NBS CIRCULAR 592

# Nickel and Its Alloys

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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UNITED STATES DEPARTMENT OF COMMERCE • Sinclair Weeks, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

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J. G. Thompson

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# Preface

Publications by the National Bureau of Standards include a series of 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" was published in 1921, when expansion and growth of the nickel industry were becoming noticeable. A second edition (revised) was issued in 1924. At the close of World War II the subject was again reviewed and Circular 485 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.

The current revision was sponsored by the International Nickel Company, Inc., and was conducted at the National Bureau of Standards under the Bureau's Research Associate plan. This revision represents a review of the literature through 1956 and includes some 1957 references and unpublished information.

A. V. Astin, *Director.*

# Contents

# Nickel and Its Alloys

J. G. Thompson*

A review is presented of available information about the occurrence, recovery and refining, properties, and uses of high-purity and commercial forms of nickel, and about the properties and industrial applications of its important alloys. The Circular is a revision of National Bureau of Standards Circular 485 issued in 1950.

## 1. Introduction

### 1.1. History

Alloys of nickel had been known and used for thousands of years before identification of nickel as a metallic element was established. There is reliable evidence that prehistoric man made use of iron-nickel alloys of meteoric origin, and the use of these meteoric alloys for the production of implements, such as arrow tips, spearheads, and knives, or for jewelry, persisted among primitive people down to relatively modern times [21, 56, 86].[1] The first manmade alloys of nickel probably were the copper-nickel and copper-nickel-zinc alloys, called "paitung" or "paktong," which were made by the Chinese in very early times by direct smelting of natural ores [755]. Probably the oldest authenticated example of a copper-nickel alloy, that is still in existence today, is a coin struck about 235 B. C. in the small Asiatic kingdom of Bactria. The composition of this ancient coin (78 percent copper and 20 percent nickel) is very similar to the 75:25 ratio of the same elements in the modern U. S. nickel coin.

The modern history of nickel dates from its identification as an element by Cronstedt in 1751, and his naming of the element 3 years later [1]. Identity of the new element was confirmed in 1775 when Bergman [2] described his own preparation of metallic nickel. Legend attributes the origin of the word "nickel" to the German word for goblins, which were known as nixes and kobalds. Ancient miners are believed to have called a supposed copper ore "kupfernickel" because they could extract no copper from it and therefore it must have been bewitched. It was the latter half of this word that Cronstedt chose as the name for his new element. However, a more reasonable explanation, recently advanced by Edward Taube [112a] is that the Saxon miners considered this material a source of pigment—not a metal—and called it kupfernickel because it was a copper-colored rock. In Middle German dialects Nickel is the diminutive of Nock (mountain) and means hill or rock fragment. Kupfernickel, or niccolite, is now known to be an arsenide of nickel.

The first appreciable use of nickel was in the early years of the 19th century when Europeans began making their own versions of the Chinese paktong. Nickel plating originated in 1843, and by 1870 had become an important use for the metal. Uses for metallic nickel were considerably expanded in 1879, when Fleitman, in Germany, added magnesium and manganese to overcome the embrittling action of sulfur and thereby produced ductile, malleable metal. This put on an industrial basis the earlier attempts to improve the ductility and malleability of nickel, by Richter in 1804 and by Wharton in 1865. Nickel structural steels began to become industrially important near the end of the 19th century, based on the pioneer investigations of Stodart and Faraday [4], von Liebig [5], Bessemer [9], Riley [7], and Wiggin [11]. The 20th century has witnessed the development and tremendous growth of a great variety of corrosion-resistant and heat-resistant alloys, including stainless steels and the "super alloys",[2] as well as Monel and other nonferrous alloys. Furthermore, there are many uses where the importance cannot be evaluated in terms of tonnage involved, for example, in magnetic alloys and in alloys with controlled rates of thermal expansion.

The growth of the nickel industry may be summarized as follows: In 1850 the World production of nickel was less than 200,000 pounds, whereas the production of the Free World for 1956 was about 452,000,000 pounds [757]. Canada, in modern times, furnishes approximately 80 percent of the total nickel supplies of the Free World, and the United States receives about two-thirds of the Canadian production, together with appreciable amounts of nickel from other sources.

### 1.2. Occurrence, Minerals, Ores

In his classic work, Clarke [30] estimated the average nickel content of the earth's crust to a depth of 10 miles as 0.019 percent. A re-estimate by Wells [109] changed this figure slightly, to 0.016 percent, which indicates an abundance of the

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*Research Associate at the National Bureau of Standards, representing The International Nickel Company, Inc.

