reach a maximal value at 37 [66] or 39 a/o of nickel [71,691, 692].

Wakelin and Yates [693] reported lattice parameters of the disordered and ordered states in the region of 50 to 80 a/o nickel. The 75 a/o nickel alloy was found to have a parameter of a = 3.5544 Å and a = 3.5522 Å in the disordered and ordered states, respectively.

Nickel is ordinarily found only in the solid-solution phase. It does not combine with carbon or oxygen, nor does it form intermetallic con pounds in simple steels. It does not greatly affe the diffusion rate of carbon in austenite, a though the diffusion rate of nickel itself, whic is very much slower than that of carbon, affected markedly by variation in carbon cor tent [694,695].

Nickel decreases the modulus of elasticity iron and iron, in turn, decreases the modulus nickel. The modulus of elasticity of iron-nick alloys are shown by Marsh [696] from selecte data (fig. 73).

4.2. Wrought Steels

Excluding the austenitic alloys, the maj contributions of nickel to steel result from th effects of nickel (1) on ferrite, (2) on the har ening reactions, (3) on the transformation ten perature ranges, and (4) on resistance to en brittlement at low temperatures.

In the ferritic alpha range, it appears fairl well established that strength is increased abou 4200 psi and hardness about 16 Brinell numbe for each 1 percent of nickel (fig. 74). With mo than 5 percent nickel, even slowly cooled allo begin to assume a martensite-like structure an when the nickel content reaches 15 to 20 pe cent, slowly cooled alloys appear to consist e tirely of martensite even though the carbo content is extremely low [698,699]. The relati effectiveness of nickel as a ferrite strengthene is shown in figure 75.

Nickel retards both the pearlite and baini transformation while steel is cooling from th austenitic state; the bainite transformation influenced more markedly than the pearlite. A indication of the effectiveness of nickel in r tarding these transformations may be obtaine by a comparison of figure 76 with figure 7 Even though the carbon content of the nick steel is lower than that of the carbon steel, th facilitating the transformation, the start of th pearlite transformation is delayed by a fact of more than ten.

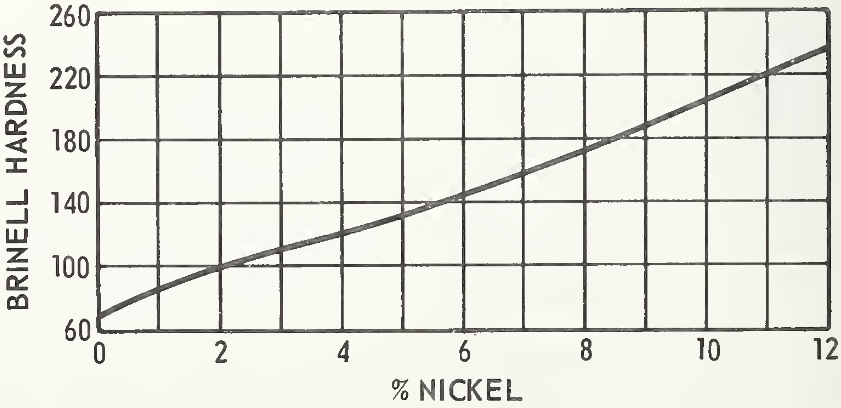

FIGURE 74. *Effect of nickel on the hardness of annealed pure iron [697].*

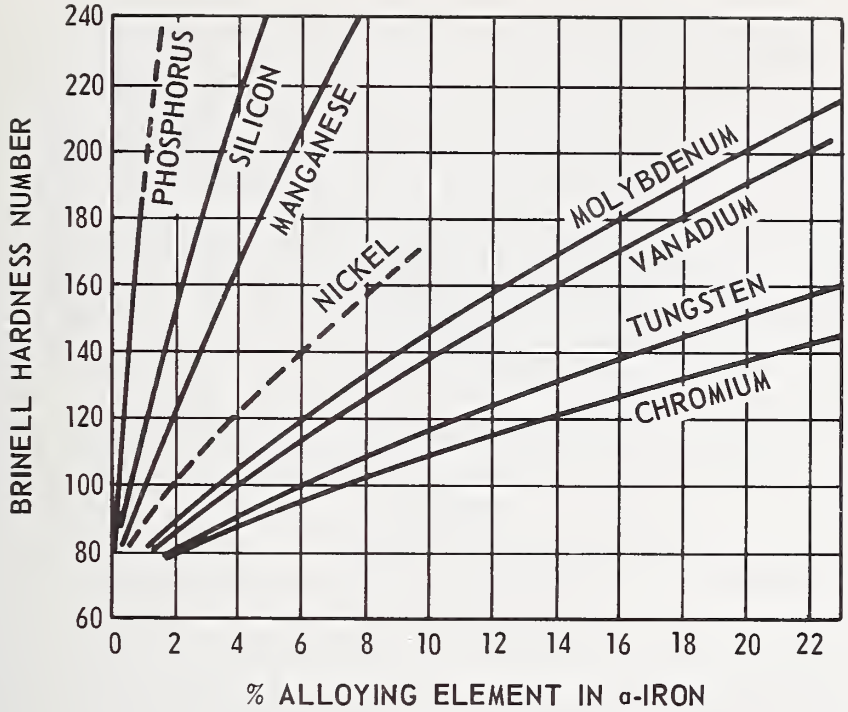

FIGURE 75. *Relative effectiveness of the alloying elements as ferrite strengtheners* [700].

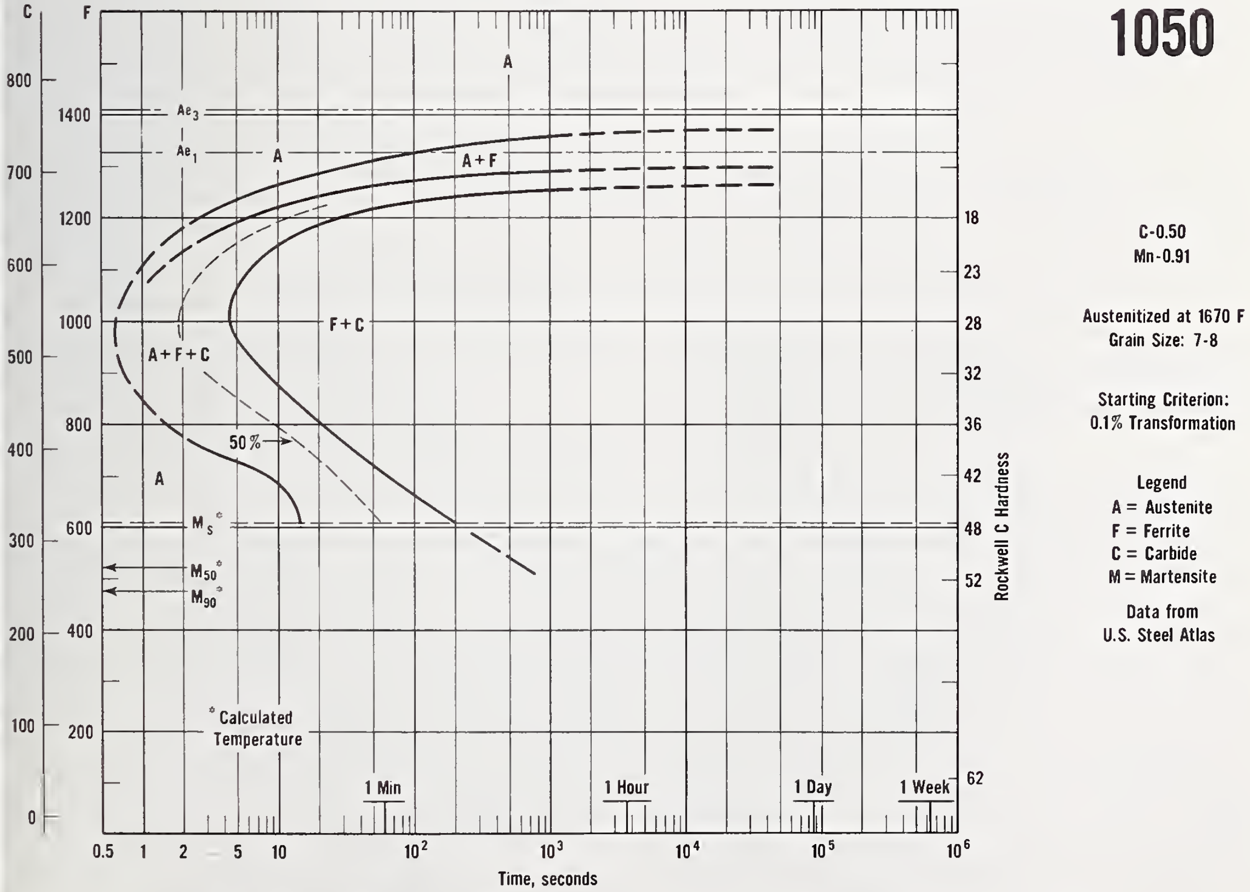

FIGURE 76. *Isothermal transformation diagram for AISI 1050 steel (0.50% C)* [701].

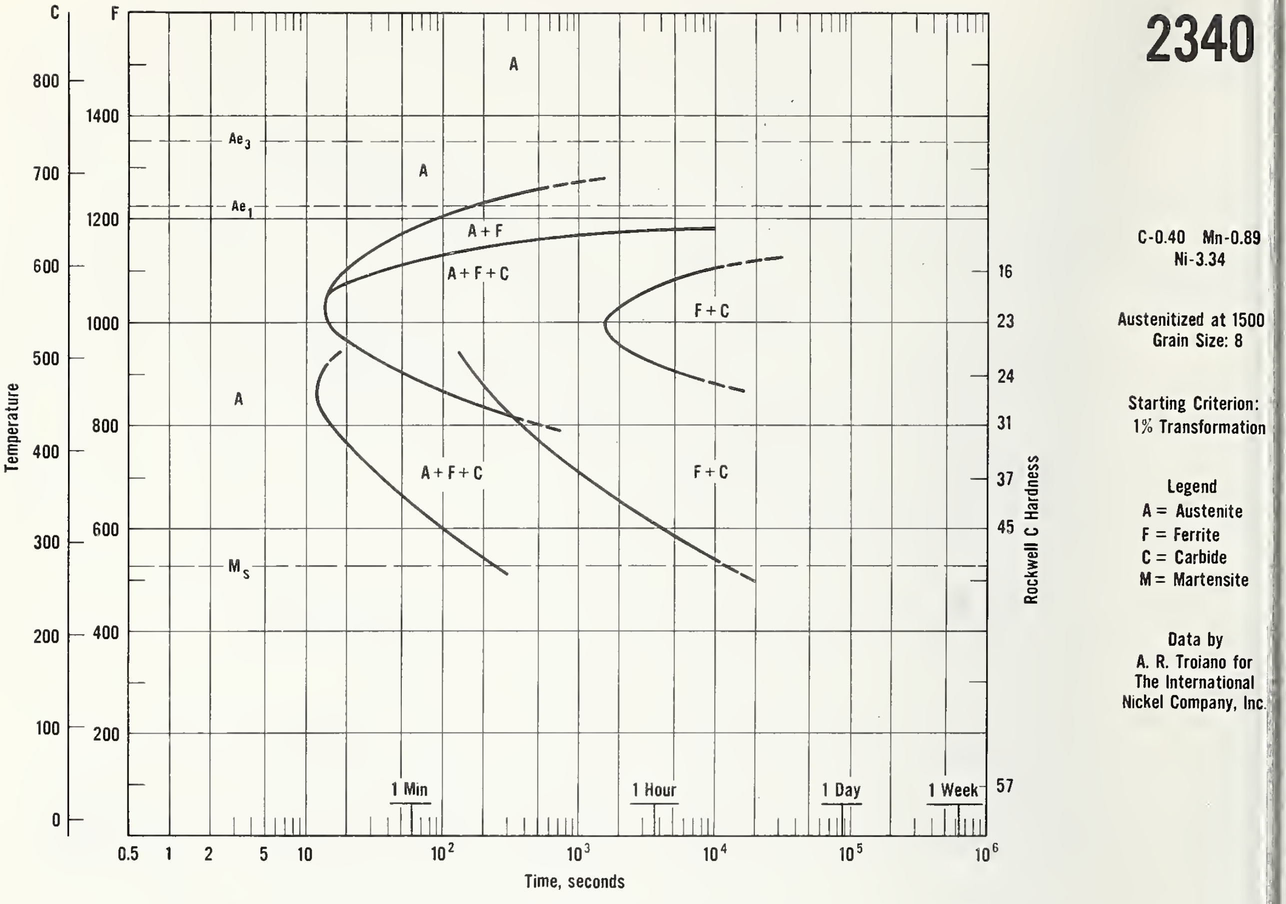

FIGURE 77. *Isothermal transformation diagram for 2340 steel (0.40% C, 3.34% Ni)* [*701*].

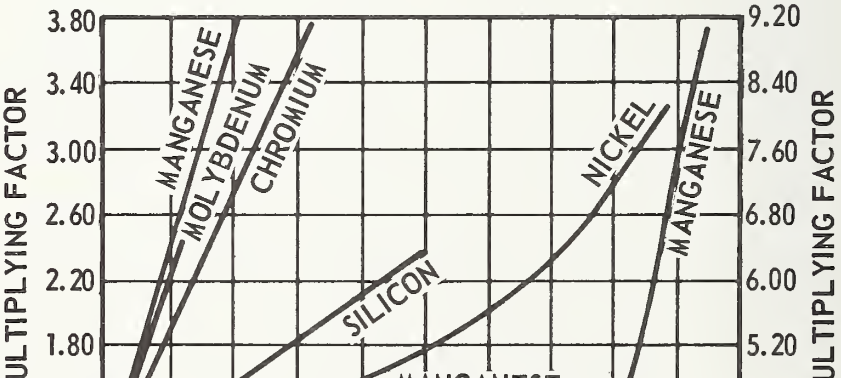

FIGURE 78. *Multiplying factors for the common alloying elements* [*700*].

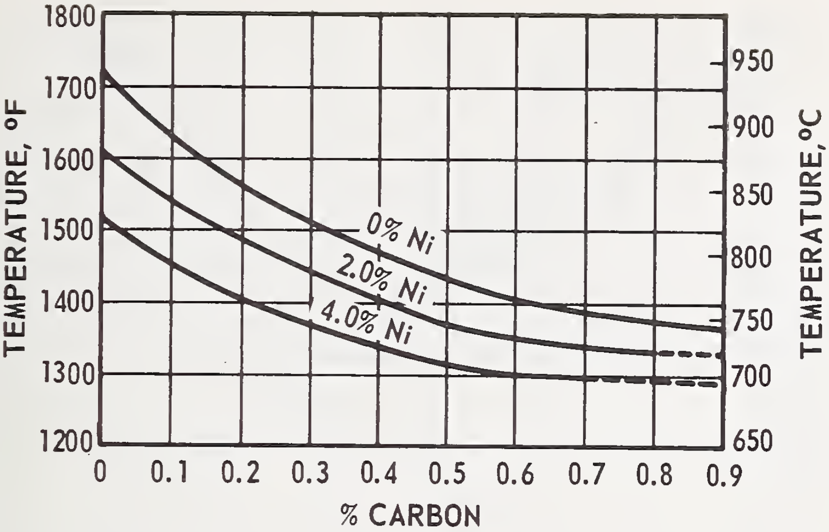

FIGURE 79. *Effect of nickel on the Ac_3 transformation in steel* [705].

Despite this, however, the hardenability of steel is increased only moderately by nickel. Multiplying factors for hardenability for several alloying elements are shown in figure 78. Related data are given in references [702,703, 704].

Because nickel lowers the transformation ranges of steels, nickel steels may be hardened by quenching from lower temperatures than their nickel-free counterparts. The effect of nickel on the Ac_3 transformation temperature is shown in figure 79. Nickel increases the volume change occurring during the $\alpha \rightarrow \gamma$ transformation in steel [706].

Nickel has no unusual effects on the tempering of martensite. No secondary hardening occurs in plain nickel steels and, consequently, there is no exceptional resistance to softening. It has no effect on the temperature range over which martensite decomposes [707].

When nickel steels are tempered for long periods of time, as is often necessary in treating heavy sections, care must be taken not to exceed the true Ac_1 temperature, which has been shown to be considerably lower (as much as 80 °F) than the apparent Ac_1 temperature indicated by conventional tests made under conditions of continuous heating [708]. This precaution is unnecessary when tempering periods do not exceed about two hours, but longer holding at temperatures slightly higher than the true Ac_1 may result in the formation of sufficient austenite to produce a hardening of the steel during subsequent cooling, thereby necessitating a second tempering operation to decompose the transformation products so formed.

Nickel depresses the temperature of both the martensite and bainite reactions. Steven and Haynes [709] studied a variety of low-alloy steels and concluded that the start of the martensite (M_s) and bainite (B_s) reactions can be calculated to within ± 25 °C with a 90 percent certainty from the following equations:

$$\begin{aligned} M_s(°C) &= 561 - 474\ (\%\ C) - 33\ (\%\ Mn) \\ &\quad - 17\ (\%\ Ni) - 17\ (\%\ Cr) \\ &\quad - 21\ (\%\ Mo) \\ B_s(°C) &= 830 - 270\ (\%\ C) - 90\ (\%\ Mn) \\ &\quad - 37\ (\%\ Ni) - 70\ (\%\ Cr) \\ &\quad - 83\ (\%\ Mo). \end{aligned}$$

The M_s temperature of high-nickel steels (up to about 31% nickel) is given by Clark [710] as:

$$\begin{aligned} M_s^2\ (°K) &= 70.1 \times 10^4 - 2.90 \times 10^4\ (\%\ Ni) \\ &\quad + 2.60 \times 10^2\ (\%\ Ni)^2. \end{aligned}$$

The M_s temperatures calculated by Clark agreed fairly well with the temperatures determined experimentally. The resulting curve is shown in figure 80.

Nickel is widely accepted as a specific for ameliorating the deterioration in toughness suffered by all ferritic steels at subzero temperatures. Generous amounts of nickel appear indispensable for the very lowest temperatures [711,712]. Nickel is particularly effective in applications where quenching is not feasible and where normalized or normalized and tempered steels must be used. Lisner [713] reported that low-carbon nickel steel could be used at temperatures down to —75 °F for 2½ percent nickel, to —150 °F for 3½ percent nickel, and to —320 °F for 9 percent nickel. The toughness of the austenitic nickel steels at very low temperatures is well known.

Thermal conductivity of steel is reduced by nickel and electrical resistivity is increased

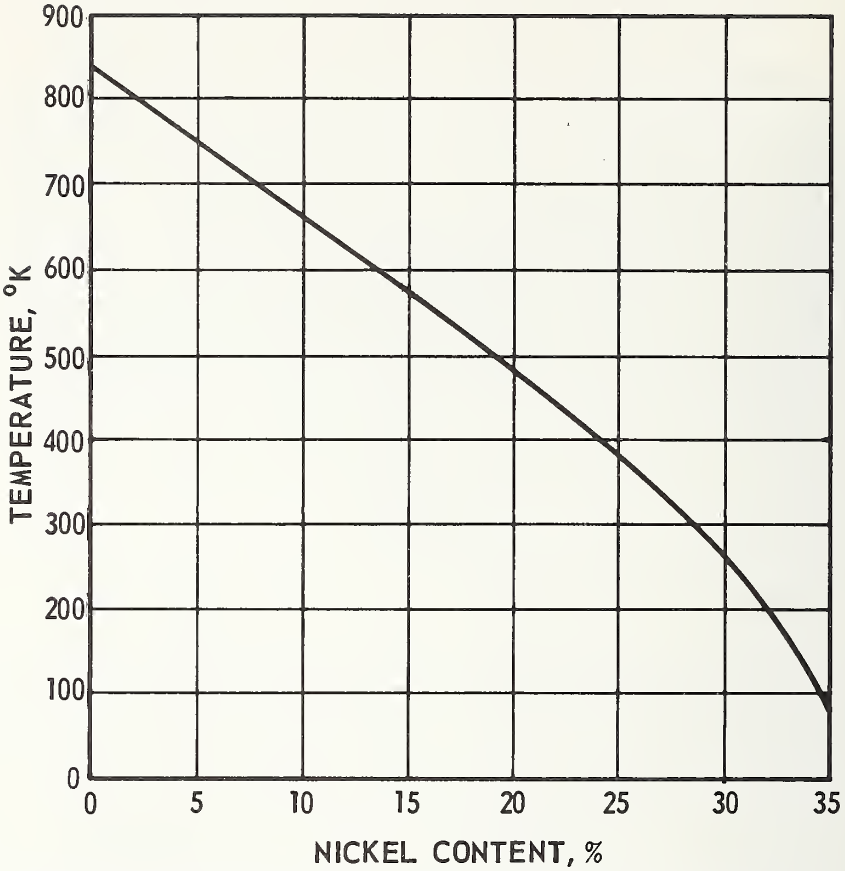

FIGURE 80. *Effect of nickel content on the Ms temperatures of steels* [*710*].

[714,715]. Specific heat appears to be unaffected [715]. Nickel decreases slightly the coefficient of thermal expansion of steels [716]. The density of nickel steels is essentially the same as for unalloyed steels of comparable carbon content.

Nickel improves somewhat the resistance to corrosion of steels in the atmosphere (fig. 81) and other environments. It is particularly effective in supplementing and intensifying the effects of other elements on resistance to corrosion.

a. Low-Alloy Steels

The first interest in nickel steels was shown by manufacturers of ordnance and armor and was a direct result of the work reported by Riley [15]. According to Hall [29], bridge designers were among the first to specify nickel steels, and the 1906 specifications for the 3½ percent nickel steel used for eye bars, stiffening trusses, and other highly stressed units of the Manhattan Bridge in New York City are similar to a modern specification, ASTM A8–54 (discontinued in 1962) for structural nickel steel for use in main stress-carrying structural members, as follows:

	Tensile strength	Yield strength, minimum	Elongation in 8 inches, minimum	Reduction of area, minimum
	psi	*psi*	%	%
1906. Manhattan Bridge.	85,000 to 95,000	55,000	17	40
1961. ASTM A8–54.	90,000 to 115,000	55,000	14	30

There was almost immediate acceptance of these steels for general engineering purposes because of their improved strength, toughness, and response to heat treatment in comparison with plain carbon steels. At the beginning of the 20th century many nickel steels were available, with nickel and carbon contents adjusted to meet the requirements of a variety of uses, both with and without heat treatment. Actually, these nickel steels were the first of the numerous alloy steels to be introduced for general engineering usage.

Until comparatively recently, nickel alloy steels of 3½ and 5 percent nickel were listed

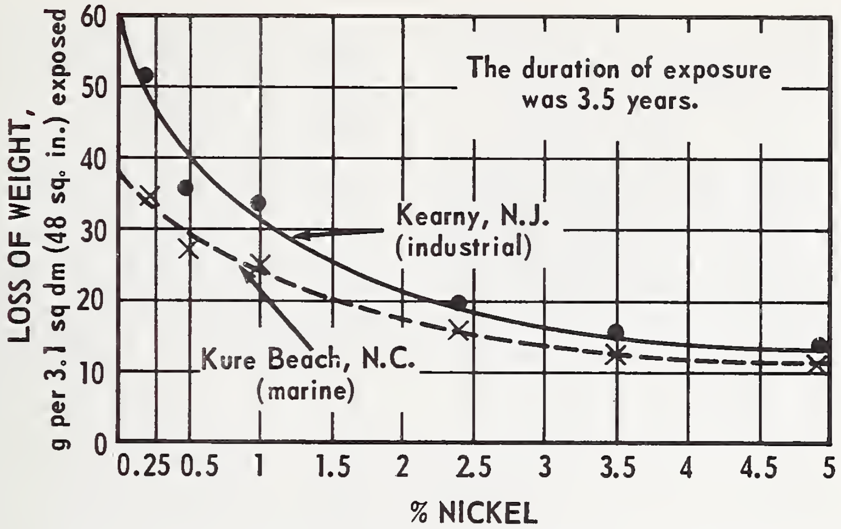

FIGURE 81. *Effect of nickel content on the corrosion of steel in marine and industrial atmospheres* [*717*].