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

[2] The term "super" has been applied to ferrous and nonferrous alloys (and to some nonmetallic materials) to indicate the possession of superior strength, resistance to creep, and other mechanical properties at very high temperatures. This and other terms, e. g., "super strength", are loosely descriptive, but not definitive. In this text the classification of super alloy has been applied primarily to alloys that possess economically useful mechanical properties at or above 1,200° F.

same order of magnitude as for zinc, boron, copper, and rubidium. Sandell and Goldich [108] estimated that nickel constitutes 0.008 percent of the uppermost crust of the earth, and Fraser [337] stated that nickel is the 23d element in order of abundance in the lithosphere and that the average nickel content of all igneous rocks is about 0.009 percent. 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 [496] and many of the stars, in sea water [395], in deep-sea silt [533, 606] and it has long been known that nickel is an important constituent of metallic meteorites. Although these are not immediately available sources of nickel, it is interesting, as a future possibility, to consider that the nickel content of sea water, reported by Ishibashi [395] to be 0.7 to 0.8 gamma per liter, can be expressed as 3 tons of nickel contained in each cubic mile of sea water.

*Minerals.* 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, and silicates (including nickeliferous iron ores), and arsenides.

The sulfide minerals include pentlandite $(Ni,Fe)_{11}S_{10}$ containing 36 percent of nickel, polydymite ($Ni_4S_5$ or $Ni_3FeS_5$), millerite ($NiS$), and linnaeite (a cobalt sulfide in which nickel may replace some of the cobalt). Pentlandite is of outstanding importance; it is the primary source of nickel in the Canadian ores which, in modern times, supply the bulk of the World's demand. A wide variety of accessory minerals are associated with nickel-sulfide in the ore, so that nickel production involves the by-product output of copper, metals of the platinum group, silver, gold, cobalt, selenium, tellurium, and, recently, iron.

The most important nickel silicate mineral is garnierite (approximately $H_2(Ni,Mg)\ SiO_4 \cdot n\ H_2O$ with a variable Ni:Mg ratio). This is the important constituent of the New Caledonia ores, which in 1956 were second in importance to those of Canada. Minerals usually associated with garnierite include noumeite, $H_6(Mg,Ni)_{10}Si_6O_{29}$, and genthite, $H_4Mg_2Ni_2\ (SiO_4)3 \cdot 4H_2O$. All of these hydrated silicates of magnesium and nickel were produced by lateritic weathering of the mineral olivine, $2(Mg,Fe,Ni)O \cdot SiO_2$. The New Caledonia ores contain considerable iron and other ores, for example, the Cuban Mayari and Nicaro ores are essentially nickeliferous iron ores. Nickel minerals of the silicate type have been found as products of the weathering of obscure and variable silicates such as the vermiculites and hydrated silicates of colloidal origin.

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 chloanthite and smaltite (arsenides of nickel and cobalt), gersdorffite (nickel-iron-cobalt sulfarsenide), and annabergite (hydrous nickel arsenate).

Additional information on the mineralogy and geology of nickel is presented by Coleman [19], Lindgren [58], Mellor [71], Dana [111], Hall [463], and a report by the U. S. Bureau of Mines [368].

*Ores.* Figure 1 illustrates the geographical distribution of the principal nickel deposits of the world and table 1 presents data on their size and approximate content of nickel. Thompson [738] reported that ores from only four countries, Canada, New Caledonia, Cuba, and the United States accounted for 98 percent of the Free-World production of 1955.

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 [626]. There is considerable variation from mine to mine, but the average content of the ore is about 1.5 percent for both nickel and copper. These deposits were discovered shortly before 1890, as a result of prospecting and of excavations made during the building of the Canadian Pacific Railroad [299, 463]. 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 in February 1956, the International Nickel Company began the sale of high-grade iron ore, in the form of sintered pellets [738].

Sulfide ore similar to the ore of the Sudbury district was found in the Lynn Lake area in northern Manitoba in 1945 [530], and has been brought into production recently by Sherritt Gordon Mines, Ltd., [530, 601]. Deposits of nickel ore have been reported in New Brunswick, British Columbia, Northwest Territories, Yukon Territory, and Saskatchewan [449]. Recently, interest has been shown in ore deposits in the Ungava peninsula and in the Great Slave Lake area of the District of MacKenzie. The public press of December 6, 1956, carried an announcement of plans of the International Nickel Company to develop new mines, in the Mystery-Moak Lakes area of Northern Manitoba, about 400 miles north of Winnepeg. It is expected that production will begin in 1960 and that by 1962 the new mines will produce 37,500 tons of nickel per year, which, together with increased production in the Sudbury area, will increase the company's current production capacity by about 50 percent.

*Table 1. Nickel-ore bodies and estimated reserves*

[368, 387, 463, 589, 616, 746]

| Location | Type of ore | Ore reserves | Average nickel content | Estimated nickel reserves |
|---|---|---|---|---|
| Canada: | | *Tons* | % | *Tons* |
| Int. Nickel Co. | Sulfide | 262,000,000 | 1.5 | 3,800,000 |
| Falconbridge | do | 40,000,000 | 1.43 | 260,000 |
| Sherritt Gordon | do | 14,000,000 | 1.20 | 200,000 |
| Alaska | do | 22,000,000 | 0.3 | 70,000 |
| Missouri | do | 12,000,000 | 0.4 | 50,000 |
| Union of South Africa | do | 150,000 | 3 | 4,500 |
| USSR[a] | do | ---------- | ---------- | ---------- |
| New Caledonia | Silicate | 1,408,000,000 | 1 to 5 | 16,700,000 |
| Cuba | Fe–Ni[b] | 3,000,000,000 | 0.8 | 24,400,000 |
| Celebes | Silicate and Fe–Ni | 500,000,000 | 0.9 to 2.0 | 7,000,000 |
| Philippine Islands | Fe–Ni | 550,000,000 | 0.8 | 4,400,000 |
| Indonesia | do | 350,000,000 | 0.55 | 2,000,000 |
| Venezuela | Silicate | 40,000,000 | 1.75 | 700,000 |
| Brazil | do | 20,000,000 | 1 to 3.5 | 540,000 |
| Oregon | Silicate and Fe–Ni | 20,000,000 | 1.5 | 300,000 |
| Japan | Fe–Ni | 30,000,000 | 0.5 | 150,000 |
| Greece | Silicate and Fe–Ni | 10,000,000 | 0.5 to 1 | 75,000 |
| Madagascar | Silicate | 900,000 | 5 | 45,000 |
| USSR[a] | Silicate and Fe–Ni | ---------- | ---------- | ---------- |

[a] Information not available on recent USSR operations, but Davis [386] estimated production for 1949 as probably 25,000 metric tons of nickel.

[b] Fe–Ni equals nickeliferous iron ores.

FIGURE 1. *Principal producers (solid circles) and minor or potential sources (open circles) of nickel ore in 1955.*

The nickel silicate ores of New Caledonia were discovered by Garnier in 1865 [47], 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 silicate. The ores originally exploited were variable in composition but appreciably richer in nickel than the Canadian ores, as indicated by the analysis reported by Guillet and Weill [52] as follows:

| | % |
|---|---|
| NiO | 5 to 10 |
| $SiO_2$ | 30 to 50 |
| MgO | 8 to 26 |
| $Fe_2O_3$ | 12 to 20 |
| $Al_2O_3$ | 0 to 1 |
| CaO | 0 to 1 |
| $H_2O$ (combined) | 6 to 12 |

Subsequently, attention was paid to ores that were not so rich, and Hall [463] reported that the New Caledonia ores ran 4 to 6 percent of nickel. Other reports increase the reserves by including large volumes of low-grade ore, as shown in table 1.

The third most important nickel ores in 1956 were the nickel-bearing iron ores of Cuba, in the districts of Mayari, Moa Bay, and San Felipe. According to Moldenke [28], the dried Mayari ore contained 49 percent of Fe, 11 percent of $Al_2O_3$, 3 percent of Si, 1 percent of Ni, and 1.5 percent of Cr. According to Davis [540], drilling in the Levisa Bay district showed 35,000,000 short tons of ore with an average content of 1.39 percent of nickel, 0.10 percent of cobalt, and 35.8 percent of iron. According to Williams [746], there are two types of ore 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. Pig iron containing both nickel and chromium was produced some years ago by direct smelting of the Mayari ores, particularly by the Bethlehem Steel Company, but it was not until 1941 that a practical process was developed to separate nickel from the Cuban ores. The process was developed by the Nicaro Nickel Company, a subsidiary of the Freeport Sulphur Company, and production reached a peak of 11,240 metric tons of nickel in 1946, according to Davis [386]. However, the process was relatively a high-cost operation and production was discontinued in 1947. Subsequently there was an increased demand for nickel and the Nicaro operations were resumed in 1952, by the Nickel Processing Corp. under contract with the General Services Administration of the United States Government. The target rate of production under this contract was 15,500 tons of nickel (as nickel oxide) per year, and this rate of production was achieved during the third quarter of 1955 [516]. This is approximately equal to the current rate of production from New Caledonia. Williams [746] stated that the ultimate goal of