TABLE 53. *American Iron and Steel Institute low-alloy nickel steels* [*718*]

AISI number	Chemical composition ranges and limits, percent							
	C	Mn	P (max.)	S (max.)	Si	Ni	Cr	Mo
3140	0.38/0.43	0.70/0.90	0.035	0.040	0.20/0.35	1.10/1.40	0.55/0.75	----------------
E3310	.08/ .13	.45/ .60	.025	.025	.20/ .35	3.25/3.75	1.40/1.75	----------------
4320	.17/ .22	.45/ .65	.035	.040	.20/ .35	1.65/2.00	0.40/0.60	0.20/0.30
4337	.35/ .40	.60/ .80	.035	.040	.20/ .35	1.65/2.00	.70/ .90	.20/ .30
E4337	.35/ .40	.65/ .85	.025	.025	.20/ .35	1.65/2.00	.70/ .90	.20/ .30
4340	.38/ .43	.60/ .80	.035	.040	.20/ .35	1.65/2.00	.70/ .90	.20/ .30
E4340	.38/ .43	.65/ .85	.025	.025	.20/ .35	1.65/2.00	.70/ .90	.20/ .30
4615	.13/ .18	.45/ .65	.035	.040	.20/ .35	1.65/2.00	----------------	.20/ .30
4617	.15/ .20	.45/ .65	.035	.040	.20/ .35	1.65/2.00	----------------	.20/ .30
4620	.17/ .22	.45/ .65	.035	.040	.20/ .35	1.65/2.00	----------------	.20/ .30
4621	.18/ .23	.70/ .90	.035	.040	.20/ .35	1.65/2.00	----------------	.20/ .30
4626	.24/ .29	.45/ .65	.035	.040	.20/ .35	0.70/1.00	----------------	.15/ .25
4718	.16/ .21	.70/ .90	.035	.040	.20/ .35	.90/1.20	.35/ .55	.30/ .40
4720	.17/ .22	.50/ .70	.035	.040	.20/ .35	.90/1.20	.35/ .55	.15/ .25
4815	.13/ .18	.40/ .60	.035	.040	.20/ .35	3.25/3.75	----------------	.20/ .30
4817	.15/ .20	.40/ .60	.035	.040	.20/ .35	3.25/3.75	----------------	.20/ .30
4820	.18/ .23	.50/ .70	.035	.040	.20/ .35	3.25/3.75	----------------	.20/ .30
8115	.13/ .18	.70/ .90	.035	.040	.20/ .35	0.20/0.40	.30/ .50	.08/ .15
8615	.13/ .18	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8617	.15/ .20	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8620	.18/ .23	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8622	.20/ .25	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8625	.23/ .28	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8627	.25/ .30	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8630	.28/ .33	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8637	.35/ .40	.75/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8640	.38/ .43	.75/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8642	.40/ .45	.75/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8645	.43/ .48	.75/. 90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8650	.48/ .53	.75/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8655	.50/ .60	.75/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8660	.55/ .65	.75/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.15/ .25
8720	.18/ .23	.70/ .90	.035	.040	.20/ .35	.40/ .70	.40/ .60	.20/ .30
8735	.33/ .38	.75/1.00	.035	.040	.20/ .35	.40/ .70	.40/ .60	.20/ .30
8740	.38/ .43	.75/1.00	.035	.040	.20/ .35	.40/ .70	.40/ .60	.20/ .30
8742	.40/ .45	.75/1.00	.035	.040	.20/ .35	.40/ .70	.40/ .60	.20/ .30
8822	.20/ .25	.75/1.00	.035	.040	.20/ .35	.40/ .70	.40/ .60	.30/ .40
E9310	.08/ .13	.45/0.65	.025	.025	.20/ .35	3.00/3.50	1.00/1.40	.08/ .15
9840	.38/ .43	.70/ .90	.035	.040	.20/ .35	0.85/1.15	0.70/0.90	.20/ .30
9850	.48/ .53	.70/ .90	.035	.040	.20/ .35	.85/1.15	.70/ .90	.20/ .30
[a]81B45	.43/ .48	.75/1.00	.035	.040	.20/ .35	.20/0.40	.35/ .55	.08/ .15
[a]94B17	.15/ .20	.75/1.00	.035	.040	.20 /.35	.30/ .60	.30/ .50	.08/ .15
[a]94B30	.28/ .33	.75/1.00	.035	.040	.20/ .35	.30/ .60	.30/ .50	.08/ .15

[a] These steels can be expected to have 0.0005% minimum boron content.

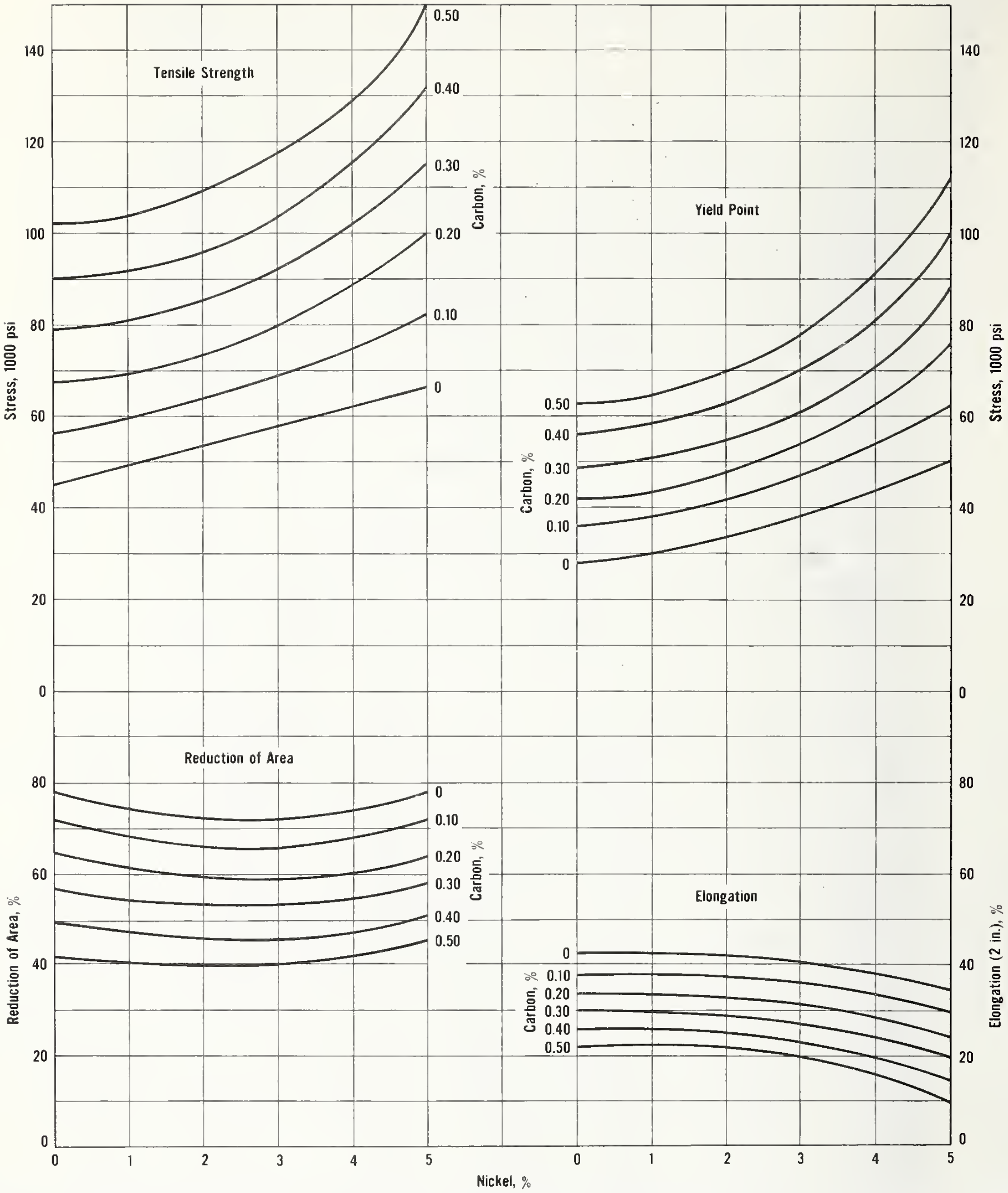

FIGURE 82. *Expected properties of normalized nickel steels treated in small sizes (½ to 1½-in diam or thickness) [719].*

by the American Iron and Steel Institute as standard steels. The most recent listing of alloy steels [718], however, does not include these straight nickel steels as standard compositions (table 53).

In complex steels, the effects of nickel and other alloying elements are complementary in a balanced composition and frequently are mutually intensifying. The contributions of nickel to hardenability are increased by the presence of manganese, chromium, and molybdenum, and the contributions of the latter three are materially increased by the presence of nickel [702,703]. The synergistic effect of alloying elements was a guiding factor in the development of the "National Emergency Steels" during World War II when the element nickel was in such short supply as to be critical. Many of the resultant lean triple-alloy steels proved to be of such merit as to warrant retention as standard steels (the 8000 and 9000 series, table 53).

The mechanical properties of the alloy steels are affected by the carbon content, the alloy content, and by heat treatment. Although hardening and tempering are usually desirable, and even necessary, to develop the maximum potential of alloy steels, there are many uses where normalized, or normalized and tempered steels, are suitable. The latter are used where improvement over carbon steel is desired but liquid quenching is either impractical or not required. Applications include some large forgings, some steels for low-temperature service, and structures fabricated so that liquid quenching is not feasible. An indication of the properties to be expected from normalized nickel steels (no other alloying element) may be obtained from figure 82. The change in strength and toughness conferred on normalized straight carbon steels by the addition of 3½ percent nickel is shown in figure 83. At 0.40 percent carbon, tensile strength is increased from about 90,000 psi to 110,000; the yield point from about 56,000 to 75,000 psi. This increase in strength is accompanied by a slight decrease in ductility; however, if the steels are compared on the basis of equal tensile strengths, the nickel steels show better ductility. For instance, the following values are taken from figure 83:

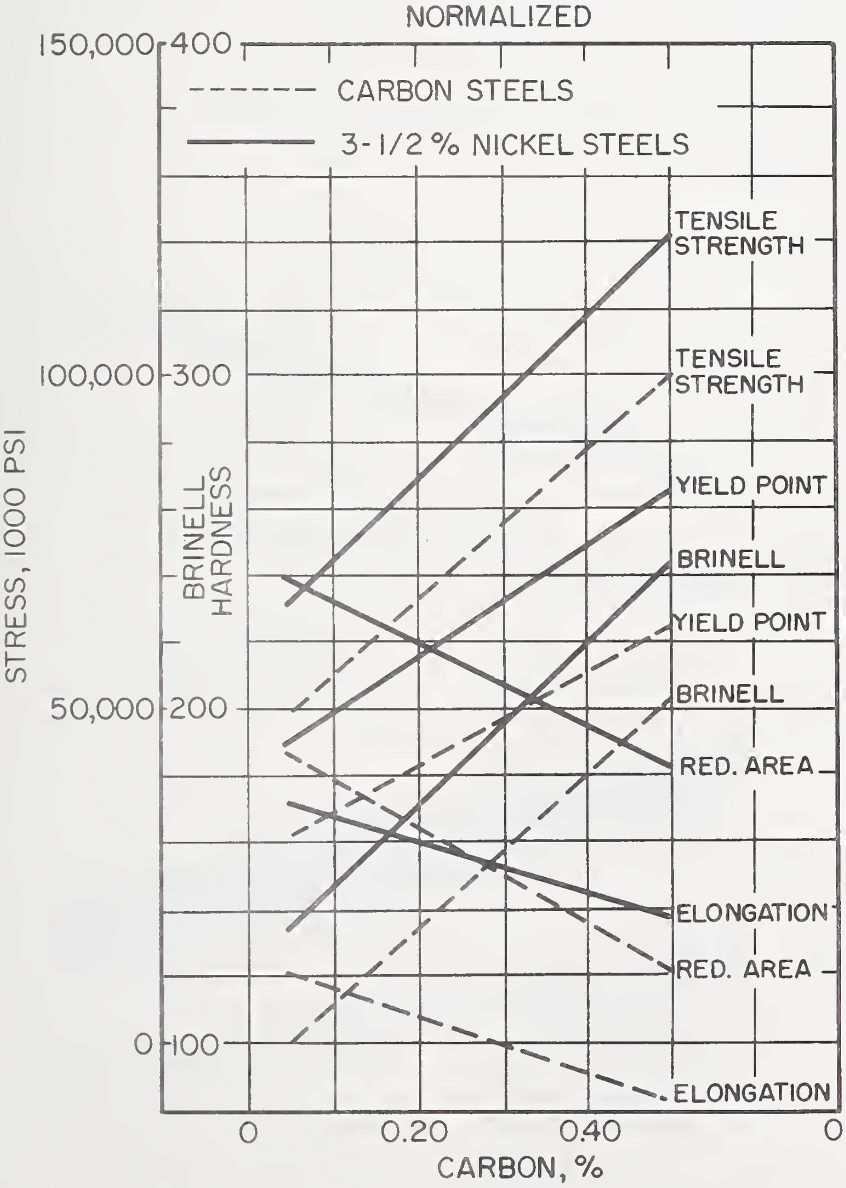

FIGURE 83. *Effect of 3½ percent nickel on the tensile properties of normalized steels treated in small sizes (½ to 1½-in diam or thickness) [719].*

Tensile strength, psi	Plain carbon steel			3½% nickel steel		
	Percent			Percent		
	C	Elong.	R.A.	C	Elong.	R.A.
70,000	0.23	34	62	0.18	35	68
100,000	.48	23	43	.33	25	54

In heat-treating alloy steels, it must be realized that transformation of austenite is retarded because of alloy content. With sufficient alloy and carbon content, steels become air hardening and the softening of such steels, for machining and forming operations, may necessitate subcritical or isothermal transformation after austenitizing. A list of suggested treatments for softening wrought nickel alloy steels, together with resultant structures and hardness, is given in reference [720].

When low-alloy steels are quenched and tempered, their resultant room-temperature mechanical properties are quite similar, provided the initial transformation was completely to martensite. The average expected properties are shown in figure 84. These curves can be used to predict the properties of any of the common alloy steels to within about ± 10 percent if the hardenability and heat treatment are such as to obtain a microstructure essentially of tempered martensite.

The low-carbon alloy steels are used mainly as carburizing steels; here the principal function of nickel is to strengthen and toughen the core whereas the principal benefits of chromium and molybdenum are in improved hardness and wear resistance of the case.

The higher carbon alloy steels are used for a variety of structural purposes. The mechanical properties of a few of these steels at a carbon content of 0.40 percent are shown in figure 85. Hardenability bands for these same steels are shown in figure 86.

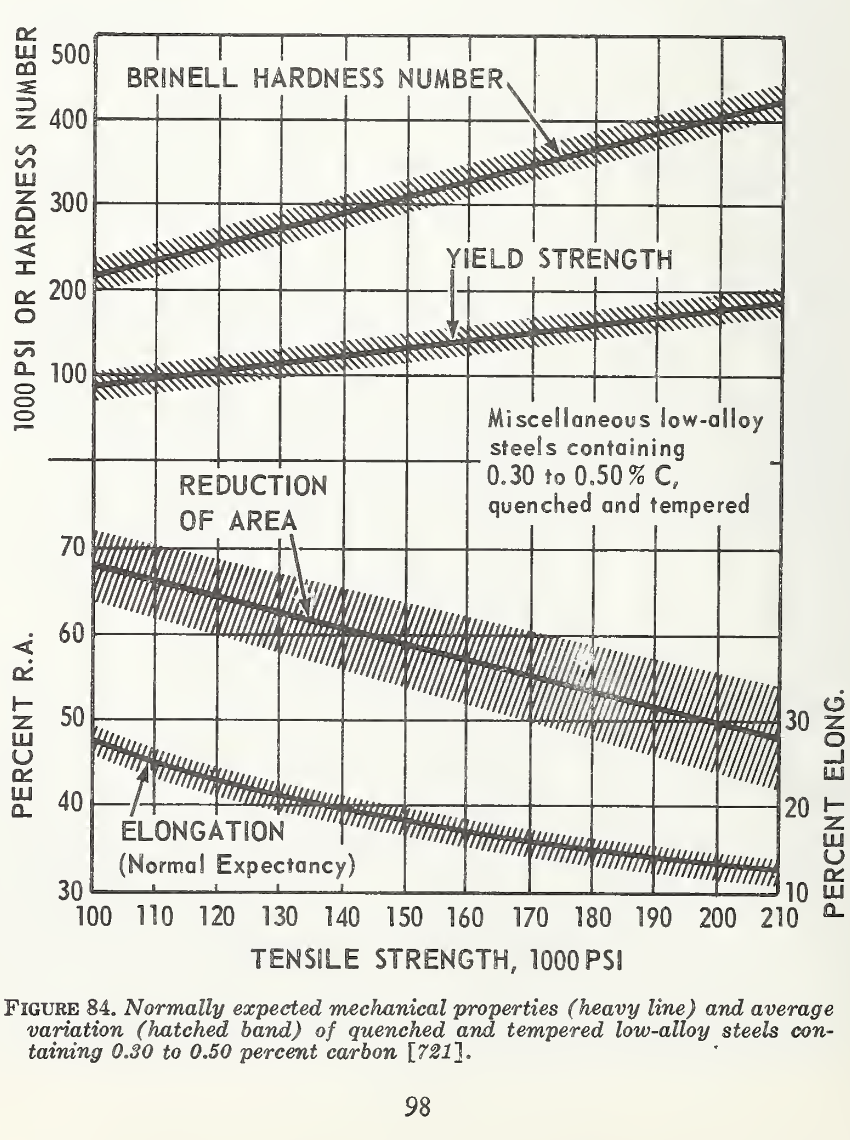

FIGURE 84. *Normally expected mechanical properties (heavy line) and average variation (hatched band) of quenched and tempered low-alloy steels containing 0.30 to 0.50 percent carbon [721].*

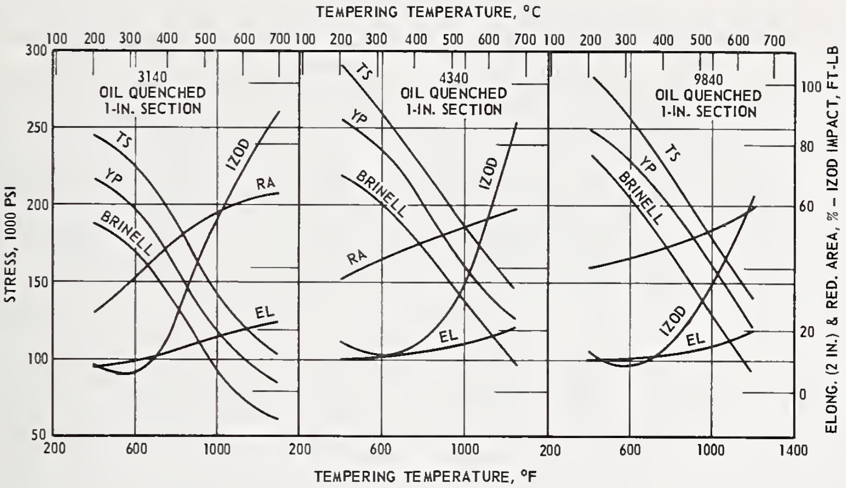

Figure 85. *Tensile and impact properties of oil-quenched and tempered 1-in sections of alloy steels as indicated* [*722*].

The low-alloy engineering steels as a class retain their room-temperature properties up to about 500 °F, but thereafter the tensile and yield strengths begin to fall off rapidly with further increases in temperature. Nevertheless, these steels are sometimes used at temperatures up to 1000 °F and the elevated temperature properties are of interest[724]. At subzero temperatures, the limitation on the use of these steels is their brittleness. This low-temperature brittleness is reduced by nickel but for use at very low temperatures, nickel in excess of the amounts present in the low-alloy structural steels is required. Parker and Sullivan [725] indicate that the lowest temperature at which a Charpy keyhole notch impact strength of 15 ft-lb may be specified is −75 and −150 °F for 2¼ and 3½ percent nickel steel, respectively. The beneficial effect of nickel in improving the impact resistance of steels is indicated in figure 87.

Beginning in the early 1930's, there has been a concerted effort on the part of the steel producers to develop high-strength low-alloy structural steels with mechanical properties that would permit substantial savings in weight in various types of construction, together with increased resistance to atmospheric corrosion that would permit the use of thinner sections without impairment of service life or safety. High-strength constructional steels previously had been carbon steels containing nickel, manganese, or silicon; in 1933 the first of the new steels appeared for use in railroad rolling stock. Applications of the high-strength low-alloy steels have been extended to include a variety of industrial equipment.

The required mechanical properties for sections of up to ½ inch in thickness, 70,000 psi minimum tensile strength and 50,000 psi minimum yield strength in the hot-rolled condition, were met by various combinations of alloying elements, some of which also improved the resistance to corrosion. For low alloy steels, functions of the different elements have been stated [727] to be as follows:

"Carbon is generally maintained at a level to insure freedom from excessive hardening after welding and to retain ductility.

"Manganese is used principally as a strengthening element.

"Phosphorus is sometimes employed as a strengthening element and to enhance resistance to atmospheric corrosion.

"Copper is commonly used to enhance resistance to atmospheric corrosion and as a strengthening element.

"Silicon, nickel, chromium, molybdenum, vanadium, aluminum, titanium, zirconium and other elements are used, singly or in combination, for their beneficial effects on strength, toughness, corrosion resistance and other desirable properties."

Some of these alloys are nickel free, or contain only residual amounts of nickel, but many include nickel as an alloying element. The nickel-containing steels as tabulated by Hall [29] are listed in table 54. For all, the minimum tensile and yield strengths are 70,000 and 50,000 psi, respectively, with elongations of about 20 percent for sections up to ½ in. in thickness. Other properties for these steels may be summarized as follows:

Fabrication and joining—satisfactory.

Notch toughness—better than carbon steels.

Resistance to fatigue and abrasion—trend toward superiority over carbon steels.

Resistance to corrosion—Resistance to atmospheric corrosion is substantially superior to carbon steels. Results of nine years of expo-

TABLE 54. *Representative low-alloy high-strength steels containing nickel* [29]

Trade name	Composition—percent								
	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
Cor-Ten	[a]0.12	0.20/0.50	0.07/0.15	[a]0.05	0.25/0.75	0.25/0.55	[a]0.65	0.30/1.25	
Double Strength	[a].12	.50/1.00	[a]0.04	[a].05		.50/1.00	.50/1.10		0.10 min.
Dynalloy	[a].20	[a]1.25	[a].10	[a].05	[a].30	[a].60	[a]1.00		[a].10
Hi-Steel	[a].12	.50/ .90	.05/ .12	[a].05	[a].15	.95/1.30	.45/ .75		.08/.18
Magari-R	[a].12	.50/1.00	.08/ .12	[a].05	.10/ .50	.50/ .70	.25/ .75	.40/1.00	
Tri-Ten	[a].25	[a]1.30	[a]0.45	[a].05	.10/ .30	.30/ .60	.50/1.00		
Yoloy	[a].15	[a]0.60	.05/ .10	[a].05		.75/1.25	1.50/2.00		

[a] Maximum.

sure of 71 low-alloy steels in industrial and marine atmospheres led Copson [738] to the conclusion that nickel additions produced low initial weight losses and, on long exposures, were particularly effective in decreasing pit depths. In sea water the average loss in weight is about the same, but the depth of pitting is about half that of carbon steels. Hudson and Stanners [729] concluded that copper, nickel, and chromium were the most useful alloying elements for resistance to atmospheric and seawater corrosion. In inland waters the low-alloy steels are at least equal to carbon steels and are superior in some contaminated, corrosive river waters. In soils the results are variable and about the same as for carbon steels. Protective coatings, such as galvanizing, for example, are readily applicable to these steels.

Manufacturing details for the low-alloy high-strength steels are given by the American Iron and Steel Institute [727].

More recently the demand for structural steels of still higher strengths resulted in the development of steels that were either precipitation hardened (held at 1000-1100 °F for 2 to 4 hr) or heat treated by quenching and tempering. A listing of some of the nickel-containing steels as compiled from various sources is given in table 55. Some of these steels have strengths as high as 140,000 psi tensile and 100,000 psi yield.

b. Ultra High-Strength Structural Steels

Until the end of World War II, the maximum strength at which steels were used for highly stressed structural components was less than 200,000 psi. Although steels could easily be treated to much higher strength levels than this, the assumption that the reduced ductility accompanying the higher strengths rendered the steels susceptible to brittle fracture prevented their use as very high strengths.

During the past twenty years the aircraft industry became particularly active in exploring the use of steels at higher strength levels, mainly because of the necessity of increasing the strength-weight ratio of structural parts in order to obtain greater efficiency of aircraft. Attempts to develop steels combining tensile strengths above 200,000 psi with sufficient ductility and toughness for safe usage have followed several courses—modification of the normal quench and temper heat treatment, modification of composition, martempering, ausforming, austempering, prestraining and retempering (also called mar-straining), and mar-aging.

Probably the first of the ultra high-strength steels was Hy-Tuf (0.25% C, 1.3% Mn, 1.5% Si, 1.8% Ni, 0.4% Mo) [730] developed by the Crucible Steel Company. The development of this steel was based on the finding by Allten

TABLE 55. *Representative low-alloy high-strength heat-treatable nickel-containing steels*

Trade name	Composition—percent										
	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	V	B
Republic "65"	0.12	0.45			0.20	1.00	1.30		0.20		
Republic "70"	.14	.75			.25	1.15	1.50		.22		
Cu-Ni-Mo	.15	.95			.22	.65	1.35		.25		
Yoloy "S"	.10	.50			.17	1.00	1.82				
"T-1"	.10/.20	.60/1.00	[a]0.040	[a]0.050	.15/.35	.15/0.50	.70/1.00	0.40/0.65	.40/.60	0.03/0.08	0.002/0.006
HY-80	[a].22	.10/ .40	[a].035	[a].040	.15/.35		2.00/2.75	.90/1.40	.23/.35		
80 HLES	[a].15	.5	[a].025	[a].020	[a].25		[b]4.00	[a].5	[a].4	[a].10	
HI-Z	.10/.18	.60/1.00	[a].030	[a].030	.15/.35	.15/ .50	.70/1.00	.40/ .80	.40/.60	.03/ .10	.002/ .006
K-O	.10/.20	.60/1.00	[a].030	[a].030	.15/.35	.15/ .50	.70/1.00	.40/ .80	.40/.60	.03/ .10	.002/ .006
MTR	.13	.65/ .95	[a].030	[a].030	[a].35	[a].25	1.10/1.60	.40/ .70	.40/.60	.04/ .10	
NK-HITEN 80	[a].18	[a]1.00	[a].035	[a].040	.15/.35	.15/ .50	[a]1.00	[a].80	[a].60	[a].10	[a].006
Superelso	[a].18	.90	.030	.025	.30	.20	1.50	1.30	.25		
Welcon 24 Super	.08/.16	.60/1.20	[a].035	[a].040	[a].55		[a]1.00	[a].5	[a].4		
Welcon 2H Ultra	.08/.16	.60/1.20	[a].035	[a].040	[a].55	.15/ .50	[a]1.50	[a].8	[a].7	[a].10	[a].006
Wel-ten 80	[a].18	.60/1.20	[a].035	[a].040	.15/.35	.15/ .50	[a]1.50	.40/ .80	[a].60	[a].10	[a].006

[a] Maximum. [b] Minimum. Where no ranges are given, values are approximate or average.