25,000 tons of nickel per year will be reached with enlarged facilities. The Moa Bay deposits [746] comprise 50 million tons of ore with an average content of 1.35 percent of nickel, 0.14 percent of cobalt, and 46.5 percent of iron, with large tonnages of lower nickel content. In contrast to the Nicaro ores, most of the nickel in the Moa Bay ores is in the limonite, and production of nickel from these ores, by the Freeport Sulfur Company, appears to be still in the pilot plant stage. The Cuban ores constitute a huge reserve of low-grade ore readily available to the United States; additional information about them is contained in the report from the U. S. Bureau of Mines, "Nickel-Cobalt Resources of Cuba" [589].

In the United States, the silicate and nickel-bearing iron ores near Riddle, Douglas County, Oreg., constitute about one-half of the known reserves and furnish the source of the only appreciable production of nickel. The Hanna Nickel Smelting Company, a subsidiary of the M. A. Hanna Company, has operated these deposits since the early 1940's, and in 1955 produced 4,400 short tons of nickel [700] in the form of ferro-nickel, under contract with the General Services Administration [357, 746]. The Riddle ores have been described [375] as being low grade and the recovery process too expensive to operate under peace time economics. The National Lead Company, with assistance from the General Services Administration, is investigating the recovery of nickel and cobalt from complex lead-copper-sulfide ores near Fredericktown, Mo., but the latest available information indicates that operations have not yet progressed beyond the pilot plant stage; up to December 1956, there had been no production of nickel to meet the requirements of National Stockpile Specification P–36–R [660]. The sulfide ores of the Lancaster Gap area in Pennsylvania are of historical interest; ore was produced from the Old Gap Mine prior to 1875 [337], but production was discontinued when ores from New Caledonia became available. Other deposits, usually low-grade nickel ores, that have been identified but not yet exploited, include the sulfide ore bodies of Alaska [120] and Lake County, Minnesota [561], silver-nickel-cobalt-uranium minerals in Grant County, New Mexico [663], and reported occurrences of nickel-bearing minerals in California, Colorado, Montana, Nevada, North Carolina, Virginia, and Washington.

Minor production, for use by the Free World, 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. Subsequently, the perfection of the electrolytic refining process made it economical to resume operations, and at their peak production for German use in World War I, nearly 80,000 metric tons of ore containing approximately 1.20 percent of nickel was produced annually [114]. However, with increasing economic competition the small nickel mines of Norway discontinued production one by one; the last one to survive was the mine at Flaad, near the town of Esje, and this mine closed in 1941. An important European source of nickel, according to Hall [463], is in Greece, particularly the magnesium silicate ores, with the chromium-nickel iron ore (similar to the Mayari ore of Cuba) of less importance. The sulfide ores in the Transvaal area of the Union of South Africa have achieved some production recently. Small amounts of nickel are recovered from the cobalt ore of French Morocco, and ore is being produced from the oxide ores of the Central Celebes. Japan in 1955 refined an appreciable amount of ore from New Caledonia [738], and perhaps from ores of Burma and the low-grade ores of the Gumma Prefecture in Japan. However, according to Thompson [738] the combined production of all minor producers in 1955 was approximately 2 percent of the total Free-World production for that year.

Ore bodies that have been explored, but not as yet brought into appreciable production, occur in Borneo, the Philippines, Madagascar, Brazil, and Venezuela. The ores of Surigao, Philippine Islands, have been opened to bids for exploitation by private operators [515]. The manganiferous ores of Brazil contain 44.8 percent of $MnO_2$, 13.7 percent of $Fe_2O_3$, 5.6 percent of $SiO_2$, 4.8 percent of CoO, 2.9 percent of NiO, and 2.3 percent of CuO [501]. Siliceous ores located near Sao Jose de Tocantins were explored by the American Smelting and Refining Company during World War II, but the deposits are approximately 1,000 miles inland, and adequate fuel was not available in the area. Further investigation of the Tocantins deposit was undertaken by Ventures, Ltd. Venezuelan ores generally consist of silicates in nickeliferous rocks, approximating iron laterites. The most important deposit, at Lomo de Hierro near the port of La Guaira, was explored by the International Nickel Company. The ore averages about 1.75 percent of nickel and appears to be amenable to the ammonia leaching process.