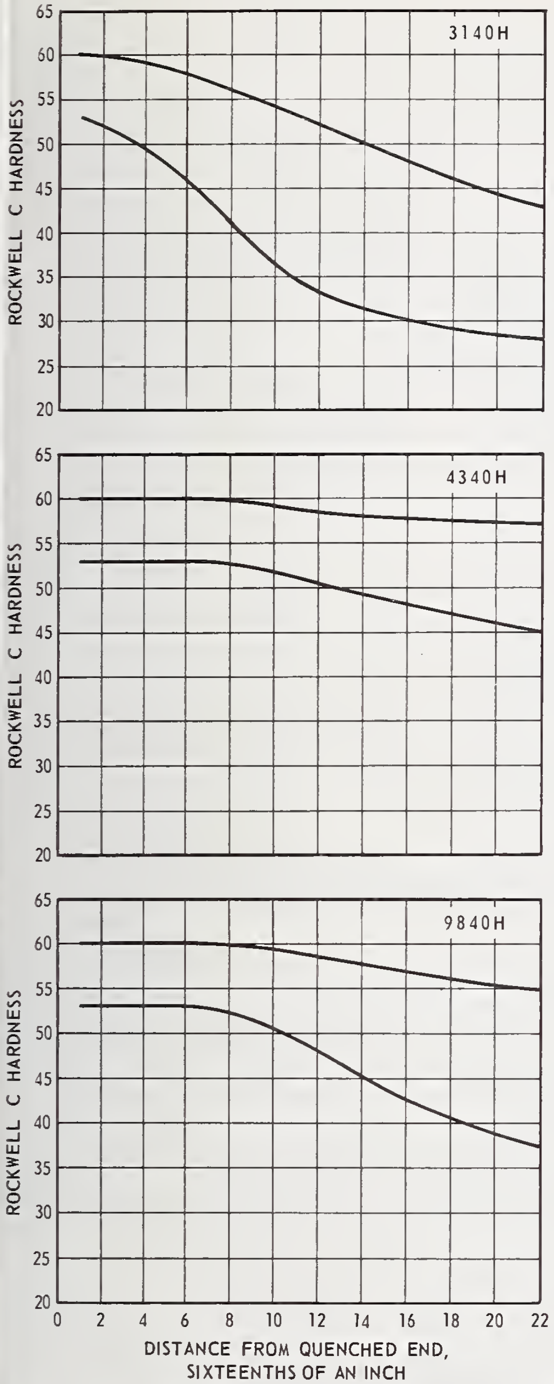

FIGURE 86. *Hardenability bands for alloy steels as indicated [723].*

and Payson [731] that silicon retards the softening of steels tempered in the range of 400 to 600 °F (fig. 88) and also that it raises the temperature at which the so-called "500 °F" embrittlement occurs, thus permitting the use of a higher tempering temperature resulting in increased toughness with no significant loss in strength. When combined with reduction in carbon content, adequate toughness for structural use was developed at a tensile strength of 230,000 psi.

Testing programs in many laboratories showed that toughness values could be shaded to allow the use of steel at still higher strength levels and a tensile strength of 300,000 psi became the magic number. Practically all of the steels developed to meet this goal contained nickel. A listing of some of these steels whose high strength may be obtained by a quench and temper heat treatment is given in table 56. Many of these steels are also susceptible to strengthening by some of the other processes noted previously.

The use of steel at very high strength and hardness levels involves careful consideration of certain factors that are relatively unimportant at lower strength levels. These include sensitivity to hydrogen embrittlement in plating operations, to damage in grinding, to the effects of surface decarburization during heat treatment, and difficulties in welding, machining, and forming. Careful handling and meticulous inspection are required, and particular effort must be made to design and fabricate to minimize notch effects and other stress raisers.

c. Maraging Steels

The term "maraging" was coined to describe the hardening process in a series of ultra high-strength steels developed by The International Nickel Company during the past several years. Essentially, the process consists of transforming a highly alloyed low-carbon austenite to martensite, which is subsequently aged to induce hardness and strength, hence the term "maraging." These steels contain large amounts of nickel (12 to 25%) plus other elements. The physical metallurgy of the maraging steels is discussed by Hall [734], Decker et al. [739], and The International Nickel Company, Inc.[739a].

The addition of such large amounts of nickel to iron depresses the $\alpha \rightleftharpoons \gamma$ transformation markedly. However, the transformation on cooling is depressed to a much greater degree than that on heating and this temperature hysteresis increases with increasing nickel content. A plot of the metastable transformation diagram is shown in figure 89.

At the lower nickel contents and, hence, the higher tansformation temperatures, the transformation process is controlled by diffusion. At higher nickel contents and correspondingly lower transformation temperatures, the extremely low diffusion rates discourage diffusion-controlled transformation and transformation occurs by shear. The result of this transformation is martensite. It is important to note that the formation of such martensite

TABLE 56. *Ultra high strength nickel-containing structural steels* [*732, 733*]

Steel	AMS No.[a]	Chemical composition—percent								Tempering temperature[b]	Mechanical properties				
		C	Mn	Si	Ni	Cr	Mo	V	B		Tensile strength	Yield strength	Elongation	Reduction of area	Charpy V-notch impact
										°*F*	*psi*	*psi*	%	%	*ft-lb*
4330 Mod	6427B	0.28/0.33	0.75/1.00	0.20/0.35	1.65/2.00	0.75/1.00	0.35/0.50	0.05/0.10	--------	600	255,000	220,000	20	50	22(Izod)
4335 Mod	6428	.32/ .38	.60/ .80	.20/ .35	1.65/2.00	.65/ .90	.30/ .40	.17/ .23	--------	500	260,000	210,000	--------	--------	--------
4340	6415E	.38/ .43	.65/ .85	.20/ .35	1.65/2.00	.70/ .90	.20/ .30	--------	--------	450	280,000	230,000	10	45	13
USS Strux	--------	.40/ .46	.75/1.00	.50/ .80	.60/ .90	.80/1.05	.45/ .60	.01/ .06	0.007 max	500	290,000	250,000	10	30	10
Ladish D-6-A	--------	.42/ .48	.60/ .90	.15/ .30	.40/ .70	.90/1.20	.90/1.10	.05/ .10	--------	500	280,000	255,000	10	30	30
Hy-Tuf	6418B	.23/ .28	1.20/1.50	1.30/1.70	1.65/2.00	.20/ .40	.35/ .45	--------	--------	500	240,000	205,000	15	50	30
300-M	--------	.40/ .45	.65/ .90	1.45/1.80	1.65/2.00	.65/ .90	.30/ .45	.05 min.	--------	500	300,000	250,000	13	35	15
NBS	--------	.40	.75	1.60	1.80	.85	.30	(0.10 Ti)	.002 max	500	285,000	235,000	10	35	16

[a] Aeronautical Material Specification.

[b] Double tempering is usually recommended.

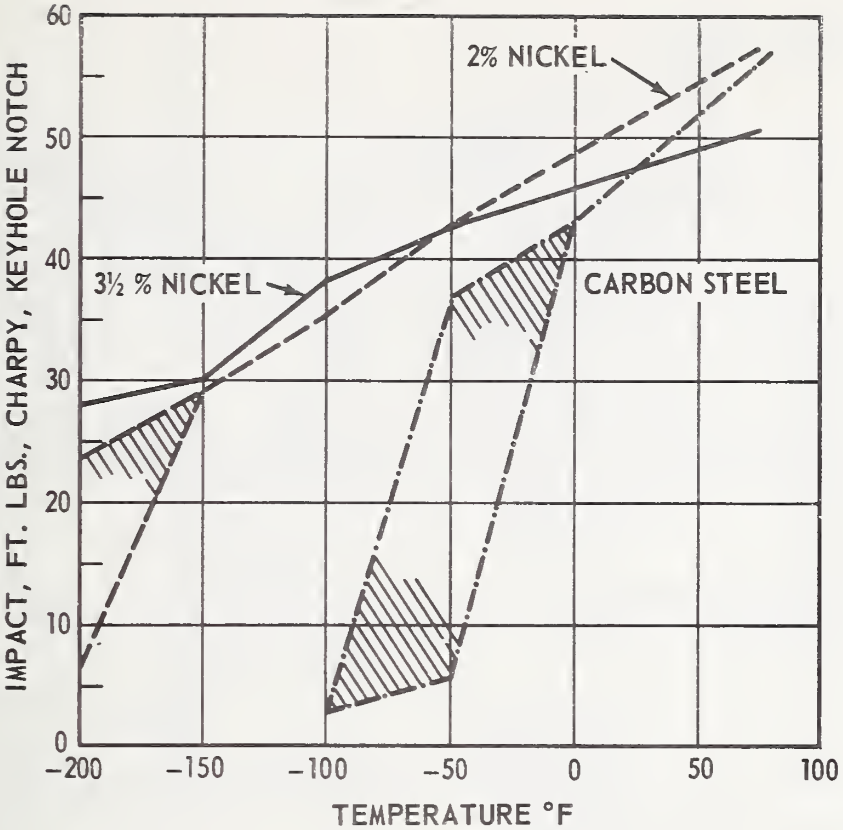

FIGURE 87. *Effect of nickel on low temperature impact properties of normalized and tempered 0.16 percent C steel treated with 0.80 percent Al* [*726*].

is not dependent upon cooling rate, but only upon composition and temperature. In the presence of low carbon, the martensite so formed has a body-centered cubic structure, but unlike the martensite of heat-treated steels, it is cubic and not tetragonal. Because of this, the volume change resulting from the formation of high-nickel martensite is much less than that in heat-treatable steels. Furthermore, because the martensite is very low in carbon, it is relatively soft and readily workable.

According to Gilbert and Owen [736], the transformation temperature (M_s) is sufficiently depressed so that martensite forms under all conditions of cooling at a minimum content of about 18 percent nickel. Nevertheless, maraging steels with 12 percent nickel have been developed [737]. Maraging steels containing as much as 28 percent nickel have been studied [738].

The martensitic transformation is not disturbed by the addition of substantial amounts of other elements, such as molybdenum, cobalt, and titanium, the presence of which provides the 18 percent nickel maraging steels with their distinguishing characteristics. The M_s temperature of these steels appears to be in the vicinity of 310 °F, while their M_f temperature is about 210 °F [739].

As shown in figure 89, a considerable hysteresis exists in the $\alpha \rightleftarrows \gamma$ transformation, which permits reheating of the martensite to fairly high temperatures before reversion to austensite takes place. This, in turn, provides considerable opportunity to develop aging and precipitation reactions within the martensite. When the maraging steels are heated to elevated temperatures below that at which reversion to austensite occurs, their hardness and strength increase markedly. Moreover, the hardening response of these steels during aging is rapid. The hardening mechanism of these steels has been the subject of considerable study [740,741,742,743]. Heat treatment of the 18 percent nickel steel has been investigated by Floreen and Decker [744].

Initially, three main types of maraging steels, containing 18, 20, and 25 percent nickel, were developed. However, only the 18 percent nickel grade has found widespread commercial usage. This steel is produced commercially at three strength levels; 200, 250, and 280 KSI. The alloy additions to the 18 percent nickel steel are mainly cobalt, molybdenum, and titanium; those to the 20 and 25 percent nickel

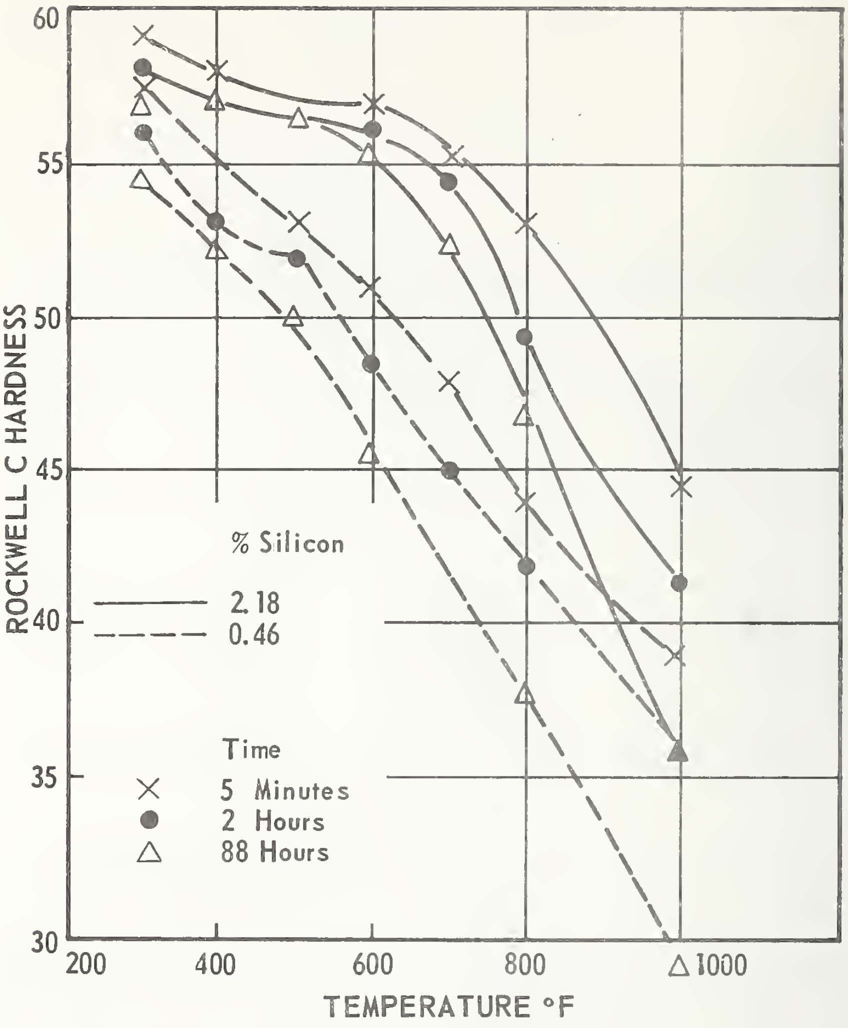

FIGURE 88. *Effect of silicon upon the hardness of 0.6 percent C, 3.0 percent Ni steel after oil quenching, subzero cooling (to —320 °F), and tempering as indicated [731].*

steels were mainly titanium, aluminum, and columbium. The 12 percent nickel steel (12-5-3) is a more recent development, as is a new 18 percent nickel grade at 350 KSI. Compositions of the most popular commercial grades are given in table 57. These steels may be aged either in the as-rolled condition, or as annealed at 1500 °F. Details on the 20 and 25 percent nickel maraging steels can be found in references 745 and 748.

The effect of residual elements on the properties of maraging steels has been reported by Novak and Diran [746].

The 18 percent nickel steel has been the most important member of the maraging steels. By minor variations in composition, it can be made

TABLE 57. *Compositions of maraging steels [734, 737, 737a, 737b]*

Designation	Chemical composition—percent										
	C[a]	Mn[a]	P[a]	S[a]	Si[a]	Ni	Co	Mo	Ti	Al	Cr
18 Ni 350	0.01	0.10	0.005	0.005	0.10	17.0/18.0	12.0/13.0	3.5 /4.0	1.6 /2.0	0 10/0.20	----------
18 Ni 280	.03	.12	.01	.01	.12	18.0/19.0	8.0/ 9.5	4.6 /5.2	.5 / .8	.05/ .15	----------
18 Ni 250	.03	.12	.01	.01	.12	17.0/19.0	7.0/ 8.5	4.6 /5.1	.3 / .5	.05/ .15	----------
18 Ni 200	.03	.12	.01	.01	.12	17.0/19.0	8.0/ 9.0	3.0 /3.5	.15/ .25	.05/ .15	----------
Cast	.03	.10	.01	.01	.10	16.0/17.5	9.5/11.0	4.4 /4.8	.15/ .45	.02/ .10	----------
12–5–3	.03	.10	.01	.01	.12	11.5/12.5	----------	2.75/3.25	.10/ .35	.20/ .50	4.75/5.25

[a] Maximum.

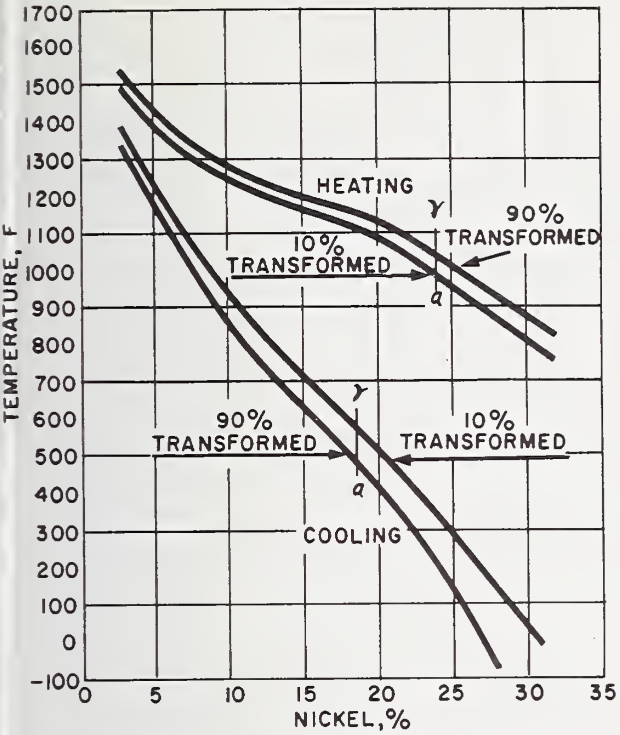

FIGURE 89. *The iron-nickel metastable transformation diagram* [735].

to three different yield strength levels—200,000, 250,000, and 300,000 psi. The lowest strength level was designed to provide maximum toughness with good strength at ambient and cryogenic temperatures; the intermediate strength level was designed to optimize high strength with good toughness, and the highest strength level was designed to obtain the highest strength-to-weight ratio with adequate toughness. The new 350,000 psi grade represents the highest strength practically obtainable with this hardening mechanism to date.

The 18 percent nickel steels can be aged either as hot rolled or as annealed at 1500 °F. Optimum properties are obtained by aging at 900 °F. The low distortion and small volume change accompanying this simple heat treatment make this steel attractive for large components. They are weldable without preheat in both the solution annealed and in the fully aged condition. Only a post-weld aging treatment is required to restore properties in the heat-affected zone and to develop good strength in the weld metal [747,748,749,750,751].

Many studies have been made of the mechanical and physical properties of the maraging steels [752,753,754,755,756,757,758,759]. A tabulation of some properties is given in tables 58, 59 and 60.

TABLE 58. *Physical and environmental properties of maraging steels* [758]

		18% Ni[a]
Density	lb/in.^{3}	0.290
Modulus of elasticity	10^6 psi	26.5
Modulus of rigidity	10^6 psi	10.2
Poisson's ratio		0.30
Coefficient of thermal expansion (70–900 °F)	10^{-6}/°F	5.6
Nil ductility transition temperature	°F	<-80
Change in length during maraging	%	0.06
Electrical resistivity	μ ohm-cm	
As annealed[b]		60–61
Annealed plus maraged[c]		38–39
Intrinsic induction	gauss	
H = 250 oersteds		16,550
H = 5000 oersteds		18,500
Remanence	gauss	5,500
Coercive force	oersteds	28.1
Stress corrosion—minimum life at stress equal to yield strength	days	
U bends in sea water		35[d]
3-point loaded in Bayonne atmosphere		>360

[a] 250,000 grade. Elastic modulus for 200,000 and 300,000 grades is 27.5 × 10^6 psi.

[b] At 1500 °F for 1 hr.

[c] At 900 °F for 3 hr.

[d] 200,000 grade showed no failures in 6 months.

TABLE 59. *Mechanical properties of annealed maraging steel* [758]

		18% Ni[a]
Yield strength (0.2%)	psi	110,000
Tensile strength	psi	140,000
Elongation in 1 in	percent	17
Reduction of area	percent	75
Hardness, Rc		28–32

[a] Bar specimen, 0.252-in. diam, 1-in. gage length.

Dean and Copson [760] reported that the maraging steels are somewhat better than high-strength low alloy steels in general corrosion behavior. Scharfstein [761] noted that susceptibility to stress-corrosion cracking was greatest in the highest-strength condition.

As cast, the maraging steels are reported to respond to the same simple heat treatments as the wrought steels and to have mechanical properties [762,763,764] comparable to those of the wrought steels.

d. Special Steels

There are many special nickel-containing steels that have been designed for specific purposes and whose compositions do not fall into any regular grouping. An example of such a steel is the 9 percent nickel steel designed for low-temperature service.

As has been mentioned previously, nickel increases the toughness of steel. At low temperatures, the 9 percent nickel steel shows toughness significantly superior to any of the ferritic steels. It may be used either as quenched and tempered (1475 °F, water; 1050 ° F, air or water) or as double normalized and tempered (1650 °F, air; 1450 °F, air; 1050 °F, air or water). Its excellent toughness at subzero temperatures is indicated in figure 90. Information on the properties of this steel is

TABLE 60. *Mechanical properties of maraging steels* [737a, 737b, 758]

Bar Stock	12–5–3	18% Ni						
		200,000 psi		250,000 psi		300,000 psi		350,000 psi
	1500 °F, 1 hr, +900 °F, 3 hr	900 °F, 3 hr[a]		900 °F, 3 hr[a]		900 °F, 3 hr (direct maraged)		1500 °F, 1 hr, +900 °F, 3 hr
				Air melt	Vacuum melt			
Yield, psi	180,000	190,000–210,000		240,000–268,000		295,000–303,000		350,000
Tensile strength, psi	188,000	200,000–220,000		250,000–275,000		297,000–306,000		356,000
Elongation in 1 inch, percent	14	14–16		10–12		12		9.5
Reduction in area, percent	65	65–70		48–58		60		50
Notch tensile strength (Kt>10)[e], psi	310,000	315,000–350,000		372,000–386,000	393,000–415,000	439,000–449,000		333,000
NTS/TS	1.65	1.58–1.62		1.41–1.53	1.49–1.54	1.44–1.51		.92
Charpy V-notch impact, ft-lb								
70 °F	60	60–110		18–26	25–30			10
−320 °F		30–60		12–15				
Endurance limit (10 ⁷ cycles), psi	90,000	95,000		95,000–100,000				
Sheet		900 °F, 3 hr[a]	50% CW +900 °F, 3 hr[a]	900 °F, 3 hr[a]	50% CW+900 °F, 3 hr[a]	900 °F, 3 hr[a b]	50% CW +900 °F, 3 hr[a c]	
Yield strength, psi								
70 °F		203,000	244,000	252,000	286,000–290,000	280,000–282,000	300,000–309,000	
−320 °F		286,000	298,000					
Tensile strength, psi								
70 °F		224,000	246,000	262,000	289,000–292,000	290,000–294,000	303,000–312,000	
−320 °F		291,000	303,000					
Elongation in 1 in., percent								
Notch tensile strength (Kt>10), psi								
NTS/TS								
Gc[f], in-lb/in²								
70 °F		> 1880	> 1680	> 2000	> 1240– > 1690	1510–1710	1100–> 1800	
−320 °F		> 2720	> 1800					
Compressive yield strength (0,2%)[d], psi				247,000				
Shear strength[d], psi				143,000				

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[a] Annealed 1 hr at 1500 °F.
[b] Annealed 1 hr at 1600 °F. Bar 0.252 in diam.
[c] Determined on bar with 0.300 in major diameter.
[d] Annealed 15 min. at 1500 °F.
[e] Test bar 0.252 in diam.
[f] Irwin's critical crack extension force.

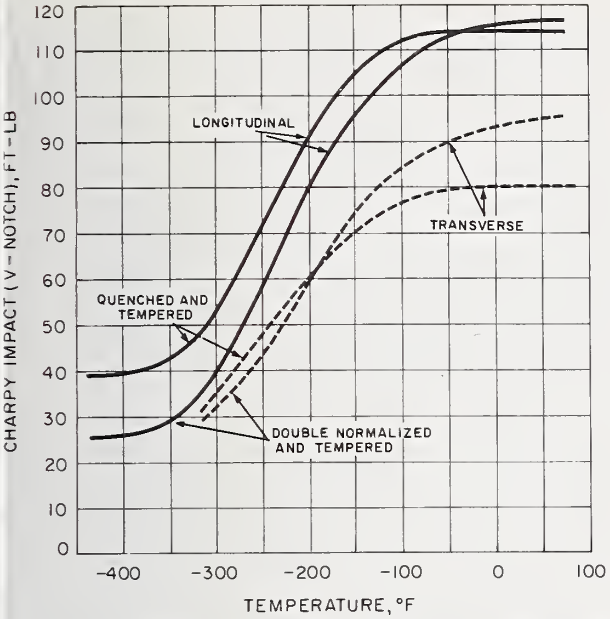

FIGURE 90. *Impact properties of 9 percent nickel steel* [*765*].

TABLE 61. *Some properties of 9 percent nickel steel* [*765*]

Composition, %			Mechanical properties (double normalized and tempered)
C	0.13	max.	Tensile strength —100,000/120,000 psi
Mn	.90	max.	Yield strength — 75,000 min.
P	.035	max.	Elongation in 2 in.— 22.0 min.
S	.040	max.	Endurance limit — 65,000 psi
Si	.15 / .30		
Ni	8.50 /9.50		

Thermal conductivity		Modulus of elasticity
Temperature –°F	Btu/in/hr/sq ft/°F	at 70 °F 27,000,000 psi at –320 °F 30,000,000 psi Density 0.284 lb/in.^{3}
–320	91	Electrical resistivity at 70° F—33.0 microhms cm
–243	134	Specific heat (double normalized and tempered)
–189	149	(mean –320 to 80 °F)—0.088 BTU/lb/ °F
–99	172	(mean 80 to 700 °F)—0.119 BTU/lb/ °F
–9	190	
81	203	

Thermal expansion (double normalized and tempered)

Temperature.°F	Instantaneous coefficient per °F	Temperature interval °F	Mean coefficient per °F
–260	0.0000040	–325 to 75	0.0000049
–150	.0000047	–200 to 75	.0000051
–50	.0000055	–100 to 75	.0000054
50	.0000058	–100 to 200	.0000058
150	.0000064	75 to 200	.0000065

Magnetic properties (double normalized and tempered)

Temperature, °F	Magnetic saturation[a] (Bs) Gauss
–303	21,360
–148	20,830
32	20,300
68	20,210
212	19,850

[a] Magnetic field strength (h) of 16,700 Oe. Bs = maximum possible intrinsic induction. The Curie temperature on heating is about 1391 °F; on cooling about 968 °F.

given in table 61. The strength properties increase as the temperature of test decreases; elongation remains essentially unchanged, being about 30 percent at temperatures as low as –300 °F.