There is very little information available for current operations of the nickel mines in Russia. It is known that the ores of Pechenga (Petsamo) in Russian Lapland, are similar to the Canadian sulfide ores of the Sudbury district [506]. The Kola deposits in the Ural mountains may be silicates and nickeliferous iron ore. Estimates of the annual production of nickel by the U. S. S. R. have been included in the annual reviews compiled by the U. S. Bureau of Mines, e. g., Davis [449].

The small deposits of nickel-bearing copper ore in China have been smelted directly for at least 2,000 years, to produce copper-nickel or copper-nickel-zinc alloys. Information about these ores is not currently available.

### 1.3. Recovery of Nickel From Its Ores

The ensuing discussion, based largely on the article by Fraser [337], has been arranged in order of the modern importance of the three basic types of nickel ores and of the principal procedures. See also Pfeil [771].

*Sulfide ores.* The sulfide ores of the Sudbury area in Canada have been the outstanding source of nickel since about 1890, with the International Nickel Company of Canada, Ltd., the dominant producer and Falconbridge Nickel Mines, Ltd., the other major producer. About 1945 Sherritt Gordon Mines, Ltd., began the development of extensive deposits of sulfide ores in the Lynn Lake district in Northern Manitoba, with commercial production of nickel beginning in 1954.

The recovery process used today by the International Nickel Company developed from a process originating before 1900. In the old procedure, the roasted ore was smelted in blast furnaces to produce a matte containing nickel, copper, and iron. Some sulfur and practically all of the iron were oxidized in Bessemer converters, with the oxidized sulfur and iron removed by the furnace gases and slag. The solidified matte from the converters was treated by the Orford process originally developed by the Orford Copper Company, at Bayonne, N. J., before this concern consolidated with the Canadian Copper Company in 1902 to form the International Nickel Company.

In the Orford process, the matte from the converters was subjected to multiple smelting in cupola furnaces, with an excess of coke and with niter cake as flux. This produced molten sodium sulfide, which is a good solvent for the sulfides of copper and iron but not for nickel sulfides. When the molten sulfides were allowed to solidify, two layers were formed, a lower layer of nickel sulfide and an upper layer of copper and iron sulfides dissolved in sodium sulfide. The nickel sulfide "bottoms" were separated, crushed, ground, and leached with hot water and with diluted sulfuric acid. The leached sulfides were roasted repeatedly to oxidize sulfur, copper, and iron, or to convert them to soluble forms that could be removed by additional leaching. Some of the resulting nickel oxide was sold to the producers of ferrous and nonferrous alloys but most of it was reduced with petroleum coke to metallic nickel for final refining by the electrolytic or Mond processes.

The Orford process was successful in separating copper and nickel but was difficult and laborious to operate. According to Mudge [593] early attempts to convert the copper-nickel matte to usable alloys, without separating the copper and nickel sulfides, achieved success in 1905 when R. C. Stanley produced a malleable, strong, corrosion-resistant alloy that was named Monel. However, the demand for nickel, as nickel rather than as a copper-nickel alloy, existed in 1905 and became more intense in succeeding years. Consequently, attempts to separate copper and nickel by means other than the Orford process continued, leading to the development of a new process which was adopted by the International Nickel Company in replacement of the Orford process late in 1948. The new process is covered by patents and has been described [368] as follows; the new process follows the path of the old process up to the Bessemer converter stage. There the matte is blown until roughly 15 percent of the mass has become a copper-nickel alloy and the remaining 85 percent is copper and nickel sulfides. The blown matte is cooled very slowly, under carefully controlled conditions, to produce three types of crystals in the final solid mass, (1) a copper-nickel alloy containing about 95 percent of the precious metals, (2) copper sulfide containing about 1 percent of nickel, and (3) nickel sulfide containing about 1 percent of copper. When the mass is finely crushed, the copper-nickel alloy is extracted in magnetic separators for further refining and recovery of the precious metals, and the copper sulfide and nickel sulfide are efficiently separated by flotation procedures. The copper sulfide goes to the copper smelter for conversion to blister copper, which is electrolytically refined. The nickel sulfide is sintered to oxide, which may be used as oxide or may be further refined by the electrolytic or Mond processes.