Considerable information on the metallurgy and properties of the 9 percent nickel steel is available and its suitability for low temperature service has been well documented [766, 767,768,769,770,771,772,773]. It is readily amenable to fabrication by welding [774,775, 776,777] and as welded, its properties are sufficiently good to allow its use for cryogenic pressure vessels without subsequent stress relief [778]. The ASME has approved its use in welded vessels down to –320 °F without stress relief in plates up to 2 in thick [779]. The 9 percent nickel steel is covered by ASTM Specification A353–64 for double normalized and tempered, A553–65 for quenched and tempered, and A522–65 for forgings.

Schumann [780] described a low-carbon 13 percent nickel steel that is characterized by greater low-temperature ductility and by a considerably higher yield point and tensile strength than the 9 percent nickel steel.

Nonmagnetizable (austenitic) steels for use under service conditions that necessitate a higher performance than that usually demanded of conventional austenitic steels are described by Kroneis and Gattringer [781]. These are very high alloy steels, many susceptible to precipitation hardening by incorporation of vanadium, titanium or aluminum. Composition ranges are carbon 0.2/0.65 percent, manganese 6/18 percent, nickel 4/10 percent, and chromium 3.5/12 percent.

A nitriding steel that can be age hardened to a tensile strength of 200,000 psi has compositional limits of carbon 0.20/0.25 percent, manganese 0.25/0.45 percent, nickel 4.75/5.25 percent, aluminum 1.8/2.2 percent, chromium 0.4/0.6 percent, molybdenum 0.2/0.3 percent, vanadium 0.08/0.15 percent [782,783]. The resistance to tempering exhibited by both the core and nitrided case makes this steel particularly suitable for use in cams, gears, shafts and bearings required to exhibit fatigue and wear resistance at temperatures up to 1000 °F.

A variation of the Hadfield manganese steel [784] with compositions of carbon 0.95/1.1 percent, silicon 1 percent maximum, 13/18 percent manganese, and 7/11 percent nickel are stated to exhibit high yield and tensile strengths, exceptionally uniform elongation and ductility, a high degree of notch toughness, and excellent energy dissipation characteristics without failure. Heat treatment consists of water-quenching from 2000 °F.

The properties of HP 9–4–25 steel were described by Savas [785]. This steel contains approximately 8 percent nickel, 4 percent cobalt, and 0.25 percent carbon. When double tempered at 1000 °F, it has yield and tensile strengths of 190,000 and 200,000 psi, respectively, over 50 percent reduction of area, and 14 percent elongation. Charpy V-notch impact is 45 ft-lb.

Steels with a coefficient of expansion approaching that of aluminum alloys have been developed. One analysis is 0.55/0.65 percent carbon, 1.00 percent silicon maximum, 5.00/6.00 percent manganese, 8.50/10.50 percent nickel [786]. Another analysis is 0.4/0.6 percent carbon, silicon 0.3 percent maximum, 4.6 percent manganese, 11/13 percent nickel, 3 percent chromium and 0.5 percent molybdenum [787].

4.3. Cast Steels and Irons

a. Cast Steels

Casting represents the most direct method of producing steel parts to final form and nickel increases the strength and ductility of steel castings in much the same manner as it does for wrought products. By 1910 the properties of cast steel containing about 3½ percent nickel were well known and the steel was widely used for cast sections in heavy ordnance. In early work on cast gun tubes at Watertown Arsenal, a 0.40 percent carbon, 2.96 percent nickel steel was used [788]. Burgess [789] reporting on tests of similar steels, noted that "certain of these treated steel castings would appear to compare very favorably in the properties with those of forged material of the same composition." Cone [790] called attention to an important characteristic of cast nickel steels, i.e., the relatively high ratio of yield to tensile strength as compared with that of carbon steels of approximately the same ductility. It is now known that the beneficial effects of nickel in cast steels result from the fact that nickel depresses the pearlite nose of the S-curve and shifts it to the right to produce a finer structure and higher yield strength when normalized.

In amounts of 2 to 3½ percent, nickel is useful alone, and in smaller amounts, 0.4 to 1.5 percent, it is effective in combination with manganese and other alloying elements. The most favorable combination of properties in cast steels, just as in wrought steels, is developed by heat treatment. Liquid quenching, followed by tempering, is usually the best treatment and is widely used when the size and shape of the casting permit. Castings of intricate shape and with sharp changes in section size may be used in the normalized or normalized and tempered condition. Cast steels, like wrought steels, may be martempered, austempered, isothermally quenched, flame hardened, induction hardened, and case hardened.

Data of early investigators on the mechanical properties of cast plain nickel steels were reviewed by Lorig and Williams [791] and the results of a number of investigations in the 1930's, together with some more recent data, are summarized in table 62. Armstrong [792, 793] reported typical properties of 30-ton naval castings and large railroad frames, made of steel containing 0.30 percent carbon, 0.90 percent manganese, and 3 percent nickel, to be as follows:

	Annealed	Normalized and tempered
Tensile strength psi	85,000	87,000
Yield strength psi	53,000	55,000
Elongation in 2 in. %	30	30
Reduction of area %	54	50

As was the case with wrought steels, uses of cast nickel steels led to interest in cast steels containing additional alloying elements. Mechanical properties of some of these steels in comparison with plain nickel steels, as reported by Lorig [794], are given in table 63. Chrominum functions as a ferrite strengthener in low-carbon steels and also has a strong tendency to form hard carbides; it therefore increases the strength and hardness of cast nickel steels but the increase in strength is

TABLE 62. *Typical properties of some cast nickel steels* [*29, 791a*]

Composition, %			Treatment	Psi		%		Charpy impact, ft lb
C	Mn	Ni		Tensile strength	Yield strength	Elongation in 2 in.	Reduction of area	
0.17	0.80	2.05	Double normalized and tempered	80,000	53,000	29	60	[a] 58
.17	.40	2.50	Double normalized and tempered	80,000	56,000	31	59	30
.09	.65	2.50	Double normalized and tempered	82,000	62.000	32	54	[b] 25
.24	.60	2.40	Double normalized and tempered	82,000	60,000	31	55	33
.16	.57	2.65	Normalized, oil quenched and tempered	81,000	65,500	29	58	37
.30	1.00	2.00	Normalized and tempered	94,000	58,000	26	48	----------
.30	.60	3.25	Annealed	95,500	61,000	22	48	----------
.39	.75	3.50	Annealed	115,000	65,000	22	35	----------
.09	.65	3.50	Double normalized and tempered	80,000	54,000	32	60	[b] 30
.33	.60	3.25	Water quenched and tempered	134,000	120,000	17	40	----------

[a] Izod. [b] At −150 °F.

Table 63. *Mechanical properties of some cast steels containing nickel [791a, 794]*[a]

Composition, %							Psi		%		Izod impact, ft-lb
C	Mn	Si	Ni	Cr	Mo	V	Tensile strength	Yield strength	Elongation in 2 in.	Reduction of area	
32	1.15	0.39	0.67	----------	----------	----------	94,500	57,000	24.5	48	----------
.31	1.60	.35	1.37	----------	----------	----------	101,000	68,000	24.5	56	----------
.30	.90	.35	2.15	----------	----------	----------	103,000	62,500	25	50	----------
.24	.74	.29	1.29	----------	----------	0.10	81,500	64,000	30.5	61	71
.32	.90	.35	1.33	0.79	----------	----------	100,000	60,000	22.5	43	----------
.29	.90	.35	1.82	----------	0.35	----------	92,000	65,000	22.5	47	----------
.30	.90	.35	1.45	.54	.21	----------	104,000	79,000	22	46	----------
.30	1.00 max	.80 max	.60	.60	.23	----------	115,000	96,000	20	52	[b] 40
.20 max	.65	.50 max	2.80	1.50	.45	----------	112,000	90,000	23	58	[b, c] 80

[a] All steels were normalized and tempered, except the last two, which were quenched and tempered.
[b] Charpy V-notch impact.
[c] At −100 °F.

accompanied by some loss in ductility. Molybdenum in the usual range of 0.10 to 0.30 percent, but sometimes as high as 0.50 percent, is effective in increasing the hardenability and resistance to some types of corrosion. Vanadium is an effective grain refiner and is frequently added to cast nickel steels, usually in amounts between 0.08 and 0.15 percent, to improve ductility and the yield to tensile strength ratio. Manganese is the cheapest of the alloying elements and its use in combination with nickel produces good ductility and high ratios of yield to tensile strength. Armstrong [795] concluded that the benefits of manganese in low-alloy steels were most apparent when the manganese content was above 1 percent.

Elman and Schelleng [796] found nickel to be essential in raising low-temperature toughness of nickel-manganese steels. Its effectiveness was found to be dependent on the particular manganese content. At a carbon level of 0.30 percent, optimum tensile and low-temperature impact properties were obtained with 1.50 percent nickel, 1.60 percent manganese. The interplay of nickel and manganese on the 15 ft-lb transition temperature of this steel as normalized and tempered is shown in figure 91.

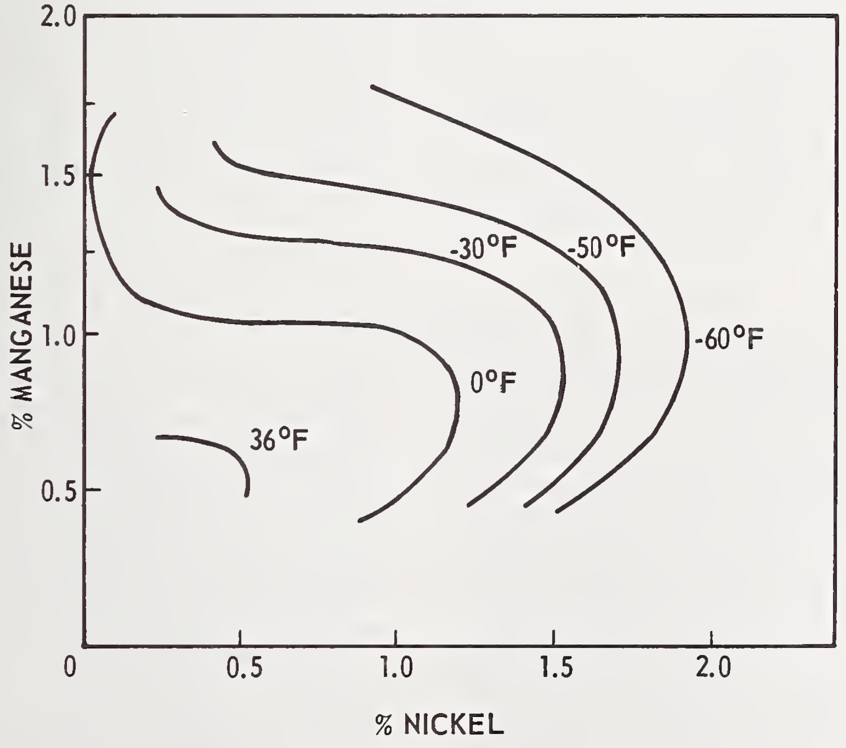

Figure 91. *Effect of nickel and manganese upon the 15 ft-lb transition temperature of 0.30 percent carbon cast steel [796].*

A low-alloy cast steel with an exceptionally good combination of strength and toughness was developed by Knoth and Schelleng [797]. Its composition is 0.25/0.29 percent carbon, 0.20/0.40 percent silicon, 0.40/0.70 percent manganese, 3.7/4.2 percent nickel, 1.9/2.1 percent chromium, 0.38/0.45 percent molybdenum, and 0.10/0.14 percent vanadium. With so much alloy, transformation from austenite is sufficiently retarded so that the steel transforms to bainite during air cooling even in heavy sections. As normalized and tempered, this steel develops a minimum yield strength of 100,000 psi in combination with 15 ft-lb Charpy V-notch transition temperatures below —70 °F and an NDT below —90 °F.

A cast steel, air hardenable in thick sections for use in armored vehicles, was developed by Rostoker [798]. The following two analyses were found to be capable of providing, in a 5-in section, an impact strength of 18/20 ft lb at —40 °F at a hardness, after tempering, of R_c 22/24:

	(1)	(2)
Carbon	0.18%	0.18%
Manganese	1.9	.5
Silicon	.5	.5
Chromium	1.0	1.0
Nickel	.5	2.5
Molybdenum	.5	.5

A cast steel containing 9 percent nickel was reported to have a 15 ft-lb Charpy V-notch transition temperature lower than liquid nitrogen temperature [799].

The design, treatment, and properties of steel castings are covered in the Steel Castings Handbook [800].

b. Cast Irons

One of the first attempts to improve cast iron by means of additions of nickel was made by Hickling [801] in 1799 when he patented the use of 2.5 to 25 percent of nickel in making hollow cast iron vessels. In 1845 Poole [802] patented an oxidation-resistant cast iron with 2-10 percent nickel. The first published paper on nickel cast iron is attributed to Fairbairn [803], who reported on the properties of various mixtures of cast iron and nickel in 1860.

The use of nickel to improve the properties of cast iron were developed empirically during the 19th century and it was not until the 20th century that the complex nature of cast iron and the interrelation of carbon, silicon, alloy content, and heat treatment began to be understood, with an accompanying rapid expansion in uses and applications. The early history of nickel cast iron was summarized in 1923 b Merica [804] and additional data were pr sented by Wickenden and Vanick [805]. Subsequent reviews include those of Merica [806 in 1937, Bairot and Berthelier [807] in 195 and Hall [29] in 1954.

Even today the iron-nickel-carbon system i not well understood and very little is known o equilibria in the iron-silicon-nickel-carbon system. According to Hall [29], nickel decrease the solubility of carbon in molten iron, lower the eutectic carbon content and raises the eutectic temperature, acts as a graphitizer with about one-half the effectiveness of silicon lowers the critical temperatures and thereby extends the austenite field, decreases the eutectoid carbon content by approximately 0.04 percent of carbon for each 1 percent of nickel and moves to the left, i.e., toward lower carbon contents, the boundaries of the field in which plain cast iron has a wholly pearlitic matrix Because nickel is a graphitizer, it acts to decrease the amount of eutectic cementite in the structure, thereby reducing or eliminating hard spots and chill and promoting uniformity in the distribution of graphite. Nickel refines the pearlitic matrix in cast iron by delaying the austenite → pearlite reaction (by displacement to the right of the upper nose and lower portions of the **T-T-T** curve), as well as by lowering the eutectoid temperature. As with steels, increasing amounts of nickel tend to make the structure martensitic or austenitic on slow cooling. The acicular structures have proved to be very desirable from the standpoint of mechanical properties.

Schelleng [808] evaluated the influence of nickel up to 37 percent in combination with silicon on the carbon content of the eutectic and proposed the following formula:

$$\% \text{ C (eutectic)} = 4.30 - 0.33\ (\% \text{ Si}) - 0.47\ (\%\text{Ni}) + 0.0055\ (\% \text{ Ni})\ (\% \text{ Si}).$$

The effect of nickel on the eutectic in iron-carbon alloys according to Schichtel and Piwowarsky [809] is shown in figure 92.

Wickenden and Vanick [805] reported that, as the nickel content of cast iron is increased to between 5 and 12 percent, a series of alloyed irons is produced that are martensitic when cooled at ordinary rates and quite hard, particularly if chromium is present. Norbury and Morgan [810] observed that when the silicon content was increased from 0 to 7 percent, the amount of nickel required to render the matrix martensitic increased from about 5 percent to about 12 percent. They also found that additions of chromium up to about 1.8 percent slightly reduced the amount of nickel required to produce a martensitic matrix, but further

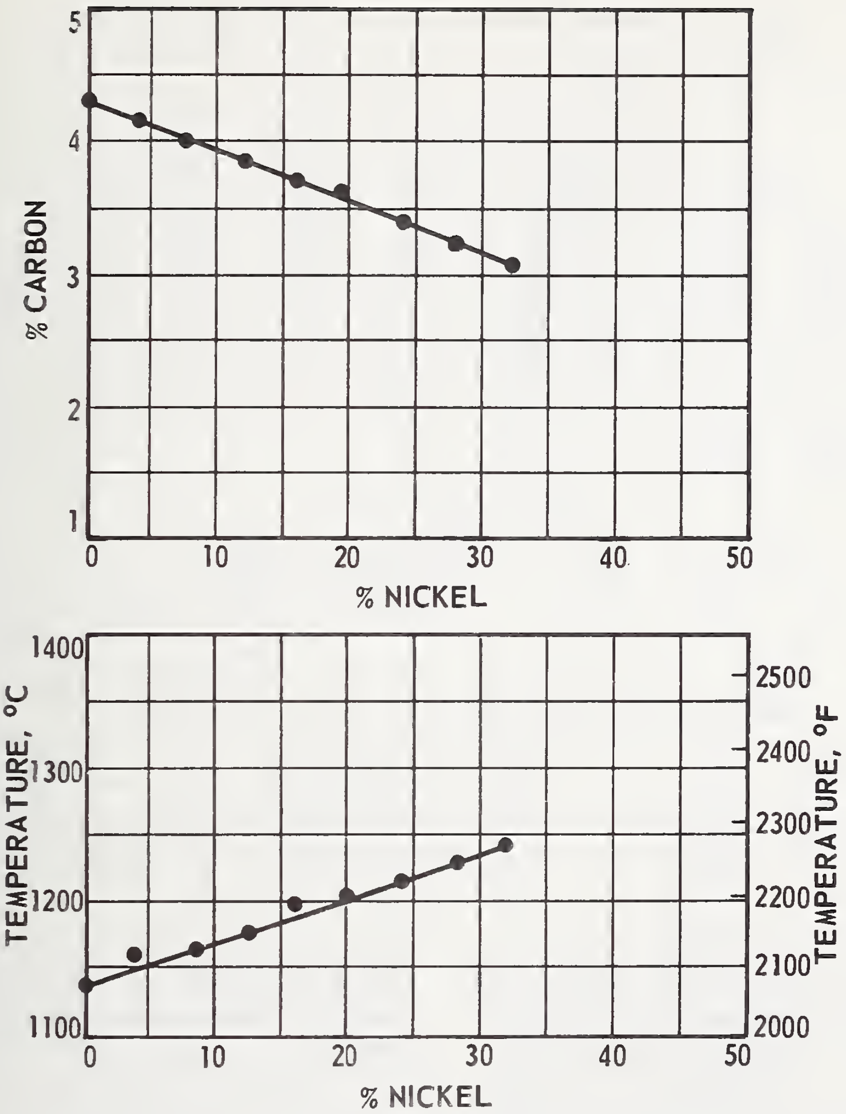

FIGURE 92. *Effect of nickel on the carbon content and temperature of the eutectic in iron-nickel alloys [809].*

additions of chromium caused no change in the required nickel content. Acicular irons, according to Flinn and Reese [811], are capable of developing 105,000 psi tensile strength. Eighteen percent of nickel is sufficient to make cast irons completely austenitic [810].

Cast irons with such high alloy contents are intended for special purposes such as resistance to corrosion, heat, and wear. The engineering cast irons have a total alloy content that normally does not exceed about 3 or 4 percent.

As has been mentioned before, nickel is effective as a graphitizer. As such, it acts to reduce or eliminate the amount of white iron in a chilled bar. The following data are indicative of its effectiveness in a cast iron of base composition about 3.55 percent total carbon and 1.05 percent silicon:

Effect of nickel on depth of chill [805]

Nickel	Depth of white iron in chilled bar	Depth of white and mottled iron in chilled bar
%	*in.*	*in.*
0.12	0.70	1.30
.32	.60	1.05
.94	.55	1.10
1.10	.45	1.15
2.47	.30	.75
3.90	0	0

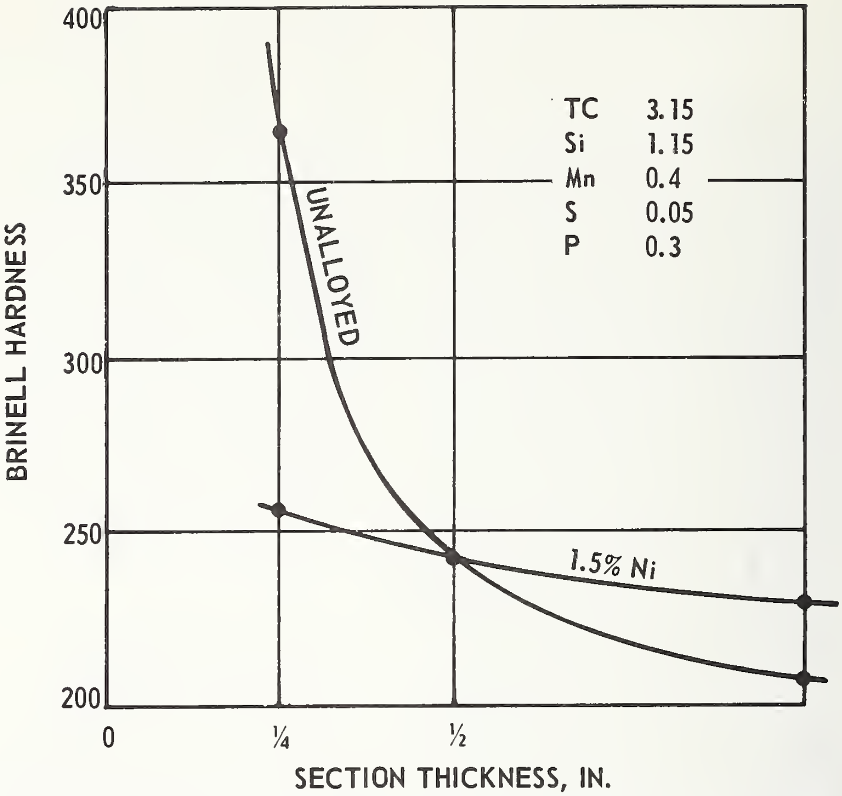

FIGURE 93. *Influence of nickel in equalizing the hardness of cast iron* [*812*].

Base composition: TC 3.15 percent, Si 1.15 percent, Mn 0.4 percent, S 0.05 percent, P 0.3 percent.

The marked effect of nickel in equalizing the hardness of cast iron is indicated in figure 93. The influence of nickel on the structure and properties of gray iron has been summarized by Form and Wallace [813].

Chromium is a powerful carbide stabilizer, thereby increasing tensile strength, transverse strength, and hardness. Molybdenum is a mild carbide stabilizer and an effective strengthener. Examples of typical compositions of high-strength irons, assembled by Hall [29] from various sources, are presented in table 64. These properties often may be improved by heat treatment.

The size, shape, and uniformity of distribution of graphite flakes have important effects on the mechanical properties of cast iron, particularly for the so-called high-duty irons that are low in carbon and silicon. Consequently, inoculants are added to cast iron in the ladle to promote the formation of graphite and its uniform distribution. Nickel itself has no inoculating properties, but a nickel-silicon alloy, Nisiloy, was at one time widely used for this purpose [814,815].

The graphite phase in cast iron may be altered completely from its usual lamellar-flake form by special ladle additions and caused to form as spheroidal nodules. In 1948 Morrogh [816] described a method of obtaining nodular graphite in hypereutectic iron by making a ladle addition of cerium or mischmetal. In 1949 a patent, originally filed in 1947, was granted to Millis et al. [817] covering controlled magnesium additions to hypoeutectic or hypereutectic irons that would cause the graphite to precipitate in spheroidal form. It was also found at that time that the nodular form of graphite could be produced in austenitic as well as pearlitic iron by the magnesium addition.

Magnesium is not readily added to liquid iron because it is extremely reactive and, in addition, boils at the temperature of molten iron. However, it can be added satisfactorily when it has been alloyed with a metal like nickel or copper, which will reduce its reactivity and raise the boiling point. Nickel-magnesium and copper-magnesium alloys containing 10-20 percent magnesium are very satisfactory for this purpose [818]. Iron-silicon-magnesium alloys are also used commercially and occasionally pure magnesium is used with the aid of special devices.

The spheroidal or spherulitic graphite (S.G.) or ductile cast irons possess high tensile

TABLE 64. *Typical compositions and properties of some high-strength cast irons [29]*

Composition, percent									Tensile strength	Brinell hardness	Transverse strength 1.25 in. bars, 12 in. span	Deflection
TC	CC	Si	Mn	P	S	Ni	Cr	Mo				
Nickel cast irons												
									psi		*lb*	*inch*
2.73	--------	1.68	1.13	0.11	0.073	0.98	--------	--------	48,500	228	4,900	0.17
3.02	--------	1.65	0.91	.11	.073	.75	--------	--------	49,100	228	5,100	.21
2.98	--------	1.66	1.17	.16	.074	1.02	--------	--------	50,000	217	5,270	.24
2.89	--------	1.58	0.77	.097	.090	1.21	--------	--------	50,800	228	5,390	.187
3.07	--------	1.64	.95	.13	.077	1.03	--------	--------	51,000	217	5,060	.19
2.86	--------	1.41	.88	.13	.096	0.97	--------	--------	52,600	217	5,210	.24
2.89	--------	2.02	.53	.033	.097	2.44	--------	--------	66,200	269	6,200	.153
2.78	--------	1.79	.49	.029	.087	2.88	--------	--------	68,000	269	5,920	.142
Nickel-chromium automotive cylinder irons												
3.10	1.05	1.13	--------	--------	--------	1.21	0.39	--------	31,550	286	4,130	0.107
3.35	0.82	2.32	--------	--------	--------	0.86	.41	--------	34,600	217	3,715	.123
3.15	.90	1.76	--------	--------	--------	1.13	.45	--------	44,450	262	5,030	.159
Nickel-molybdenum irons, as-cast												
2.26	0.72	2.27	--------	--------	--------	1.09	--------	0.33	71,000	286	4,050	[a]0.26
2.30	.75	2.31	--------	--------	--------	1.03	--------	1.36	71,800	321	4,700	[a].33
2.28	.74	2.31	--------	--------	--------	2.06	--------	0.82	74,400	340	4,600	[a].36
2.31	.76	2.30	--------	--------	--------	1.04	--------	.81	80,600	321	4,600	[a].32
2.30	.77	2.32	--------	--------	--------	2.03	--------	1.31	82,000	387	4.800	[a].35
Nickel-chromium-molybdenum cast irons, cupola produced												
3.36	--------	2.04	0.87	0.105	0.063	1.52	0.29	0.74	56,750	248	5,220	--------
3.21	--------	1.85	.85	.087	.056	1.61	.24	.78	61,050	248	5,575	--------
3.24	--------	1.99	1.00	.093	.067	1.52	.19	.73	63,350	269	5,280	--------
3.20	--------	1.97	0.93	.089	.064	1.53	.19	.74	65,550	262	5,335	--------
3,24	--------	1.75	.93	.087	.057	1.42	.25	.82	66,100	262	5,640	--------
3.24	--------	1.87	.84	.089	.066	1.56	.28	.80	67,400	269	5,770	--------
3.28	--------	1.88	1.09	.072	.064	1.55	.26	.73	70,350	293	6,120	--------
2.97	--------	2.01	0.93	.087	.069	1.63	.29	.77	74,900	286	5,785	--------
3.12	--------	1.74	.92	.080	.084	1.63	.28	.90	77,000	302	5,930	--------
2.94	--------	1.78	1.00	.080	.054	1.62	.28	.79	79,150	286	5,990	--------

[a] On 18-in. span.

strength and ductility and at the same time retain the machinability and much of the castability of the standard gray irons. Tensile strengths of 70,000–120,000 psi can be obtained by the nodularizing treatment without heat treatment in irons that normally would have 20,000-40,000 psi tensile strength, and annealing 1 hr at 1650 °F, followed by slow cooling, gives an elongation of about 20 percent with a tensile strength of about 70,000 psi [818]. High ductility can also be achieved by a subcritical heat treatment when no carbide exists in the iron. Heat treatment (quenching and tempering) will give even higher strengths, as much as 175,000 psi. In nickel ductile irons, the nickel content is relatively low (about 0.4 to 2%), but the austenitic type of ductile iron contains about 18 to 22 percent of nickel. Indeed, it is this high nickel content that makes it austenitic. This iron has excellent heat and corrosion resistance. The seven generally recognized grades of ductile iron are tabulated in table 65. It will be observed that types 100–75–04 and 120–90–02 are identical in composition. The higher strength of the latter type is attained by heat treatment. The ASTM lists five grades of ductile irons by properties only, as indicated in table 66.

The cast irons generally have better corrosion resistance than steels. Greene and Sefing [820] reported that low-alloy irons could be used up to about 1100 °F as grate bars, annealing boxes, etc., whereas higher alloyed irons could be used at higher temperatures. Wilks, Mathews, and Kraft [821] reported that ductile high-nickel irons were useful up to 1200 or 1300 °F.

The compressive strength of cast irons containing nickel extends over a range of 80,000-200,000 psi [29]. As a rule, the ratio of compressive to tensile strength becomes smaller as the tensile strength increases, varying from 4.5 to about 2.5 times the tensile strength. Shock resistance is somewhat better than for unalloyed iron; the ratio of shear strength to tensile strength decreases as the tensile strength increases, from about 1.6 or 1.7 for low-strength irons to about 1.0 for high-strength irons; the torsional strength generally bears a linear relation to the tensile strength; the high damping capacity of gray iron varies with the amplitude of vibration, and the fa-

TABLE 65. *Compositions and properties of ductile irons* [819]

Type	Chemical composition, percent								Mechanical properties					Characteristics
	TC	Mn	P	Si	Ni	Cr	Mo	Mg	Tensile strength	Yield strength	Elongation in 2 in	BHN	Charpy impact	
									psi	*psi*	%		*ft-lb*	
65–45–12	3.4/3.8	0.2/0.6	0.08	1.8/2.5	0/1.0	--------	--------	0.02/0.07	60,000/ 80,000	45,000/ 60,000	10/25	140/190	[a]60/115	Maximum toughness and machinability. Good weldability. Structure essentially ferritic.
60–40–18	3.4/3.8	--------	.02/.06	1.8/2.5	0/1.0	--------	--------	.02/ .07	60,000/ 70,000	42,000/ 50,000	18/25	150/180	[a]75/115	Excellent machinability and good weldability. High shock resistance at low temperatures achieved by annealing.
80–55–06	3.3/3.8	.2/ .5	.08	2.0/3.0	0/1.0	--------	--------	.02/ .07	90,000/110,000	60,000/ 75,000	3/10	200/270	[a]15/ 65	High strength in as cast condition; good wear resistance, machinability and toughness. Essentially pearlitic structure which responds readily to flame or induction hardening.
100–70–03	3.4/3.8	.3/ .6	.08	2.0/2.75	0/2.5	--------	0/1.0	.02/ .07	100,000/120,000	75,000/ 90,000	6/10	200/240	[a]35/ 50	Excellent combination of strength, toughness, and wear resistance. Readily flame or induction hardened. Is usually normalized and tempered, although it may be quenched and tempered.
120–90–02	3.4/3.8	.3/ .6	.08	2.0/2.75	0/2.5	--------	0/1.0	.02/ .07	120,000/150,000	90,000/125,000	2/7	240/325	[a]25/ 40	Usually quenched and tempered. Has excellent wear resistance and is readily flame or induction hardened to Rockwell C 56/58.
Heat Resistant Type.	2.8/3.8	.2/ .6	.08	2.5/6.0	0/1.5	--------	--------	.02/ .07	60,000/100,000	45,000/ 75,000	0/20	140/300	[a]5/115	Maximum resistance to oxidation and growth.
Austenitic Type.	2.4/3.0	.7/1.25	.08	1.5/3.0	18/22	1.75/2.75	--------	.02/ .07	58,000/ 68,000	32,000/ 38,000	8/20	140/200	[b]10/28	Excellent corrosion and heat resistance. Non-magnetic. Most readily weldable type of ductile iron.

[a] Unnotched.
[b] V-notch.

TABLE 66. *Tensile requirements for ductile iron castings (ASTM A536–65T)*

	Grade 60–40–18	Grade 65–45–12	Grade 80–55–05	Grade 100–70–03	Grade 120–90–02
Tensile strength, min psi	60,000	65,000	80,000	100,000	120,000
Yield strength, min psi	40,000	45,000	55,000	70,000	90,000
Elongation in 2 in, min ______percent	18	12	6.0	3.0	2.0

tigue strength increases with increasing tensile strength, although both drop off rapidly when the temperature exceeds about 800 °F.

Gray irons containing nickel are widely used for automobile engine cylinder blocks, diesel engine cylinder liners, piston rings, crankshafts, camshafts, couplings, gears, machinery frames, and a variety of uses involving metal-to-metal contact and resistance to wear and abrasion. Many of the properties, and particularly the resistance to wear and abrasion, are improved by increasing the carbon and alloy content. For instance, Ni-Hard is a generic designation for a martensitic white cast iron that is widely used in applications requiring resistance to abrasion, particularly in such severe service as in grinding and crushing equipment. Its composition is 2.8-3.6 percent carbon, 0.5-0.7 percent manganese, less than 0.4 percent phosphorus, 4 to 5 percent nickel, and 1.8 to 2.6 percent chromium [822]. A summary of its properties is given by The International Nickel Company, Inc. [823].

Many cast irons with higher alloy contents have been developed since about 1930 for improved heat and corrosion resistance to meet the increasingly severe requirements of service in the chemical industry and as annealing retorts, grate bars, and other furnace parts. Hallett [824] reviewed established and experimental materials with varying combinations of increased nickel, chromium, and silicon with additions of other elements, including copper and molybdenum. Some of these are gray irons, but in many instances the alloy content is high enough to make the irons austenitic.

Ni-Resist is a generic name applied to a group of high-nickel alloy cast irons containing sufficient nickel to produce an austenitic structure as well as a complete change in chemical and physical characteristics. Ranges of chemical compositions are given in table 67 and are covered by ASTM Specification A436–63. By reason of their high alloy content and austenitic structure, they provide a unique combination of engineering properties: resistance to corrosion, erosion, heat and oxidation; strength and toughness, resistance to wear, good mechinability, high electrical resistance, and, by suitable choice of the nickel content, non-magnetic characteristics and varying thermal expansivities. Types 1 and 2 are corrosion resistant, the heat resistance of type 3 is considerably improved over that of types 1 and 2, and types 4 and 5 are notably resistant to both heat and corrosion, although the latter is used primarily for parts requiring high dimensional stability and low thermal expansion. Considerable information on Ni-Resist is given by Barton [826]. Ni-Resist can be treated with magnesium to change the graphite from flakes to spheroids [827] with improvement in strength, elongation, and toughness at room and elevated temperatures. This iron is covered by ASTM Specification A439–62. According to Wilks, Mathews, and Kraft [821], tensile, rupture, and creep tests show that the utility of the standard ferritic and pearlitic grades of cast iron is limited to about 1000 °F for long-term load-carrying applications when both scaling resistance and strength are considered, but the high-nickel austenitic irons should be useful to about 1200 to 1300 °F. Their results for the effect of temperature on the tensile strength and ductility of ductile cast irons are shown in figure 94.

The development of a special Ni-Resist ductile cast iron for use at low temperatures was described by Rickard [828]. A ductile austenitic cast iron was patented by Schelleng and Abbott [828a].

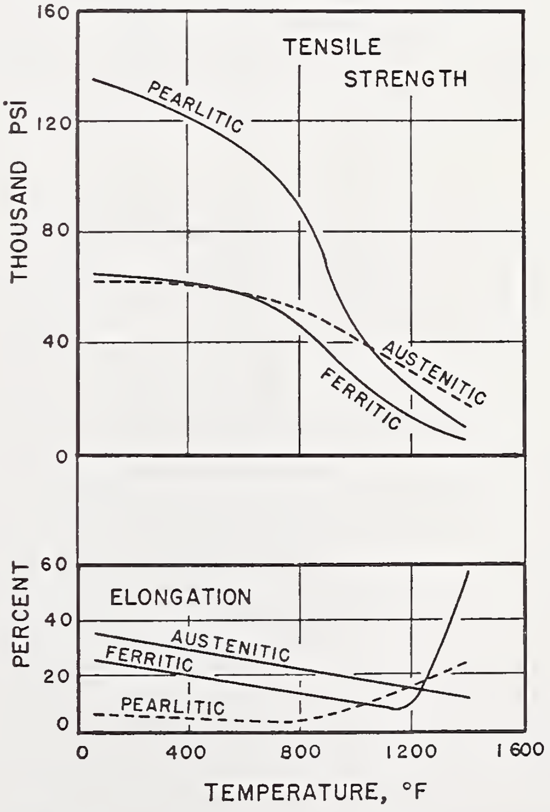

FIGURE 94. *Effect of temperature on the tensile strength and elongation of ductile cast irons [821].*

TABLE 67. *Composition ranges of Ni-Resist irons* [825]

Type	Chemical composition, percent					
	Total carbon	Manganese	Silicon	Nickel	Copper	Chromium
1	[a] 3.00	1.00/1.50	1.00/2.80	13.50/17.50	5.50/7.50	1.75/2.50
1b	[a] 3.00	1.00/1.50	1.00/2.80	13.50/17.50	5.50/7.50	2.75/3.50
2	[a] 3.00	.80/1.50	1.00/2.80	18.00/22.00	[a] .50	1.75/2.50
2b	[a] 3.00	.80/1.50	1.00/2.80	18.00/22.00	[a] .50	3.00/6.00
3	[a] 2.60	.40/ .80	1.00/2.00	28.00/32.00	[a] .50	2.50/3.50
4	[a] 2.60	.40/ .80	5.00/6.00	29.00/32.00	[a] .50	4.50/5.50
5	[a] 2.40	.40/ .80	1.00/2.00	34.00/36.00	[a] .50	[a] .10

[a] Maximum.

4.4. Stainless Steels

a. General

The outstanding characteristic of the stainless steels (more properly termed corrosion-resisting steels) is their ability to resist attack by oxidizing media. This property is conferred by the addition of chromium and the presence of large amounts of this element is a common characteristic of all of the many stainless steels. The minimum content of chromium in any of the stainless steels is about 11.5 percent. Standard compositions of the nickel-bearing stainless and heat-resisting steels are given in table 68.

The stainless steels can be divided into four general classes, namely, martensitic, ferritic, austenitic, and precipitation-hardening. None of the ferritic stainless steels contain nickel and are not, therefore, included in this discussion.

b. Martensitic Stainless Steels

Only two of the standard martensitic stainless steels (and none of the ferritic type) contain nickel (table 68). Type 414 is not used a great deal, but type 431 (frequently referred to as 16–2) finds extensive use as high-strength stainless forgings and fittings. It is normally used as heat treated to a strength level of about 200,000 psi. When properly made and processed, this steel exhibits amazing toughness at high strength levels. Charpy V-notch values in excess of 70 ft-lb have been recorded on steels treated to a hardness of Rockwell C36 and 40 ft-lb at a hardness level of C43. It is important that this steel should never be tempered in the range of 600 to 1000 °F as tempering in this range results in excessive brittleness. The constitution of 16–2 has been studied by Johnson and Rosenberg [831] and the properties of 16–2 have been discussed by Angstadt [832]. The function of the nickel content is to decrease, or even eliminate, the delta ferrite in the microstructure.

Two modifications of the 16–2 steel, one for forgings and one for cold-rolled sheet, were described by Morley [833]. The compositions are as follows:

	FV520(B)	FV520(S)
Carbon	0.07% max	0.04/0.08%
Manganese	1.0 max	.8 /1.8
Silicon	.6 max	.6 max
Chromium	13.5/14.5	15.3/16.0
Nickel	5.0/ 5.8	5.0/ 5.8
Molybdenum	1.2/ 2.0	1.2/ 3.0
Copper	1.2/ 2.0	1.5/ 2.2
Niobium	.2/ .9	----------
Titanium	----------	.2 max

A steel of somewhat similar composition was patented by Irvine [834] (carbon 0.07-0.16%, chromium 14-17.5%, nickel 3.5-4.5%, nitrogen 0.05%). It is characterized by a content of manganese, with or without one or more of the elements silicon, tungsten, and molybdenum, in certain specified proportions. Another hardenable nickel-bearing stainless steel was patented by Aktiebolaget Bofors [835] (carbon 0.03-0.25%, manganese 0.25-2.00% silicon 0.10-0.70%, chromium 11-14%, nickel 4-8%, molybdenum 0.5-3.5%). Mott [836] described a hardenable stainless steel resistant to erosion, corrosion, and abrasion by acid and other corrosive slurries (carbon 0.07% max, manganese 0.2-4%, silicon 0.2-7%, chromium 15-32.5%, nickel 25-35%, molybdenum 2-20%, copper 1-5%). This steel is hardened by proper adjustment of the alloying elements and not by heat treatment.

c. Austenitic Stainless Steels

The chromium-nickel (austenitic) stainless steels are widely used because of their resistance to corrosion, ease of formability, desirable mechanical properties, and the ability to retain these properties at temperatures above and below ambient. Although chromium is the principal alloying element, the austenitic stainless and heat-resisting steels account for about one-fourth of all the nickel consumed (fig. 3) in the United States.

The addition of substantial amounts of nickel to high-chromium steels effects a marked change in both mechanical and physical properties. Nickel enhances fabricating characteristics and increases corrosion resistance significantly in the presence of chromium, but the principal function of nickel in stainless steel is to stabilize the austenitic structure normally existent only at high temperatures. The austenitic stainless steels originally developed during the 1920's contained about 18 percent chromium and 8 percent nickel and this led to the use of the term "18–8" to decribe these steels.

During times of national emergencies, the shortage of nickel presented a serious problem to the producers and consumers of the 300

TABLE 68. *Nickel bearing standard stainless and heat-resisting steels* [829, 830]

AISI type	Chemical composition							
	% C (max)	% Mn (max)	% P (max)	% S (max)	% Si (max)	% Cr	% Ni	Other
				Austenitic steels				
201	0.15	5.50/ 7.50	0.060	0.030	1.00	16.00/18.00	3.50/ 5.50	N 0.25% max.
202	.15	7.50/10.00	.060	.030	1.00	17.00/19.00	4.00/ 6.00	N 0.25% max.
301	.15	2.00	.045	.030	1.00	16.00/18.00	6.00/ 8.00	
302	.15	2.00	.045	.030	1.00	17.00/19.00	8.00/10.00	
302 B	.15	2.00	.045	.030	2.00/3.00	17.00/19.00	8.00/10.00	
303	.15	2.00	.20	[a].15	1.00	17.00/19.00	8.00/10.00	Mo 0.60% max (optional).
303 Se	.15	2.00	.20	.060	1.00	17.00/19.00	8.00/10.00	Se 0.15% min.
304	.08	2.00	.045	.030	1.00	18.00/20.00	8.00/12.00	
304 L	.030	2.00	.045	.030	1.00	18.00/20.00	8.00/12.00	
305	.12	2.00	.045	.030	1.00	17.00/19.00	10.00/13.00	
308	.08	2.00	.045	.030	1.00	19.00/21.00	10.00/12.00	
309	.20	2.00	.045	.030	1.00	22.00/24.00	12.00/15.00	
309 S	.08	2.00	.045	.030	1.00	22.00/24.00	19.00/22.00	
310	.25	2.00	.045	.030	1.50	24.00/26.00	19.00/22.00	
310 S	.08	2.00	.045	.030	1.50	24.00/26.00	19.00/22.00	
314	.25	2.00	.045	.030	1.50/3.00	23.00/26.00	19.00/22.00	
316	.08	2.00	.045	.030	1.00	16.00/18.00	10.00/14.00	Mo 2.00/3.00%.
316 L	.030	2.00	.045	.030	1.00	16.00/18.00	10.00/14.00	Mo 2.00/3.00%.
317	.08	2.00	.045	.030	1.00	18.00/20.00	11.00/15.00	Mo 3.00/4.00%.
321	.08	2.00	.045	.030	1.00	17.00/19.00	9.00/12.00	Ti 5 x C min.
347	.08	2.00	.045	.030	1.00	17.00/19.00	9.00/13.00	Cb-Ta 10 x C min.
348	.08	2.00	.045	.030	1.00	17.00/19.00	9.00/13.00	Cb-Ta 10 x C min Ta 0.10% max Co 0.20% max.
				Martensitic steels				
414	.15	1.00	.040	.030	1.00	11.50/13.50	1.25/ 2.50	
431	.20	1.00	.040	.030	1.00	15.00/17.00	1.25/ 2.50	
ACI type				Cast steels				
CA-15	.15	1.00	.04	.04	1.50	11.5 /14	[b] 1	Mo 0.5% max[d].
CA-40	.20/.40	1.00	.04	.04	1.50	11.5 /14	[b] 1	Mo 0.5% max[d].
CB-30	.30	1.00	.04	.04	1.50	18 /22	[b] 2	
CB-7 Cu	.07	1.00	.04	.04	1.00	15.5 /17	3.6 / 4.6	Cu 2.3/3.3%.
CC-50	.50	1.00	.04	.04	1.50	26 /30	[b] 4	
CD-4 M Cu	.040	1.00	.04	.04	1.00	25 /27	4.75/ 6.00	Mo 1.75/2.25; Cu 2.75/3.25.
CE-30	.30	1.50	.04	.04	2.00	26 /30	8 /11	
CF-3	.03	1.50	.04	.04	2.00	17 /21	8 /12	
CF-8	.08	1.50	.04	.04	2.00	18 /21	8 /11	
CF-20	.20	1.50	.04	.04	2.00	18 /21	8 /11	
CF-3 M	.03	1.50	.04	.04	1.50	17 /21	9 /13	Mo 2.2/3.0.
CF-8 M	.08	1.50	.04	.04	2.00	18 /21	9 /12	Mo 2.0/3.0.
CF-8 C	.08	1.50	.04	.04	2.00	18 /21	9 /12	Cb 8 x C min, 1.0% max.
CF-16 F	.16	1.50	.17	.04	2.00	18 /21	9 /12	Mo 1.5% max, Se 0.30/0.35%.
CG-8 M	.08	1.50	.04	.04	1.50	18 /21	9 /13	Mo 3.0/4.0%.
CH-20	.20	1.50	.04	.04	2.00	22 /26	12 /15	
CK-20	.20	1.50	.04	.04	2.00	23 /27	19 /22	
CN-7 M	.07	1.50	.04	.04	(c)	18 /22	21 /31	Mo-Cu[c].
CY-40	.40	1.50	.015	.015	3.00	14 /17	Bal	Fe 11.0% max.
CZ-100	1.00	1.50	.015	.015	2.00	------------	[a] 95	Fe 1.50% max.
M-35	.35	1.50	.015	.015	2.00	------------	Bal	Cu 26/33%, Fe 3.50% max.
HA	.20	.35/ .65	.04	.04	1.00	8 /10	------------	Mo 0.90/1.20%.
HC	.50	1.00	.04	.04	2.00	26 /30	[b] 4	Mo 0.5% max[d].
HD	.50	1.50	.04	.04	2.00	26 /30	4 / 7	Mo 0.5% max[d].
HE	.20/.50	2.00	.04	.04	2.00	26 /30	8 /11	Mo 0.5% max[d].
HF	.20/.40	2.00	.04	.04	2.00	19 /23	9 /12	Mo 0.5% max[d].
HH	.20/.50	2.00	.04	.04	2.00	24 /28	11 /14	Mo 0.5% max[d]; N 0.2% max.
HI	.20/.50	2.00	.04	.04	2.00	26 /30	14 /18	Mo 0.5% max[d].
HK	.20/.60	2.00	.04	.04	2.00	24 /28	18 /22	Mo 0.5% max[d].
HL	.20/.60	2.00	.04	.04	2.00	28 /32	18 /22	Mo 0.5% max[d].
HN	.20/.50	2.00	.04	.04	2.00	19 /23	23 /27	Mo 0.5% max[d].
HT	.35/.75	2.00	.04	.04	2.50	13 /17	33 /37	Mo 0.5% max[d].
HU	.35/.75	2.00	.04	.04	2.50	17 /21	37 /41	Mo 0.5% max[d].
HW	.35/.75	2.00	.04	.04	2.50	10 /14	58 /62	Mo 0.5% max[d].
HX	.35/.75	2.00	.04	.04	2.50	15 /19	64 /68	Mo 0.5% max[d].

[a] Minimum. [b] Maximum. [c] There are several proprietary alloy compositions falling within the stated chromium and nickel ranges, and containing varying amounts of silicon, molybdenum, and copper. [d] Molybdenum not intentionally added.

For the cast steels, designations with the initial letter "C" indicate alloys generally used to resist corrosive attack at temperatures less than 1200 °F. Designations with the initial letter "H" indicate alloys generally used under conditions where the metal temperature is in excess of 1200 °F. The second letter represents the nominal chromium-nickel type, the nickel increasing in amount from "A" to "Z". Numerals following the letters indicate the maximum carbon content of the corrosion-resistant alloys.

series of stainless steels. Since the main function of nickel in the 300 series steels is to form austenite at high temperatures, retain it at ambient temperatures, and to retard its transformation during cold working, and since nitrogen is effective in forming austenite at high temperatures and manganese serves to retain austenite at room temperature and retard its transformation during cold-work, substitute stainless steels containing nitrogen and manganese (the 200 series) were developed. Experience with these steels was described by Spencer [837] and Paret [838].

As the chromium-nickel stainless steels are austenitic at room temperature, they cannot be hardened by heat treatment. However, they can be hardened by cold work. Part of this strengthening results from the cold work itself and some from the transformation of the austenite. The degree to which austenite can be decomposed by cold work is largely dependent on its chemical composition. Both the percentages of the alloying elements and the ratios in which they are present have an important influence on the response to cold working. Elements tending to stabilize austenite and thereby decrease the work-hardening rate differ in their relative effect. As the nickel content is increased up to the limit permitted by the specification for a given stainless steel, the steel becomes more stable and shows a lower rate of strengthening by cold work. The effect of chromium depends on the nickel and chromium content. With nickel contents of 9 to 10 percent or greater, increasing the chromium content increases the rate of work hardening. On the other hand, if the nickel content is below 7 percent, the rate of work hardening decreases as the chromium content is increased from 17 to 20 percent. Depending on the amount of cold work, the tensile strength of austenitic stainless steels varies from about 80,000 psi for fully annealed to as high as 300,000 psi for severely work-hardened steel; the highest strengths can be secured only with small cross sections.

Chromium itself causes a significant decrease in the thermal conductivity of steel and this characteristic of the straight chromium martensitic or ferritic steels is accentuated in the austenitic chromium-nickel steels; in addition, the coefficient of thermal expansion of the austenitic steels is considerably higher than that of the martensitic or ferritic steels. Inasmuch as these steels are austenitic, they are also nonmagnetic. However, many of the compositions are somewhat marginal so that partial transformation of the austenite may occur during cold working or exposure to subzero temperatures; this tendency may be counteracted by increasing nickel, manganese, or carbon, or by decreasing chromium or molybdenum.