Electrolytic refining is conducted in a nickel sulfate-chloride electrolyte with anode and cathode compartments separated by canvas. The electrolyte is circulated and is continuously purified. Cathode starting sheets are made by stripping thin sheets of electroplated nickel from stainless-steel blanks. The product of electrolytic refining is nickel of 99.95-percent purity, including cobalt which formerly was present in amounts up to 0.5 percent, but in the most modern practice is 0.1 percent, or less. Metals of the platinum group and other valuable metals are recovered from the sludge. For further details, see Peek [46], and publications by the International Nickel Company [119, 446].

The Mond process was developed from the original discovery in 1890 by Mond and his associates [8]. In modern operations, the process briefly is as follows: Nickel oxide sinter is reduced by water gas at carefully controlled temperatures. The reduced nickel is then reacted with carbon monoxide at about 80° C, forming volatile nickel carbonyl, which passes to another vessel maintained at a temperature high enough to cause decomposition of the carbonyl compound. The nickel content is deposited onto seed grains of nickel, which are moved around in the decomposers until the deposited layers build them up to marketable size. The Mond process produces nickel of 99.7- to 99.9-percent purity, with carbon and oxygen as the principal impurities. With proper control of operating temperatures and gas composition, metals other than nickel do not form volatile carbonyl compounds, or, if they do, their carbonyl compounds do not decompose when the nickel carbonyl does. Mond nickel was noted for many years as being the only available form of cobalt-free nickel, but in recent years, and in part because of the intensified demand for cobalt, other means of separating nickel and cobalt have been developed, for example, as described by Bercovici [262], and by Schaufelberger and associates [602, 603].

Many and radical changes have been made in recent years in the International Nickel Company's processes. In addition to the new recovery process that replaced the Orford process, these changes include completion in 1954 of the conversion from open-pit to underground mining in the Sudbury District [449], and the development of improved mining techniques [408]. According to Davis [541], major alterations that greatly increased the operation efficiency of the Mond refinery, Clydach, Wales, were completed in 1952, and revision and enlargement of the International Nickel Company's electrolytic refining plant at Port Colborne, Ontario, was in progress. Davis also reported the completion of a 7½-mile pipeline for improved transportation, by pumping, of the bulk concentrate from the 3½ million tons of ore handled annually by the newly built Creighton concentrator to the reduction plants at Copper Cliff. Procedures have been developed [433, 683] to separate pyrrhotite from other nickel-bearing sulfides by selective flotation, and to treat the pyrrhotite concentrates by leaching procedures that result in the recovery of both iron and nickel. The iron oxide is recovered as sintered pellets that contain 68 percent of Fe, with only 1.5 percent of $SiO_2$, 0.003 percent of P, 0.65 percent of $Al_2O_3$, 0.01 percent of S, and with no other element present in excess of 0.3 percent. The high iron content and the low silica and phosphorus make this product attractive for use in the open-hearth. According to Thompson [738], the first commercial-scale shipment of sintered pellets of this high-grade iron ore was made in February 1956 from the International Nickel Company's iron-ore recovery plant near Copper Cliff.

Copper is the second most important product produced by the International Nickel Company from the Sudbury ores. Valuable by-products of the recovery and refining processes include metals of the platinum group, gold, silver, selenium, tellurium, sulfuric acid, liquid sulfur dioxide, and the newest by-product, high-grade iron ore.

Falconbridge Nickel Mines, Ltd., treats the Canadian sulfide ores in a different manner, using the Hybinette process [237]. The initial treatment of the ore, by mechanical and magnetic concentration, flotation, and smelting of the copper-nickel concentrate in the blast furnace, is similar to the International Nickel Company's process, but copper is not separated from nickel in the smelting operations. In former practice the roasted matte was leached with diluted sulfuric acid to remove most of the copper and a small amount of nickel, but, according to Davis [541], during 1952 a leach solution containing both sulfates and chlorides was substituted for the diluted sulfuric acid, primarily to facilitate the recovery of cobalt. The insoluble remainder from the leaching operation is melted and cast into anodes that contain about 65 percent of nickel and from 3 to 8 percent of sulfur. The anodes are dissolved electrolytically, copper is removed from the electrolyte by cementation, and refined nickel is deposited on the cathodes, with recovery of precious metals from the slimes on the bottom of the Hybinette cells.