The austenitic stainless steels can be hot worked readily, although more power is required than for unalloyed steels. In some of the highly alloyed stainless steels the hot-working properties are improved by small amounts of rare earth metals of the cerium group [839] or of boron [840].

Other common characteristics are high resistance to shock, good weldability, and better strength and resistance to scaling at high temperatures and better corrosion resistance than the martensitic or ferritic stainless steels. They are somewhat difficult to machine unless they contain sulfur or selenium (types 303 and 303Se). When heated in the temperature range of about 800 to 1400 °F, they are susceptible to carbide precipitation and consequent intergranular corrosion unless they have been stabilized by additions of titanium or columbium (types 321 and 347). Metallographic etching methods and reagents for the detection of austenite, ferrite, sigma phase, and carbides were reviewed by Braumann and Pier [841]. Commercial procedures for cleaning, grinding, pickling, descaling, polishing, buffing, plating, coloring, etc., were discussed by DuMond [842].

The physical and mechanical properties of the wrought stainless steels are of interest for their engineering applications in corrosive environments. The literature on this subject is extremely voluminous.

Considerable information from various sources on the physical and mechanical properties of the austenitic stainless steels has been summarized in publications of The International Nickel Company, Inc.[843,844,845]. The effect of temperature on some physical properties of selected steels is shown in figures 95 to 99, inclusive.

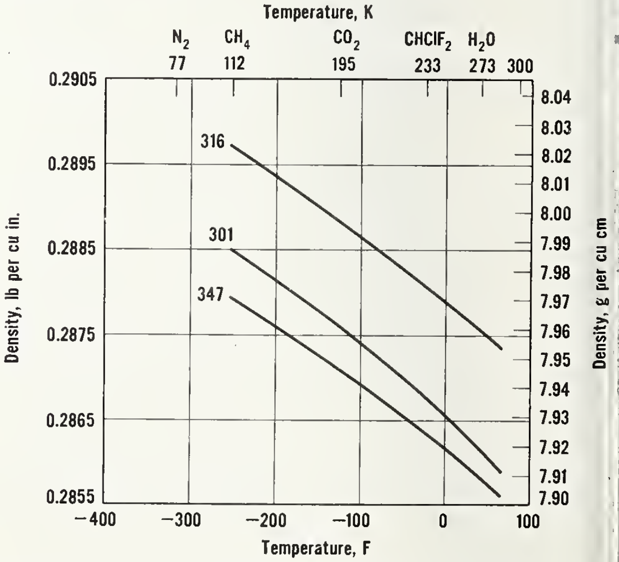

FIGURE 95. *Effect of temperatures on the density of some stainless steels [844].*

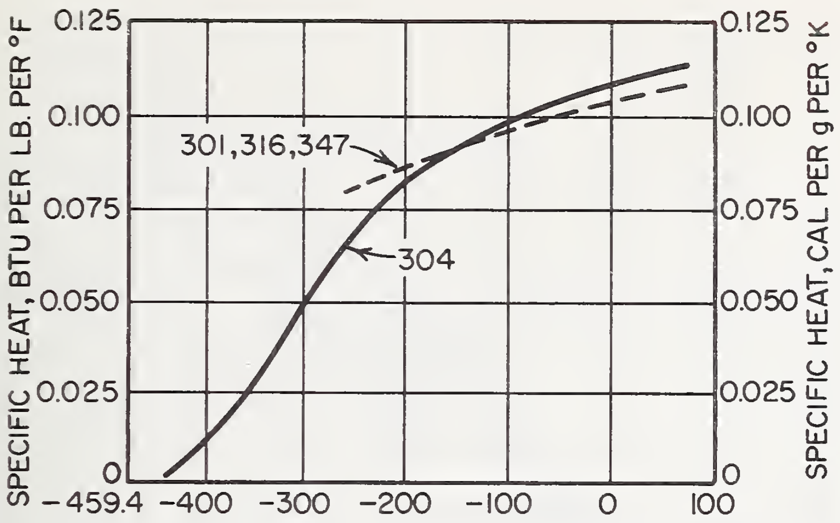

Figure 96. *Effect of temperature on the specific heat of some stainless steels [844].*

The austenitic stainless steels find many uses because of their nonmagnetic characteristics. The effect of temperature on the permeability of selected steels is shown in figure 100. An interesting use of stainless steels is for standards of mass. Necessary qualities were specified density and low magnetic permeability. Steels have been developed for densities of 8.4 g/cm³ [846] and 8.0 g/cm³ [847], containing 32 and 25 percent nickel, respectively.

As with other metals, the strength of the austenitic stainless steels increases at subzero temperatures. Because of its austenitic structure, however, ductility is not greatly affected; neither is toughness. It is for this reason that these steels are such favorites for low-temperature use [848]. The effect of low temperature on the tensile and impact properties of a type 304 stainless steel is shown in figure 101. The mechanical properties of many materials have been surveyed in two monographs by the National Bureau of Standards [319, 849]. Watson and Christian reported on the low-temperature properties of cold rolled stainless steel sheet [850].

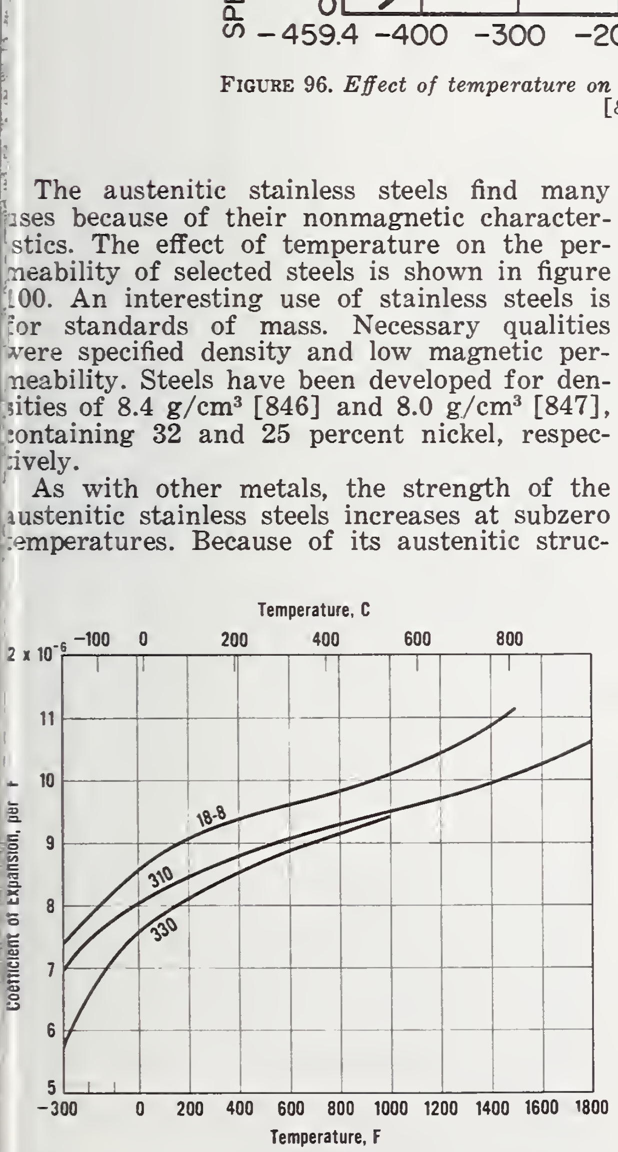

Figure 97. *Effect of temperature on the coefficient of expansion of some stainless steels [843].*

At elevated temperatures the strength of the austenitic stainless steels falls off. Typical properties of some are shown in figures 102, 103, and 104. Many of these data were taken from the work of Simmons and Cross [851]. The strength-rupture values of the various steels tend to merge at about 1200 °F. Freeman and Voorhees' summary [852] of relaxation properties showed that the replacement of initial elastic strain by the plastic strain of creep occurs at approximately this temperature, with resultant reduction in stress level. Improvement in the properties from cold working is still evident up to about 800 °F, provided that the degree of cold working and the conditions of exposure are not conducive to extensive recrystallization [853].

Recent work on the elevated temperature properties of the austenitic stainless steels was presented at the 1963 Joint International Conference on Creep [854,855,856,857]. An exhaustive series of stress-rupture tests was made on a type 304 stainless steel to evaluate its potential as a so-called "standard" stress-rupture specimen [858].

Pfeil and Harries [859] studied the effect of neutron irradiation on austenitic stainless

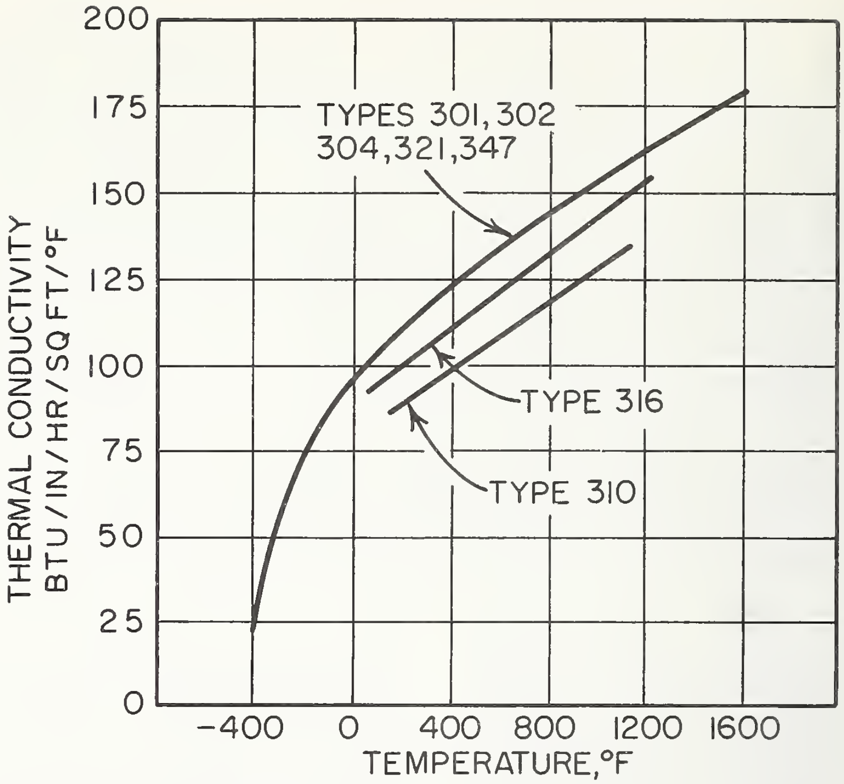

FIGURE 98. *Effect of temperature on the thermal conductivity of some stainless steels [843].*

steels and reported an adverse effect on the tensile ductility at test temperatures above 600 °C (1110 °F) and a detrimental effect on the stress-rupture properties. Irvin, Bement, and Hoagland [860] also reported a marked reduction in ductility with increasing exposure and test temperature. Confirmatory evidence of the damaging effect of neutron irradiation on the ductility has been given by Martin and Weir [861] and by Venard and Weir [862].

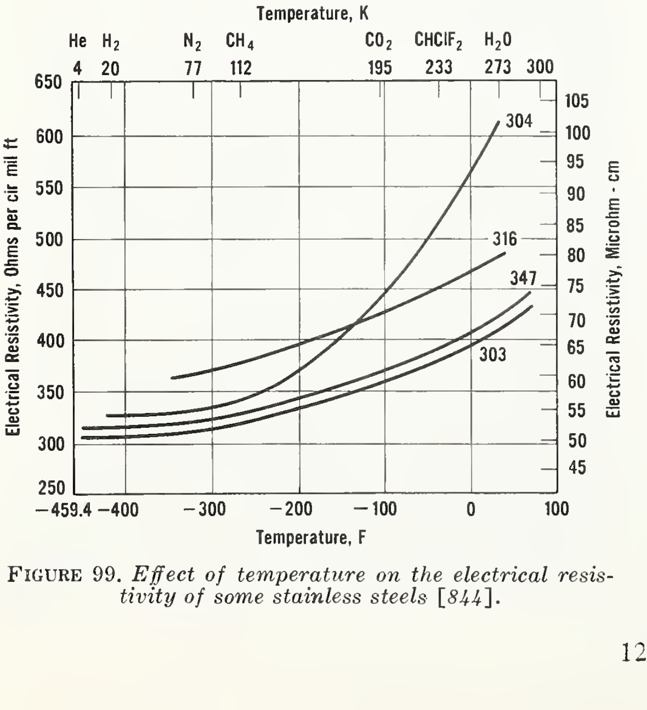

FIGURE 99. *Effect of temperature on the electrical resistivity of some stainless steels [844].*

The tendency of some austenitic stainless steels to become embrittled at high temperatures, through the formation of the intermetallic sigma phase [863,864,865], is detrimental to some of the properties. However, heating sigma-embrittled steels to about 1800 °F eliminates sigma and restores the original toughness. Aborn [839] reported that sigma rarely occurs in plain 18–8 stainless steel. It would be expected that increase in chromium increases the susceptibility to sigma formation, especially if ferrite is present. This was found to be so by Rosenberg and Irish [866], who found sigma to be a stable phase in high-purity 18 percent Cr-10 percent Ni alloys. Sigma formation in commercial nickel-chromium-iron alloys was summarized by Foley and Krivobok [867].

As a group, the modulus of elasticity in tension or compression of the annealed wrought stainless steels is about 29,000,000 psi. Poisson's ratio is about 0.30.

The resistance to corrosion of stainless steels with chromium contents in excess of about 11-12 percent is due to the presence of

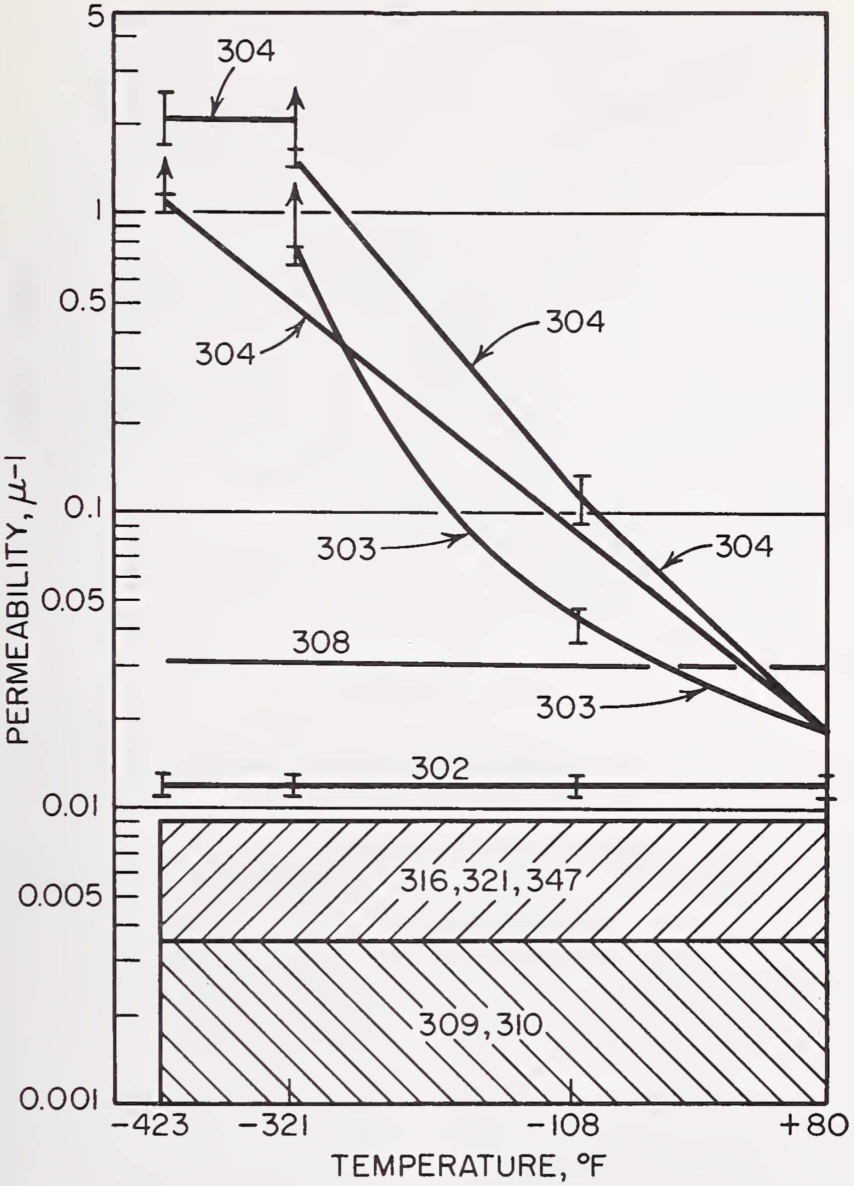

FIGURE 100. *Effect of temperature on the permeability of some annealed stainless steels [844].*

passive oxide film that is richer in chromium han the underlying metal [839]. Protection fforded by this film is complete at room and oderately elevated temperatures, but the film creases in thickness as the temperature creases and becomes a scale at very high mperatures. Eiselstein and Skinner [868] eported that scaling of stainless steels did ot become pronounced until temperatures of 800 °F or higher were reached. Paret [838] eported that the scaling resistance of the high-anganese types 201 and 202 was equivalent that of types 301 and 302 up to about 550 °F, but that above that temperature the high-manganese steels scaled faster. Keith, Siebert, and Sinnot [869] reported that intergranular oxides formed by 100 hours exposure at 1900 °F had the same composition as the external scale, both being high in chromium and manganese, and low in nickel as compared with the underlying metal.

In some of the early uses of austenitic stainless steel at elevated temperatures, it was observed that they became embrittled and subject to intergranular corrosion. This intergranular embrittlement was the result of the precipitation of chromium carbides at the grain boundaries of steels heated in the range

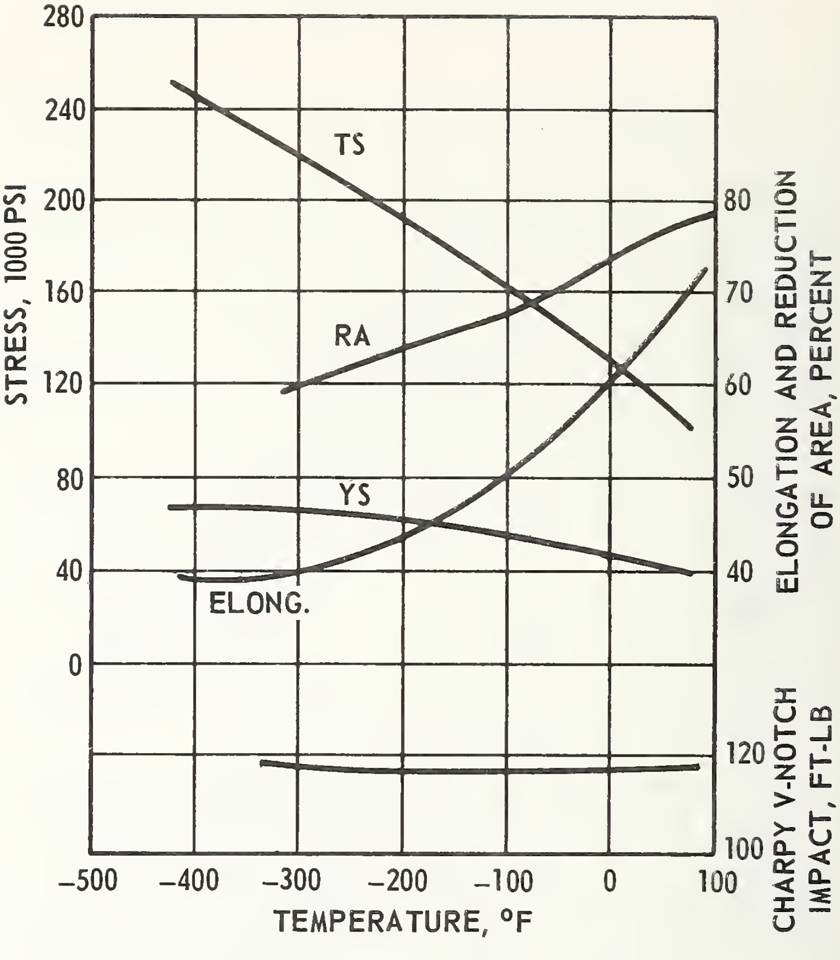

Figure 101. *Effect of low temperature on the tensile and impact properties of type 302 stainless steel* [*844*].

of 800 to 1400 °F and became evident when such steel was subsequently subjected to acidic environments. This problem was attacked in two ways: (1) by reduction in the amount of carbon available to form carbides, i.e., by the development of low-carbon steels such as 304L and 316L, and (2) by the addition of titanium or columbium (types 321 and 347) that formed their own stable carbides and thus prevented the formation of chromium carbides. Testing procedure to determine the susceptibility of austenitic stainless steel to intergranular attack, using acidified copper sulfate solution, is covered by ASTM Specification A393–63. The susceptibility to intergranular embrittlement was explored in detail by Rosenberg and Darr [870], by Binder, Brown, and Franks [871], by Tupholme and Bouchier [872], and by Schwaab, Schwenk, and Ternes [873].

The resistance of austenitic stainless steel to corrosion in a great many media has resulted in extensive uses in the chemical, transportation, and petroleum industries; in food processing and dairy equipment; in hospital, surgical, and pharmaceutical equipment; in the fatty acid industry; in the production of atomic power; in the paper making and textile industries; in domestic uses, and many others. The resistance to a particular corrosive medium may vary with the concentration of the corrodent; the presence of impurities, including oxygen; the temperature, composition, prior history, and surface condition of the steel; contact with dissimilar metals; and with other factors. Stainless steel has been studied for use in the human body; Fischer and Zitter [874] suggested the use of slightly modified type 316 for implants.

The low-carbon stainless steels generally show improved resistance to corrosion, as do the steels with increased alloy content. The addition of molybdenum (types 316 and 317) improves the resistance of 18 : 8 to many media, including sulfurous, sulfuric, phosphoric, formic, and various hot organic acids [875]. The 18 : 8 steels have good resistance to nitric

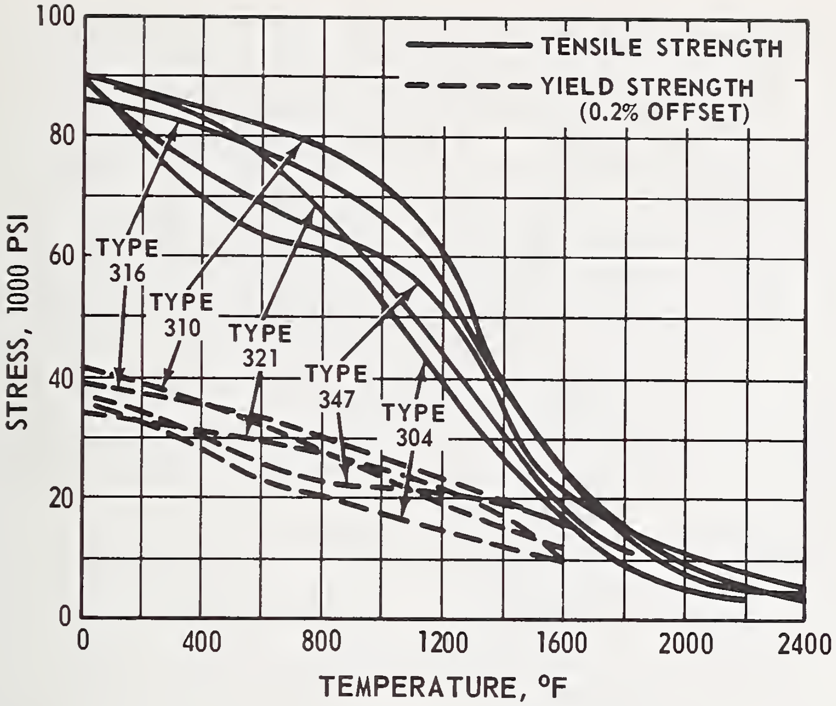

FIGURE 102. *Effect of temperature on the short-time tensile properties of several annealed austenitic stainless steels* [*845*].

cid, but have no resistance to hydrochloric. Tsukamoto [876] described a special stainess steel, designated NTK–M7, that has good esistance to hydrochloric acid; its composiion is carbon 0.06 percent max, manganese .0 percent max, silicon 1.0 percent max, chronium 9-11 percent, nickel 16-18 percent, moybdenum 6-8 percent. Types 316 and 317 are esistant to pitting corrosion and give useful ervice at room temperature in sulfuric acid f concentrations lower than 20 percent and igher than 85 percent. Between these limits hey are subject to rapid attack. The Carpener Steel Company developed a steel of comosition carbon 0.07 percent max, manganese .75 percent, silicon 1 percent, chromium 20 ercent, nickel 29 percent, molybdenum 2 perent min, copper 3 percent min, that is resistnt to sulfuric acid; recent work by Class and Grafen [877] indicates that this steel with 1 ercent columbium added (Carpenter Stainess 20 Cb) exhibits satisfactory resistance to ulfuric acid.

A comprehensive review of the effect of lloying elements upon the corrosion resistnce of stainless steels was published by Class 878]. A review of the literature relating to netallurgical factors involved in welding the 8–8 steels was prepared by Ball [879].

Many of the stainless steels are subject to tress-corrosion cracking and this has been he subject of considerable research. A compilation of case histories was published in 1960 [880] and many recent papers are of interest [881,882,883,884,885]. Hochmann and Bourrat [886] reported that the addition of 3.3 to 4.1 percent silicon significantly increased the resistance of 18:10 to stress corrosion. Snowden [887] noted that the more stable austenite resulting from increased nickel content has greater resistance to stress-corrosion cracking, and Eckel [888] reported that the nucleation of stress-corrosion cracking was delayed by an increase in nickel content.