Sherritt Gordon Mines, Ltd., uses still another process to recover nickel from Canadian sulfide ore, at Lynn Lake, Manitoba. The nickel refinery at Fort Saskatchewan began operating in August 1954 and reached rated capacity early in 1955. Lynn Lake flotation concentrate (unroasted), containing percentages of 12 to 16 nickel, 1 to 2 of copper, 0.2 to 0.5 of cobalt, 33 to 40 of iron, 28 to 34 of sulfur, 8 to 20 of insolubles, and less than 0.02 oz of precious metals per ton, is leached with strong aqueous ammonia at 160° to 175° F, in a closed vessel with air agitation under pressure. This oxidizes the iron to insoluble hydrated ferric oxide. The iron-free leach solution may be treated in several ways to separate the nickel, cobalt, and copper. Nickel can be precipitated as nickel-ammonium-sulfate, and thereby separated from the copper and cobalt. Alternatively, the iron-free leach solution may be boiled to drive off some of the ammonia and decompose the thiosulfate; the copper precipitates quantitatively as copper sulfide, and the nickel and cobalt may be recovered from solution separately by a hydrogen-precipitation process. The hydrometallurgical processes have been described [376, 454, 554, 743], and in several patents, for example, [389, 404, 555]. The process is also known as the Chemical Construction Corp. process and is being investigated at Fredericktown, Mo. [541].

Silicate ores such as those of New Caledonia are sulfur- and copper-free. The ore is mixed with sulfurous materials such as gypsum or pyrites, is briquetted, and smelted with coke to produce a matte, which is treated in Bessemer-type converters with added silica to slag off the iron. The converter matte, which contains approximately 80 percent of nickel and 20 percent of sulfur, is roasted to remove most of the sulfur and to oxidize the nickel. The nickel oxide is reduced at about 1,250° C to form cubes or rondelles containing about 99.25 percent of nickel [114]. Most of the matte is refined at LeHavre, France, but approximately one-fourth of the New Caledonia ore produced in 1952 was refined in Japan [387, 541]. In modern practice, a large tonnage of "fonte" (ferronickel containing 30 percent of Ni) is produced from New Caledonia ore or matte, for European consumption. The New Caledonia operations are conducted by La Societe le Nickel.

The low-grade, nickeliferous iron ores that are found in Brazil, Cuba, Oregon, The Philippine Islands, and Venezuela present additional problems, partly economic, because of the higher iron content and lower nickel content, with the nickel so minutely dispersed that the usual concentration procedures, including flotation, are not successful. Prior to World War II, the Bethlehem Steel Company smelted Cuban Mayari ore successfully, in spite of the high content of alumina and other slag-formers, to produce an alloy pig iron containing about twice as much chromium as nickel, that was useful in the production of alloyed foundry-irons. However, for the production of steel, only the nickel content was of value as most of the chromium was lost through oxidation during the steel-making processes. As a result of the recent intensified demand for nickel, the Hanna Nickel Smelting Company under contracts with U. S. Government agencies, has recovered nickel in the form of ferro-nickel from Riddle, Oreg., ores. According to Rasmussen [357], the nickel-iron ratio of the silicate ores in the Riddle area is high enough to produce a 15-percent nickel pig iron without using selective reducing smelting. According to Davis [449], the process used to produce ferro-nickel from the Riddle ores, which contain 1.5 percent of NiO, 35 percent of FeO, and 35 percent of $SiO_2$, is the Ugine-Perrin process [500]. Briefly, the process is carried out in electric furnaces with additions of carbon as a deoxidizer and to form carbon monoxide, which mixes and stirs the melt, and of ferrosilicon or aluminum, whose exothermic oxidation compensates for heat losses in the converter. According to information supplied by the General Services Administration [660], typical ferro-nickel produced at Riddle, Oreg., contains 45 percent of Ni, 0.006 to 0.009 of S, 0.018 to 0.043 of P, 0.010 to 0.038 of C, and 0.10 percent of Cr, a composition that is well within specifications for stockpiling purposes. A modification of the Ugine-Perrin process was proposed recently [723] for treatment of Cuban ores containing 0.5 percent of NiO, 25 percent of FeO, 40 percent of $SiO_2$, and large amounts of MgO. It is proposed to melt the ore and add molten ferro-nickel (35 percent nickel). Reaction between the ferro-nickel and the ore reduces the NiO content of the ore to 0.2 percent and raises the nickel content of the ferro-nickel to 36.5 percent. Pyrometallurgical treatment of lateritic ore or nickel-bearing serpentine from Surigao, Mindanao, Philippine Islands, was investigated recently by the U. S. Bureau of Mines [523], who reported that electric smelting experiments indicate a recovery of about 35 pounds of nickel from a ton of dried ore. Fukabori [455] proposed heating serpentine with rock phosphate to produce a usable phosphate slag and an iron-nickel-phosphorus alloy, which could be oxidized to ferro-nickel.