According to Truman and Kirby [889], stress-corrosion cracking of the stainless steels is not the hazard it might seem to be from the number of papers that have been published. They indicate that it is likely to occur only under certain specific conditions, the limits of which are fairly well defined. Fairman [890] reported that stress-corrosion cracking may be prevented by suitable cathodic protection. The effect of irradiation on the stress-corrosion cracking of type 316 and a 20 percent Cr-25 percent Ni-1 percent Nb stainless steel developed specifically for reactor applications was studied by Davies, Landsman, and Seddon [891]. They found that the susceptibility to stress-corrosion cracking of the former steel was greatly increased, whereas the latter steel proved to be immune both in the unirradiated and in the irradiated conditions.

Considerable data on the corrosion resist-

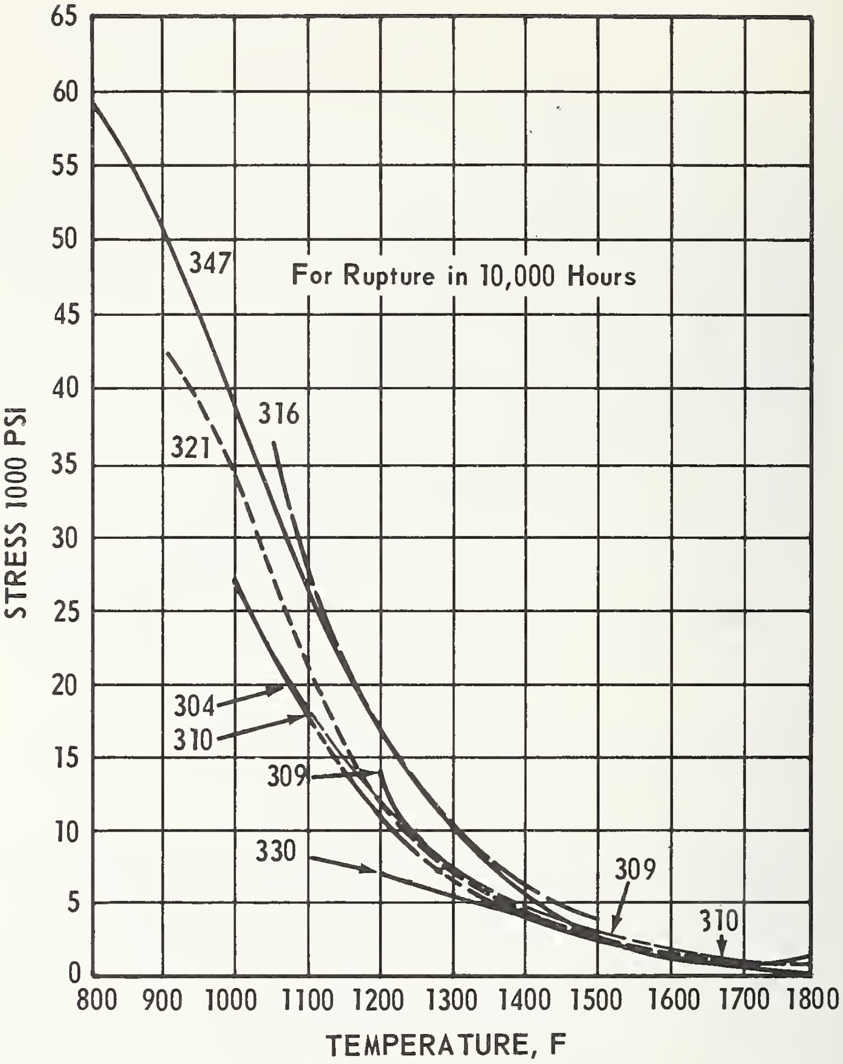

Figure 103. *Stress-rupture curves for several annealed austenitic stainless steels [845].*

ance of the austenitic stainless steels have been summarized by The International Nickel Company, Inc.[892,893,894,895].

Stainless steel is expensive and for many applications the use of carbon or low-alloy steels, clad with stainless, represents a successful compromise between cost and corrosion resistance. Stainless clad steels are described by Ma [896].

The cast stainless steels, as indicated in table 68, fall into two broad groups—the corrosion-resistant and the heat-resistant. Many of the compositions correspond generally to those of the wrought steels. Resistance to both corrosion and heat increases as the total alloy increases; maximum resistance is obtained with castings extremely high in nickel.

Detailed and specific information on the physical constants and mechanical properties, as well as heat treatment and fabricating procedures and design consideration, are give for all of the cast steels in the form of dat sheets issued by the Alloy Casting Institut [897]. Criteria for the selection of the heat resisting grades, as well as their short- an long-time strength characteristics at temperatures up to 1880 °F, are given by Schoeffe [898,899]. The effect of low temperatures o the mechanical properties of cast stainless stee has been studied by Mayer and Balajva [900 and by Hall [901], both of whom reported tha the cast steels retained useful ductility an toughness down to the lowest test temperatur (−430 °F for Hall).

d. Precipitation-Hardening Stainless Steels

The precipitation hardenable stainless steel are a series of iron-chromium-nickel alloys t

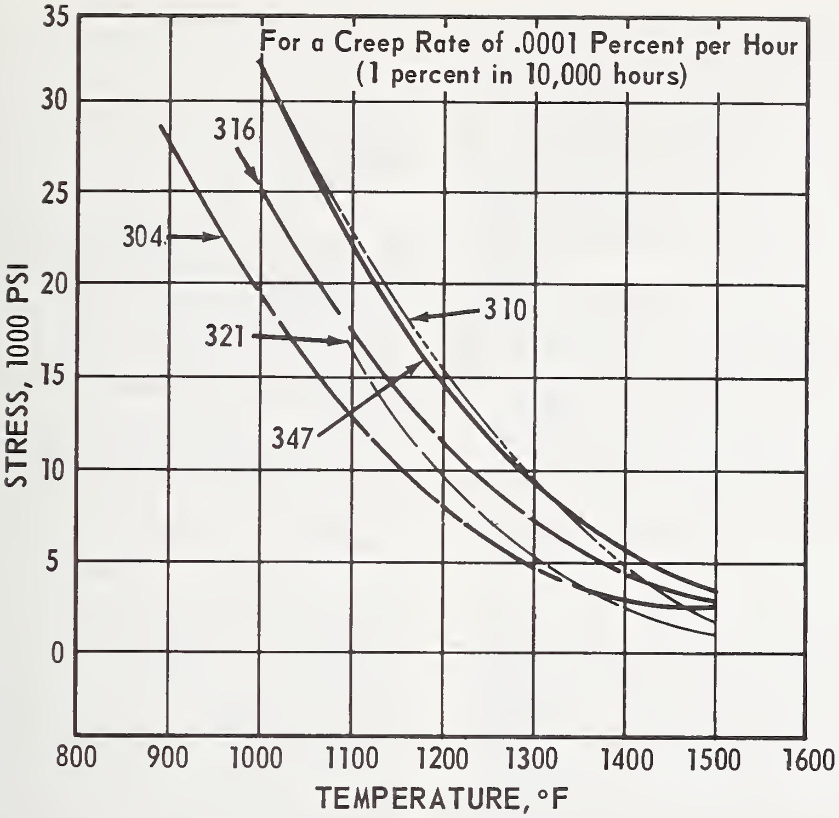

FIGURE 104. *Creep rate curves for several annealed austenitic stainless steels [845].*

which additional elements have been added to provide hardening by precipitation reactions. The steels are divided into three broad groups: martensitic, semi-austenitic, and austenitic steels. Nominal compositions are given in table 69. Development work in this field has been extremely active and there are literally dozens of other precipitation-hardening stainless steels.

The compositions of the martensitic steels are so adjusted that the M_s transformation is above ambient. Actually, both stainless W and

TABLE 69. *Nominal compositions of some of the precipitation hardening stainless steels [902]*

Designation	Producer	Chemical composition, %													
		C	Mn	P	S	Si	Cr	Ni	Cu	Mo	Ti	Al	Cb+Ta	N	V
Martensitic steels															
Stainless W	U.S. Steel	0.07	0.50	0.010	0.010	0.60	17.0	7.0	------	------	0.70	0.20	------	------	------
17-4 PH	Armco	.04	.25	.020	.010	.60	16.0	4.0	3.2	------	------	------	0.25	------	------
Semiaustenitic steels															
AM-350	Allegheny Ludlum	.10	.80	.020	.010	.25	16.5	4.3	------	2.75	------	------	------	0.10	------
AM-355	Allegheny Ludlum	.13	.95	.020	.010	.25	15.5	4.3	------	2.75	------	------	------	.10	------
17-7 PH	Armco	.07	.60	.020	.010	.40	17.0	7.0	------	------	------	1.15	------	------	------
PH 15-7 Mo	Armco	.07	.60	.020	.010	.40	15.0	7.0	------	2.20	------	1.15	------	------	------
Austenitic steels															
HNM	Crucible	.30	3.50	.25	.025	.50	18.5	9.5	------	------	------	------	------	------	------
17-10 P	Armco	.12	.75	.25	.030	.60	17.0	10.0	------	------	------	------	------	------	------
17-14 Cu Mo	Armco	.12	.75	.020	.010	.50	16.0	14.0	3.0	2.5	.25	------	.50	------	------
A-286	Allegheny Ludlum	.06	1.50	.020	.020	.70	15.0	26.0	------	1.2	1.8	.020	------	------	0.30

17–4 PH are severely unbalanced AISI 301 types. The austenite in both steels is so unstable that it transforms to martensite at about 200 to 300 °F upon cooling from the solution annealing temperature (about 1900 °F). In this condition it has relatively high strength and low ductility. A simple aging treatment at about 900 to 1000 °F promotes the precipitation of intermetallic compounds and causes full hardening.

The semiaustenitic stainless steels are essentially similar to those in the martensitic group except that the composition is so adjusted that the M_s temperature is depressed. Solution annealing below 1700 °F results in transformation above room temperature; annealing at higher temperatures depresses the M_s transformation to subzero temperatures. As annealed, these steels are soft and ductile and therefore are amenable to fabricating operations.

These characteristics permit the use of a variety of heat treatments. The steels can be transformed by conditioning the austenite at about 1700 °F, followed by refrigeration at −100 °F, or by conditioning at 1300 to 1400 °F followed by cooling to about 60 °F. This conditioning treatment allows some of the carbon originally in solution in the austenite to precipitate as chromium carbides. The depletion of chromium and carbon from the austenite reduces its stability, i.e., it raises the M_s temperature. Upon cooling to room temperature or below, the austenite-to-martensite transformation reaches completion. The transformation can also be effected by severely cold working the steel as annealed at 1950 °F. Full hardening is then effected by a subsequent aging treatment at 900 to 1050 °F.

The compositions of the austenitic steels are adjusted so as to assure retention of the austenitic structure under all conditions of heat treatment. These steels are solution annealed at temperatures above 2000 °F. As so annealed, the steels are soft and ductile and therefore amenable to fabricating operations. Complete hardening is effected by aging at 1300 to 1450 °F.

The physical metallurgy of the precipitation-hardening stainless steels has been discussed by Ludwigson and Hall [903], by Dulis [904], and by Lena [904a]. Data on physical and mechanical properties are given by Roach and Hall [905], Brisbane [906], Roberts, Roach, and Hall [907], Holmberg [908], and International Nickel [902].

The strengths and ductilities of the precipitation-hardening stainless steels vary over a considerable range, depending on treatment. Maximum strengths are approximately as follows [902]:

	Tensile	Yield
	psi	*psi*
Martensitic steels	210,000	200,000
Semi-austenitic steels	265,000	260,000
Austenitic steels	150,000	100,000

One of the semiaustenitic steels (AM–355) can be treated to as high as 350,000 psi tensile and 335,000 psi yield by very severe cold working prior to aging [903]. As with other materials, the higher strengths in all these steels usually are obtained at some sacrifice in ductility.

The strength properties increase as the temperature decreases [319,849,902]. Ductility and toughness decrease, but Campbell and Rice [909] note that many of these steels have reasonably good ductility and toughness down to −108 °F (the temperature of CO_2). Below this, ductility and toughness decrease rapidly.

An important attribute of the precipitation hardenable stainless steels is retention of strength at moderately elevated temperatures (600 to 1000 °F). Since this temperature range extends into the precipitation hardening range, additional aging can occur in service. This may or may not be beneficial. In several of the grades, long time aging can impair the usefulness of the alloy for service in the range 600 to 800 °F because of embrittlement.

These steels also have excellent stress-rupture and creep properties at moderately elevated temperatures [672]. At higher temperatures (up to 1300 °F), the austenitic precipitation-hardening stainless steels retain their strength properties to a greater degree than the other types of precipitation-hardening steels. Data on the mechanical properties of the precipitation-hardening stainless steels are contained in the booklet of International Nickel [902]. Additional data have been reported by Pearl, Kappelt, and King [910].

The corrosion resistance of these steels is inferior to that of the 300 series (the 18–8 steels), but is still markedly superior to that of the 400 series (the straight chromium steels).

Precipitation-hardening stainless steels may be used in the cast condition, although compositions may vary somewhat. Thus, CB–7Cu (table 68) is somewhat similar to 17–4 PH (table 69). Data on the mechanical properties of castings of this steel are given by Ekey and Black [911], and of CD–4M Cu by Schoefer [912,913]. Four precipitation-hardening stainless steels for casting were described by Mott [914].

The semiaustenitic precipitation hardening stainless steel designated PH 14–8 Mo [915] is a modification of PH 15–7 Mo. It gives better toughness at high strength levels and also possesses increased stability at high temperatures. Its composition is carbon 0.05 percent max, manganese and silicon 1.0 percent max, phosphorus 0.015 percent max, sulfur 0.010 percent max, chromium 13.5 to 15.5 percent, nickel 7.5 to 9.5 percent, molybdenum 2.0 to 3.0 percent, aluminum 0.75 to 1.5 percent.

The weldability of the precipitation hardening stainless steels varies with composition, but all of them except those high in phosphorus can be readily welded by conventional methods [916,917].

Two stainless maraging steels designated as AM 362 and AM 363 combine the mechanical properties of nickel maraging steels with the corrosion resistance of stainless steels [918]. These two steels are readily weldable.

4.5. Thermal Expansion and Constant Modulus Alloys

The fact that iron-nickel alloys containing about 36 percent of nickel have extremely low coefficients of thermal expansion was observed by Guillaume [919] in 1897 in a search for less expensive materials than the platinum-iridium alloy that was then the standard for metrology. Additional data were published subsequently [920]. Because the 36 percent alloy had such a low coefficient of expansion at room temperature that the linear dimensions were almost invariable over ordinary changes in temperature, Guillaume named it Invar. In a study of the elastic properties of this alloy, Guillaume found that the addition of 12 percent of chromium produced an alloy that had an invariable modulus of elasticity over a considerable range of temperature, as well as reasonably low thermal expansion. This alloy he named Elinvar. It is now known that these low coefficients of expansion represent an approximate balance between expansion from thermal agitation and contraction from magnetostriction.

Subsequent investigations here and abroad confirmed and extended Guillaume's original observations. Owen, Yates, and Sully [120] showed that increasing the temperature above room temperature increased the minimum coefficient of expansion and shifted it toward that of the higher nickel contents. Figure 105 shows their data for alpha and for gamma alloys. Compositions between about 18 and 28 percent of nickel are mixtures of alpha and gamma. Atomic precentages of nickel in iron-nickel alloys are approximately the same as weight percentages; for instance, 36 atomic percent is 35 weight percent.

Scott [921] showed that, as the nickel content is increased above 36 percent, the coefficients of expansion increase but are retained to higher temperatures. This is important where a low-expansion material is needed at temperatures in excess of that at which the 36 percent alloy is effective. Figure 106, according to Hunter [922], shows the effect of temperature on the thermal expansion of alloys containing 36 to 52 percent of nickel, in comparison with a plain carbon steel.

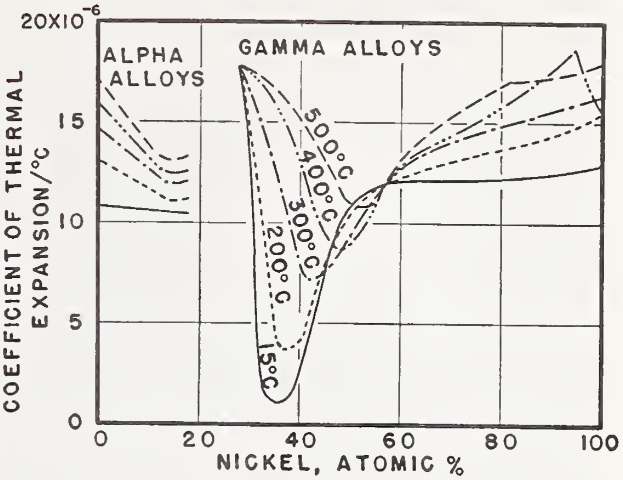

FIGURE 105. *Coefficient of thermal expansion of iron-nickel alloys at temperatures up to 500 °C [120].*

The 36 percent nickel alloy Invar (also marketed under the designation Nilvar) is the most widely used alloy for applications requiring low thermal expansivity up to about 400 °F. This alloy finds extensive use as the low expansion side of thermostatic bimetals, measuring devices, electronic equipment, and other applications requiring extreme dimensional stability over temperature ranges up to 400 °F. Super-Invar (also sold under the designation Super-Nilvar) has near zero expansivity over the Invar temperature range. It contains 31 percent nickel plus cobalt.

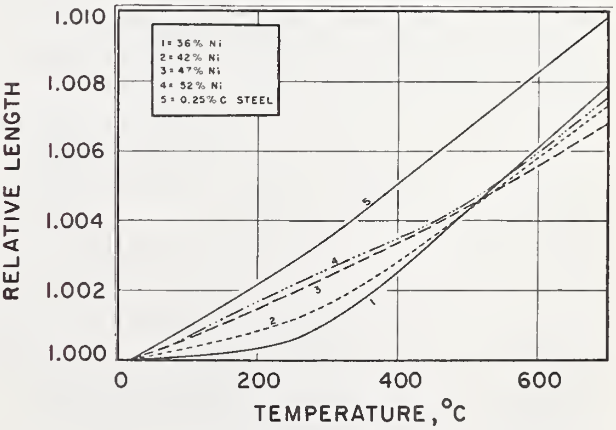

FIGURE 106. *Thermal expansion of iron-nickel alloys [922].*

TABLE 70. *Approximate physical and mechanical properties of three low-expansion alloys in the annealed condition [923]*

		36% Nickel	42% Nickel	49% Nickel
Average coefficient of expansion per °F between				
−200 and 0 °F		1.1×10⁻⁶	3.4×10⁻⁶	5.4×10⁻⁶
0 and 200 °F		.7	3.2	5.6
200 and 400 °F		1.5	3.0	5.6
400 and 600 °F		6.4	3.2	5.6
600 and 800 °F		8.6	5.5	5.6
800 and 1000 °F		9.5	8.6	7.3
Curie temperature	°F	530	755	965
Tensile strength	psi	71,000	68,000	77,000
Yield point	psi	40,000	35,000	33,000
Elongation in 2 in	%	43	45	45
Reduction of area	%	75	75	75
Brinell hardness		132	138	144
Modulus of elasticity	psi	21,000,000	22,000,000	24,000,000
Temperature coefficient of the modulus of elasticity	per °F	+270×10⁻⁶	+150×10⁻⁶	−130×10⁻⁶
Modulus of rigidity	psi	8,100,000	8,500,000	9,300,000
Temperature coefficient of the modulus of rigidity	per °F	+300×10⁻⁶	+50×10⁻⁶	−50×10⁻⁶
Poisson's ratio		0.290	0.290	0.290
Electrical resistance:				
ohms/mil-ft		490	420	290
microhm-cm		81	70	48
Temperature coefficient of electrical resistance	per °F	0.67×10⁻³	0.66×10⁻³	1.66×10⁻³
Specific heat between 77–212 °F	Btu/lb/°F or cal/g/°C	0.123	0.121	0.120
Thermal conductivity between 68–212 °F	Btu/hr/ft²/in/°F	93	106	124
	cal/sec/cm²/cm/°C	.0323	.0366	.0428
Density:				
lb/ft³		508	507	514
g/cm³		8.13	8.12	8.23

From 400 to 650 °F, the 42 percent nickel alloy is used, and from 650 to 1000 °F, the alloys containing 47 to 50 percent of nickel are used. These alloys are generally designated by their nickel content, such as "52 Alloy." They find extensive use as the low expansion side of thermostatic bimetals operating at temperatures above the Invar range, as glass sealing alloys suitable for use in conjunction with many soft glasses, and other applications requiring low but not minimum expansivity. Practical experience has shown that these three compositions will satisfy most requirements. The approximate physical and mechanical properties of these three alloys are shown in table 70. The physical and mechanical properties of the Invar type alloys are discussed in detail by McCain and Maringer [924].

TABLE 71. *Effect of heat treatment and impurities on the thermal expansion of Invar [925]*

Compositon, percent				Coefficient of expansion, millionths per °C from −40 to +40 °C		
C	Mn	Si	Ni	Annealed [a]	Water quenched [b]	Quenched and stabilized [c]
Commercial Invar						
0.07	0.44	0.24	36.8	1.9	0.9	1.1
Experimental alloys						
0.02	0.09	0.01	36.0	0.8	0.1	0.0
.10	.12	.08	36.1	1.0	.1	.0
.15	.08	.17	36.0	1.5	.1	.0
.25	.05	.20	36.6	1.4	.1	1.0

[a] Furnace cooled after 30 min at 830 ° C.
[b] Water quenched after 30 min at 830 ° C.
[c] Treatment b, then stabilized by reheating at 95 °C for 48 hr, followed by air cooling.

The linear expansion of Invar, and particularly the minimum expansion values, are affected by the presence of impurities and by additions of alloying elements. The expansivity of fully annealed Invar is appreciably higher than that of quenched or cold-worked material. These extremely low expansion values of quenched or cold-worked material are unstable with respect to time and temperature, but the alloys can be stabilized by low-temperature annealing. The effect of heat treatment and of minor changes in composition is shown by the data of Lement, Roberts, and Averbach [925] in table 71. The water-quenched high-purity alloys have coefficients of expansion close to that of fused quartz for the temperature range indicated. Additions of manganese, chromium, silicon, tungsten, or molybdenum tend to shift the area of minimum expansivity toward higher nickel contents, whereas copper and carbon have the reverse effect [94]. Some of the aging effects observed in Invars are attributed to the precipitation of carbon or carbides, others to intermetallic compounds. Cobalt lowers the coefficient of Invar at ordinary temperatures [921,926], and titanium raises the minimum value of the coefficient and shifts it toward that of the higher nickel contents [927].

A series of age-hardening alloys with a constant modulus of elasticity, each containing about 2.5 percent of titanium, was reported by Mudge and Talbot [927]. Three of these alloys are called Ni-Span-Lo with appropriate numbers to designate their nickel contents of 42, 45, and 52 percent. With proper cold working and heat treatment these alloys have tensile strengths approaching 200,000 psi. Other alloys reported by Mudge and Talbot were a relatively high expansion alloy, Ni-Span-C alloy 902, containing 8 to 9 percent of chromium, and a constant modulus alloy, Ni-Span-C that contains 42 percent of nickel and 5.5 percent of chromium. The constant modulus alloys generally contain 36 to 42 percent of nickel plus one or more of the following: Cr, W, Mo, Ti, Al. The use of constant modulus alloys as spring materials was reviewed by Carlson [928] as follows, with compositions as listed by Woldman [929]:

> "Elinvar—the first of the constant modulus materials and used for horological springs, weighing scales, tuning forks, bourdon tubes, and other applications requiring invariant elasticity with temperature variations. The original composition of 36% Ni, 12% Cr, balance iron was austenitic and hardenable only by cold work; modern Elinvar Extra contains 42% Ni, 5% Cr, 2.5% Ti, 0.5% Al, balance iron.
>
> "Ni-Span-C alloy 902—42 percent Ni, 5.5 percent Cr, 2.4 percent Ti, 0.6 percent Al, balance iron alloy developed by the International Nickel Company. Most popular of the constant modulus alloys. Usually formed in the 50% cold-worked condition and precipitation hardened at 900 °F for 8 hr, or at 1250 °F for 3 hr to produce a hardness of 40 to 44 R_c, permitting safe torsional loads of 60,000 to 80,000 psi. The alloy is ferromagnetic up to 400 °F and nonmagnetic at higher temperatures. Its thermal expansion at room temperature is 3.8 to 4 × 10^{-6} per °F.
>
> "Iso-Elastic—36% Ni, 8% Cr, 4% Mn-Si-V, 0.5% Mo, balance iron alloy developed by John Chatillon and Sons. Easier to fabricate than Ni-Span-C and popular for scales, dynamometers, and instruments. Used at 30 to 40 R_c to withstand torsional stresses of 40,000 to 60,000 psi.
>
> "Elgiloy—40% Co, 20% Cr, 15% Ni, 7% Mo, 15% Fe, 2% Mn, 0.05% Be alloy also called 8J alloy, Durapower, and Cobenium. Developed at Battelle Memorial Institute [930] for the Elgin Watch Company in cooperation with wire producers. The alloy is nonmagnetic. It is worked and precipitation hardened at 900 °F to produce a hardness of 48 to 50 R_c. It is used in Elgin watches and instruments for torsional stresses below 75,000 psi from subzero temperatures to about 1,000 °F.
>
> "Dynavar—Fe, Ni, Cr, Co, alloy developed by the Hamilton Watch Company. Nonmagnetic; precipitation hardened at 900 °F. Useful from subzero temperatures to about 1,000 °F."

Clark [931] patented an alloy with the desired composition of 42.2 percent Ni, 2.8 percent Ti, 6.5 percent Cr, remainder iron, that exhibits a substantially zero thermoelastic coefficient and low mechanical hysteresis in the age-hardened condition. Eiselstein and Bell [932] patented an age-hardenable iron-nickel-cobalt base alloy stated to have a constant thermoelastic coefficient over a wide range of temperature. The composition is 16 percent Ni min, 12.5 percent Co min, 0-6 percent Cb and/or 0-12 percent Ta, 0.5-1.5 percent Ti, 0-1 percent Si, 0-1 percent Mn, 0-1 percent Al, 0-0.2 percent C, 0–0.1 percent Ca, remainder (at least 31%) Fe.

Several of the iron-nickel and modified alloys are used for making glass-to-metal seals for electrical connections into vacuum tubes, laboratory apparatus, etc. For stress-free and vacuum-tight joints the expansion curves of the metal and glass must be close together, and any particular alloy cannot be used above its Curie temperature, where an inflection in the expansion occurs. The presence on the surface of some metallic oxide, produced during heating, probably is essential to the production of a good seal, and preoxidation of the metal frequently facilitates the sealing operation. Copper has been added to some of the alloys or used as a coating to facilitate the formation of a good seal. The alloy known as Dumet, which is 42 percent Ni (25% Cu clad) is used as leads to electric light bulbs and electronic tubes, and other glass sealing applications requiring high electrical conductivity.

The alloys of 42 percent Ni, 5.5 percent Cr, balance iron, known as Sylvania HC4, Sealmet HC4, Carpenter 426, are suitable for seals in many soft glasses. Alloys of 29 percent nickel plus 17 percent cobalt are suitable for sealing hard, heat resistant glasses. Fernico (28% Ni, 18% Co, 54% Fe) and Kovar (29% Ni, 17% Co, 0.3% Mn, balance Fe), are two of these alloys. Others are known as Therlo and Rodar. Grosvenor [664] reported that the 42-percent nickel irons were used with soft glasses, the 52 percent nickel iron and Kovar or Fernico with certain hard glasses, and cited data supplied by G. V. Luerssen to illustrate the close match in expansion of a 42-percent nickel alloy with soft glass, as shown in figure 107. For borosilicate

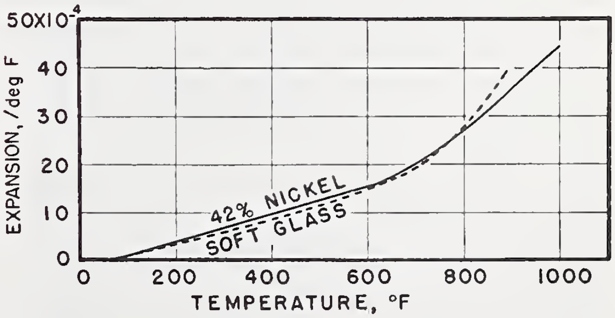

FIGURE 107. *Thermal expansion curves of 42 percent nickel-iron alloy and soft glass [664].*

TABLE 72. *Iron-nickel sealing alloys according to ASTM Specification F30–63T*

	Composition—percent										Average linear coefficient of thermal expansion cm/cm/°C × 10⁻⁶	Temperatur range, °C
	Ni	Mn	Si	C	Cr	Co	P	S	Al	Fe		
42 alloy	41	0.80	0.30	0.05	0.10	0.50	0.025	0.025	0.10	bal	4.0– 4.7 6.7– 7.4	30–30 30–45
46 alloy	46	.80	.30	.05	.10	.50	.025	.025	.10	bal	7.1– 7.8 8.2– 8.9	30–35 30–50
48 alloy	48	.80	.30	.05	.10	.50	.025	.025	.10	bal	8.2– 9.2 9.6–10.3	30–40 30–55
52 alloy	50.5	.60	.30	.05	.10	.50	.025	.025	.10	bal	9.6–10.1 10.2–10.7	30–45 30–55

The nickel contents are nominal. All others, except iron, are maximum.

glasses, an alloy containing 30 percent Ni, 17 percent Co, and 53 percent Fe has been recommended [933,934].

The American Society for Testing and Materials lists the chemical requirements and expansion characteristics of glass-to-metal sealing alloys in Specification F30–63T, as shown in table 72. This society also lists Specification F31–63T, covering the 42% Ni-6% Cr-Fe sealing alloy. The composition is given as

Nickel	42%	(nominal)
Chromium	5.6	(nominal)
Carbon	.07	(max)
Manganese	.25	(max)
Phosphorus	.025	(max)
Sulfur	.025	(max)
Silicon	.30	(max)
Aluminum	.20	(max)
Iron	remainder.	

The average linear coefficient of expansion, expressed as cm/cm/°C, falls within the following limits: 9.7 to 10.4 $\times 10^{-6}$ for 30 to 425 °C, and 8.5 to 9.2 $\times 10^{-6}$ for 30 to 350 °C.

Patents covering sealing alloys have been issued to Williams [935] for a zirconium-containing glass-to-metal sealing alloy producing bubble-free seals; to Smith [936] for an iron-nickel-cobalt alloy for sealing to high-alumina ceramics; to Wloka [937] for alloys for sealing to both soft and hard glass; to Scott [938] for an alloy capable of withstanding a wide range of temperature variation, and to the Pittsburgh Plate Glass Company [939] for an alloy known as "4750" suitable for sealing to lead-borosilicate plate and window glass. The characteristics and applications of 8 sealing alloys (7 of which contain nickel) were described by Eberly [940]. A technique for producing reliably air-tight seals between nickel and glass was described by Certa [941].

Minovar is an austenitic iron that contains 36 percent Ni, 1.5 percent Si, 0.5 percent Cr, and 2.40 percent maximum total carbon [942]. Its coefficient of expansion is 2.2 $\times 10^{-6}$ per °F, about one-third that of ordinary irons, and Minovar therefore is useful for such applications as spindle housings of precision drilling, boring, and grinding machines. Alloys containing 27 percent Ni, 5 percent Mo, 67 percent Fe, or 42 percent Ni, 5 percent Mo, 53 percent Fe have been used for the high-expansion side of thermostatic bimetals [943].

4.6. Magnetic Alloys

Useful magnetic materials either have high permeability and are magnetized and demagnetized easily, or are permanent magnets and magnetize with difficulty but retain their magnetism tenaciously [944]. Most of the ferromagnetic substances are alloys containing one or more of the elements iron, nickel and cobalt; some are nonmetallic compounds of these three elements, sometimes plus others; and some are alloys that contain no iron, nickel, or cobalt but are composed of manganese and other elements that are individually nonmagnetic. This discussion will be confined to the magnetically soft and permanent magnet ferrous materials in which nickel is a major constituent. An excellent condensation of this subject has been prepared by The International Nickel Company, Limited [945]. For applications of magnetic nickel-iron alloys, see Smith [946]. For discussions for magnetic alloys, see Stanley [173, 947].

a. Magnetically Soft Materials

It became generally recognized about 1920, as a result of the work of Arnold and Elmen [948], that nickel-iron alloys containing from 35 to 90 percent of nickel had high permeabilities at low field strengths and several of these alloys were called Permalloys, with numerical prefixes to indicate the nickel content. The 78-Permalloy (78% nickel) developed maximum permeabilities approaching 100,000, together with low hysteresis losses, low saturation values, very low magnetostriction, and low electrical resistivity. These properties were obtained after heating the alloy to 900 °C and cooling it slowly, followed by reheating to 600 °C with final rapid cooling to room temperature [696]. Even more remarkable properties were exhibited by Permalloys when the material was exposed to a magnetic field of several

TABLE 73. *Magnetic properties of some iron-nickel alloys* [947]

Alloy	Composition, percent			Hydrogen heat treatment	Relative permeability		Coercivity	Saturation induction	Electrical restivity	Curie temperature	Density
	Ni	Fe	Other		Initial	Maximum					
				°C			*Oersteds*	*Gausses*	*Microhm-cm*	°C	*g/cm* ^{3}
45 Permalloy	45	54	----------	1,050	2,500	25,000	0.30	16,000	50	440	8.17
Hiperink	50	50	----------	1,200	4,000	80,000	.05	16,000	35	500	8.25
78 Permalloy	78	21	----------	1,050+600	8,000	100,000	.05	10,000	16	580	8.60
4–79 Permalloy	79	16	4 Mo	1,100	20,000	150,000	.05	8,700	57	420	8.72
Mu metal	75	18	2 Cr, 5 Cu	1,100	20,000	150,000	.03	7,200	60	430	8.58
Supermalloy	79	15	5 Mo	1,300	100,000	1,000,000	.004	8,000	60	400	8.87

oersteds during the reheating to 600 °C. This magnetic anneal greatly increased the maximum permeability, diminished the coercive force, and converted the hysteresis loop to a substantially rectangular shape, the effects being at a maximum for alloys containing 65 to 70 percent of nickel, as shown in figure 108. During World War II a great improvement was made in the Permalloys by heat treating them in pure hydrogen at about 1,200 °C. The 78-Permalloy has been widely used in transformers transmitting weak signals of communication apparatus, whereas Hypernik, which contains 50 percent of nickel and was developed by Yensen, has been used in the transmission of power [944].

Additions of chromium, copper, molybdenum, or vanadium reduce the sensitivity of the iron-nickel alloys to heat treatment variables and thereby simplify the control of cooling rates to obtain high permeabilities. These elements also increase electrical resistivity, which is desirable for alternating current applications. Of the alloys summarized in table 73, the 4–79 Permalloy and Mumetal alloys are the most widely used and Supermalloy is the most responsive to the hydrogen anneal, with initial permeabilities of more than 1,000,000 obtainable commercially even in thin sheets [174,944].

Elmen [949] found that iron-nickel-cobalt alloys, which he called Perminvars, had permeabilities that were independent of field strength over a relatively large range, particularly when the usual heat treatment at about 1,000 °C was followed by about 24 hr at about 400 °C. The Perminvar containing 45 percent Ni, 30 percent Fe, and 25 percent Co is a good example; a permeability of 300 is obtainable for a field of about 3 Oe, corresponding to a flux density of 1,000 G. The resistivity of Perminvars is low but can be increased by additions of molybdenum or chromium [173]. Useful alloys in the Perminvar class include the nickel-iron-alloys Conpernik (50% Ni) and Isoperm (40% Ni).

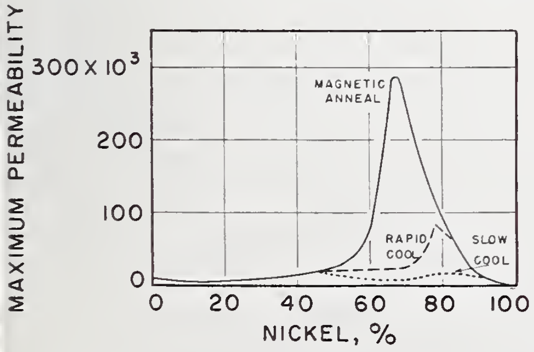

FIGURE 108. *Effect of annealing treatments on the maximum permeability of iron-nickel alloys* [944].

Iron-nickel-manganese alloys containing 5 to 15 percent of manganese generally have lower permeabilities than the iron-nickel-chromium or iron-nickel-molybdenum alloys, but have been used commercially. Addition of 1 or 2 percent of manganese improves the forging and mechanical properties of iron-nickel alloys [173].

Other useful alloys in the Permalloy or Hypernik class include Sinimax (43% Ni, 3.25% Si, Fe), Nicalloy (47% Ni, Fe), Monimax (47% Ni, 3% Mo, Fe), and 1040 (72% Ni, 14% Cu, 3% Mo, Fe). Gyorgy and Nesbitt [950] found that the coercive force of Permalloy could be raised to the level desirable for magnetic memory devices, without adverse effects on the rectangularity of the hysteresis loop, by the addition of gold and patented an alloy with the following ranges: 0.5-20.0 percent gold, 35-85 percent (preferably 63-85%) nickel, remainder iron, the ratio of nickel to iron being between 2:1 and 6:1.

Many of the iron-nickel alloys have anisotropic magnetic properties, that is to say, properties which are different along the different crystallographic axes. By suitable alignment of structure, properties can be obtained which are distinct from those of the material in the random condition. These effects can be produced either by cold work or by heat treatment, or by a combination of the two.

Magnetically soft materials generally are used as solid metals. For some uses, for example, inductances in telephonic and radio frequency circuits, cores made of finely divided material are required to minimize eddy current losses. To facilitate the preparation of powders with particle diameters in the range from 0.0002 to 0.0004 in, the alloys frequently are embrittled by the addition of a few tenths of 1 percent of sulfur. The powder is annealed, mixed with a suitable bonding agent such as

Bakelite, and molded in a die under pressure. The permeability of the compact depends upon the particle size and shape, thickness, and molding pressure. Useful permeabilities are 20 to 80 for telephonic use and 5 to 20 for radio frequencies. The ferromagnetic oxides or ferrites are also used in powdered form for high-frequency applications because of their high electrical resistance and consequent low eddy losses. Typical examples are $NiO \bullet Fe_2O_3$, $MgO \bullet Fe_2O_3$, and $NiO \bullet ZnO \bullet Fe_2O_3$, but many oxides with low loss and high permeability have been identified, for example, by Snoek [951]. All Fe_2O_3 ferrites have negative magnetostriction, but magnetite (Fe_3O_4) is positive, and mixtures of the negative magnetostriction materials with magnetite readily produce substances with zero magnetostriction [173].

The magnetically soft nickel-irons have been established for some time. Consequently, recent literature has been more concerned with the theory of magnetic behavior than with the development of new alloys. Bozorth [952] studied the effect of cooling rate on the magnetic anisotropy, magnetostriction, and permeability of single crystals of Permalloy and other compositions. The behavior of a cold-rolled single crystal of the intermetallic compound Ni_3Fe was studied by Chikazumi and Suzuki [953] in connection with the strong magnetic anisotropy developed by cold rolling iron-nickel alloys. Schindler and Salkovitz [954] reviewed published data on the Hall coefficients of binary alloys and offered explanations for anomalous behavior. The galvanomagnetic properties and Goldhammer effect in iron-nickel alloys were discussed by Grum-Grzhimailo [955].

Clark and Fritz [956,957] conducted a comprehensive investigation of the influence of temperature on the magnetic properties of iron-nickel alloys and Schindler et al.[958] reported on the effect of irradiation on the magnetic properties of iron-nickel alloys.

b. Permanent Magnets

Magnetically hard or permanent magnet materials have a large coercive force sometimes because of internal stress involving lattice distortions. In the martensitic steels that were the early permanent magnets, internal stress developed during the heat treatment that produced the martensitic structure. In later permanent magnets, the internal stresses developed from the precipitation-hardening and aging processes.

The quality of a permanent magnet is characterized not only by the residual induction, Br, and coercive force, Hc, but also by the so-called energy product, the product of B and H for various points on the demagnetization curve. The maximum energy product is probably the best single criterion of magnetic quality for these materials. Factors that produce undesirable demagnetization of permanent magnets include high temperatures, vibration and impact, stray magnetic fields, and accidental contact with another magnet to produce new poles [173, 944].

Uses of permanent magnets are (a) converting mechanical to electrical energy, e.g., dynamic microphones, phonograph pickups, etc., (b) converting electrical to mechanical or acoustical energy, i.e., electric motors, electrical instruments, radio loudspeakers, etc., (c) tractive efforts to attract or repel other magnets or magnetic materials, e.g., magnetic chucks, magnetic separators, pressure controls, switches, thermostats, etc., (d) control of charged particles, i.e., focusing of electrons and ions in some types of scientific apparatus, and (e) modification of the normal characteristics of matter.

The first permanent magnets were martensitic plain carbon steels. The tungsten magnet steels, introduced after 1855, were an improvement over the plain carbon steels, both the remanence and coercive force being increased. When tungsten became difficult to obtain, chromium was found to be a cheaper and almost equivalent substitute and the iron-chromium-carbon alloys were developed during World War I. In 1916, Honda and Saito, in Japan, introduced the KS magnet steel, which contained 35 to 41 percent Co, 2.0 to 3.75 percent Cu, 3.75 to 7.0 percent W, and 0.9 percent C. In the early 1930's it was found that excellent permanent magnets could be made from carbon-free alloys, notably the iron-nickel-aluminum alloys discovered by Mishima [959] and developed by Ruder [960,961] in this country. These iron-nickel-aluminum alloys and their modifications are the most popular and most widely used for all permanent magnet materials. They were named Alnico, which is a generic term describing the ternary alloys of aluminum, nickel, and iron. These alloys (25 to 30 percent Ni, 10 to 15 percent Al, remainder Fe) correspond roughly to Fe_2NiAl, and are precipitation hardening. Compositions and properties of the Alnicos and other nickel-containing permanent alloys are given in table 74.

The Alnico alloys are glass-brittle and difficult to fabricate; however, they have sufficient strength for most applications. They are usually fabricated by sand or shell mold casting; a few are fabricated by powder metallurgy techniques. The cast alloys are unmachinable and must be finished by grinding. They can be pulverized, and magnets can be pressed from this powder, bonded with Bakelite or other suitable binders. Such bonded cores are inferior to cast ones in that the residual induction is greatly reduced, but this difficulty can be partly overcome by increasing the cross-sectional area. By heating some Alnico compositions close to the melting point, it has been possible to hot work them. In general, vacuum-melted alloys hot

TABLE 74. *Compositions and properties of some nickel-containing permanent magnet alloys* [947]

Alloy	Composition, percent						Residual flux density	Coercivity	Maximum energy product, gauss oersteds (millions)	Flux density, B_o,[b]	Fabrication and heat treatment
	Al	Ni	Co	Cu	Ti	Fe					
							Gausses	*Oersteds*		*Gausses*	
Alnico I	12	22.5	5	---	---	remainder	6,600	540	1.40	4,100	Cast; cooled from high temperature; aged.
Alnico II	10	18	13	6	---	remainder	7,000	650	1.70	4,300	Cast; cooled from high temperature; aged.
Alnico III	12	26	3	---	---	remainder	6,400	560	1.35	3,900	Cast; cooled from high temperature; aged.
Alnico IV	12	28	5	---	---	remainder	5,500	730	1.35	3,200	Cast; cooled from high temperature; aged.
Alnico V[a]	8	15	24	3	---	remainder	12,000	720	5.00	9,100	Cast; heat treated in magnetic field.
Alnico V DG[a]	8	14.5	24	3	---	remainder	13,100	700	6.50	11,000	Cast with directional grain; heat treated in magnetic field.
Alnico V–7	8	14	24	3	---	remainder	13,400	780	7.50	11,400	Cast with directional grain; heat treated in magnetic field.
Alnico VI[a]	8	17	23	3	4	remainder	7,500	975	2.75	4,600	Cast; heat treated in magnetic field.
Alnico VII[a]	8.5	18	24	3.25	5	remainder	7,500	1,100	3.00	4,300	Cast; heat treated in magnetic field.
Alnico VIII	7	15	35	4	5	remainder	8,700	1,450	4.50	5,200	Cast; heat treated in magnetic field.
Alnico XII	6	18	35	---	8	remainder	6,100	1,000	1.65	3,200	Cast; cooled from high temperature; aged.
Nipermag	12	30	---	---	.4	remainder	5,600	660	1.34	3,400	Cast; cooled from high temperature; aged.
Sintered Alnico II	10	17	12.5	6	---	remainder	7,200	550	1.50	4,400	Sintered; cooled from high temperature; aged.
Sintered Alnico IV	12	28	5	---	---	remainder	5,500	730	1.25	3,100	Sintered; cooled from high temperature; aged.
Sintered Alnico V[a]	8	14	24	3	1	remainder	10,500	600	3.8	8,150	Sintered; heat treated in magnetic field.
Cunico I	---	21	29	50	---	---	3,400	710	.85	2,000	Rolled.
Cunico II	---	24	41	35	---	---	5,300	450	.99	3,400	Rolled.
Cunife I[a]	---	20	---	60	---	20	5,700	590	1.85	4,200	Rolled.
Cunife II[a]	---	20	2.5	50	---	27.5	7,300	200	.78	4,700	Rolled.
New KS	3.7	17.7	27.2	---	6.7	remainder	7,150	785	2.03	4,300	Quenched.

[a] Directional magnetic properties.

[b] B_o is the flux density at the point of maximum energy product.

work more easily than air-melted. The alloys have been extruded, rolled, and swaged. Properties of hot-worked Alnico are similar to those of the cast product. Ritzow [962] evaluated the temperature regions for complete homogenization of the structures in sintered Alnicos.

The Alnico alloys are age hardening because of the precipitation of the Ni-Al or Ni-Ti compounds or complexes like (Fe, Ni, Co)$_3$Ti [963, 964,965]. In general, the heat treatment given these alloys is to quench from about 1,200 °C and then age them for the proper time at about 650 °C. Geisler [963] reported that overaging appreciably reduced all of the magnetic properties, for example, the energy product for Alnico V was reduced from 5.00 to 0.09×10^6 and for Alnico IV from 1.30 to 0.02×10^6. The principal function of the cobalt is to decrease the cooling rate necessary to obtain optimum properties, thus permitting the casting of larger magnets.

According to Stanley [947], the Alnicos are the most popular and most widely used of all permanent magnet materials. Hadfield [966] suggested that magnetically anisotropic Alnicos may be about the maximum obtainable in solid magnets, but that further improvement may result from powder metallurgy techniques. Sugiyama and Shida [967] reported that the addition of 0.5 to 2.0 percent of columbium improved the properties of cast Alnico V.

Nickel-copper-iron alloys (Cunifes) can be hot and cold worked and machined. Their properties in very small wire sizes were studied by Cooter and Mundy [968]. Legat [969] found optimum magnetic properties at 15 percent nickel and 15 percent copper. The copper-nickel-cobalt alloys (Cunicos) have magnetic and physical properties similar to those of the Cunifes. They are used as castings, sintered powder metallurgy products, and in wrought condition. They are malleable when cold, but cannot be hot worked.

Precipitation hardening gold-nickel magnets, with compositions in the vicinity of 70 percent gold and 30 percent nickel, are of interest on theoretical grounds [970].

The stability of nickel-containing permanent magnets, both at ambient and elevated temperatures, has been the subject of numerous investigations [971,972,973,974,975]. The effect of radiation on permanent magnets was reported by Sery et al.[976]. A review tabulating available data on various permanent magnet materials was written by Fabian [977].

5. Multicomponent Systems

In the review of recent technical literature, references pertaining to the phase diagrams of systems of which nickel is a component were noted as follows:

Binary systems, nickel and:

Aluminum [978,979,980]
Beryllium [981,982]
Boron [983,984]
Chromium [980,985,986,987,988,989,990]
Cadmium [991]
Cobalt [992]
Columbium [993]
Gadolinium [994,995]
Gallium [996]
Gold [997]
Hafnium [998]
Indium [999]
Iron [689,992,1000,1001,1002,1003]
Lead [1004,1005]
Manganese [1003,1006,1007]
Molybdenum [1008,1009,1010]
Osmium [1011]
Palladium [1012,1013,1014]
Phosphorus [1015]
Platinum [1016]
Rhenium [1017]
Ruthenium [1018]
Silicon [1019,1020]
Sulfur [1021]
Tantalum [1022]
Tin [1023]
Titanium [980,1024,1025,1026,1027,1028,1029, 1030,1031]
Tungsten [182,980,1032,1033]
Uranium [1034,1035]
Vanadium [1036,1037]
Yttrium [1038,1039]
Zinc [1040,1041]
Zirconium [998,1017,1042,1043]

Ternary systems, nickel with

Aluminum and boron [1044]
Aluminum and chromium [1045]
Aluminum and copper [1046]
Aluminum and Iron [1048,1049,1050,1051, 1052]
Aluminum and molybdenum [1047]
Aluminum and nitrogen [1053]
Aluminum and silicon [1054]
Aluminum and titanium [1055]
Aluminum and zinc [1056]
Boron and zinc [1057]
Cadmium and nitrogen [1053]
Carbon and chromium [1058]
Carbon and indium [1059]
Carbon and iron [1060,1061,1062]
Carbon and manganese [1063]
Carbon and titanium [1064]
Carbon and zinc [1065]

Chromium and cobalt [1066]
Chromium and copper [1067]
Chromium and iron [866,1068]
Chromium and molybdenum [1066]
Chromium and nitrogen [1069]
Chromium and palladium [1014]
Chromium and silicon [1054]
Chromium and titanium [1070,1071]
Cobalt and manganese [1072]
Cobalt and sulfur [1073]
Cobalt and zinc [1074]
Copper and lead [1075]
Copper and manganese [1014,1076]
Copper and palladium [1014]
Copper and sulfur [1014]
Copper and tin [1077]
Gold and iron [1078]
Iron and lead [1061]
Iron and molybdenum [1062,1079]
Iron and nitrogen [1080,1081,1082,1083]
Iron and phosphorus [1084]
Iron and silicon [1085]
Iron and zinc [1086]
Magnesium and copper [1087]
Magnesium and nitrogen [1053]
Magnesium and zinc [1087]
Manganese and palladium [1014,1088]
Molybdenum and cobalt [1089]
Molybdenum and iron [1089]
Molybdenum and silicon [1047]
Molybdenum and titanium [1054]
Nitrogen and zinc [1053]
Palladium and silver [1014]
Palladium and titanium [1047]

Quaternary systems, nickel with

Aluminum, chromium and titanium [1090]
Aluminum, copper, and iron [1091]
Aluminum, copper, and manganese [1092]
Carbon, chromium, and iron [831,866,1093]
Carbon, iron, and lead [1061]
Chromium, iron and molybdenum [1094]
Chromium, iron and nitrogen [1095]

Quinary systems, nickel with

Aluminum, chromium, iron, and titanium [1096]

Systems with intermetallic compounds

Cr–NiAl [1097]
Cr_3Nb_2–Ni [993]
Ni–NiAl [1097]
Ni_3Cr–Ni_3Al [1098]
Ni–NiCl [1099]
TiC–Ni [1100]
Ni–Cr–NiAl [1097]

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