Because of the intensified demand in recent years for nickel rather than for ferro-nickel, much attention has been given to the possibility of recovering nickel from low-grade ores by leaching processes. The most successful of these to date has been the application of the Caron [29, 261] or ammonia-leaching process to the Nicaro ores in Cuba. The process depends upon the fact that nickel in the metallic state reacts with ammonia to form soluble complexes. The hot ore is treated with reducing agents to convert nickel oxide and silicate to nickel metal. This can be accomplished with very little reduction of the iron oxides by controlling the $CO_2 : CO$ and $H_2O : H_2$ ratios in the reducing gas. The reduced ore is leached with an ammonium carbonate-ammonium hydroxide solution, which converts the metallic nickel particles into a soluble complex, approximately $NiCO_3 \cdot 3NH_3$. The use of compressed air during the leaching process facilitates solution of the nickel and retention of the iron as insoluble oxide. The nickel complex in the leach solution is stable only in the presence of an excess of ammonia. When the leach solution is heated, ammonia and carbon dioxide are driven off, and the nickel is precipitated as basic carbonate, approximately $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$, which is calcined to produce a marketable nickel oxide [472]. The Nicaro plant was built during World War II, by the Defense Plants Corp. and was operated by Freeport Sulphur Company until it was put in standby condition early in 1947. In 1952 the plant was rehabilitated by the Cuban Nickel Company, a U. S. Government corporation, for operation by the Nickel Processing Corp. with ore supplied by Nicaro Nickel Company, a subsidiary of Freeport Sulphur Company [514, 541, 746]. This has been the outstandingly successful recovery of nickel by leaching operations, with a 1955 production of 30,000,000 lb of nickel in the form of nickel oxide and sinter, that meet the requirements of National Stockpile Specification P–36–R, with typical compositions [660] as follows:

| | Ni+Co | Co | Fe | S | C |
|---|---|---|---|---|---|
| Oxide | 77.66 | 0.69 | 0.22 | 0.03 | ---- |
| Sinter | 90.27 | .76 | .43 | .05 | 0.10 |

Modifications and improvements on the Caron process include a patent [228] granted to the International Nickel Company, for the recovery of nickel from lateritic ores, and patents granted to the Chemical Construction Company [404, 588, 702], which are in use by Sherritt Gordon Mines at Lynn Lake, Manitoba, and are being investigated by the National Lead Company in their operations at Fredericktown, Mo. Leaching with ammonia is used by the International Nickel Company [683] in a process for the recovery of both nickel and iron from nickeliferous pyrrhotite, and is under investigation by Calumet & Hecla, Inc., [453] for the recovery of nickel and copper.

Other leaching processes that have been proposed but have not yet reached the production stage include a chlorination process proposed by Daubenspeck [650] for the treatment of low-grade nickeliferous laterites or serpentines; a nitric acid-autoclave process proposed by Mancke [698] for the treatment of Mayari-type ore; and a leach with mineral acid in an autoclave to extract nickel and cobalt from oxidized ores [154]. See also [772].

The recovery of nickel from arsenical ores is of historical interest because nickel was first identified, by Cronstedt, in arsenical ores of Norway. None of the Norwegian mines appears to be operating today, and the arsenical ores of Canada, Europe, and French Morocco are of negligible importance in the modern production of nickel. The usual procedure [337] was to smelt the roasted ore in a blast furnace to form a speiss, similar to the matte formed in smelting sulfide ores. The speiss was concentrated by roasting and resmelting, with additions of carbonaceous matter, sodium nitrate, and soda ash to volatilize the arsenic or to convert it to a water-soluble form. When other elements were not present in excessive amounts, the resulting nickel oxide was mixed with carbonaceous material and reduced to metallic nickel. If complicating elements were present, appropriate steps were taken.

## 1.4. Statistics of Production and Consumption

World production of nickel was less than 100 tons per annum in 1850, when Norway was the chief source and the principal demand was for copper-nickel and copper-nickel-zinc alloys, modernizations of the old Chinese paktong. In the latter part of the 19th century, the development of nickel plating, malleable nickel, and nickel structural steels created an increased demand for nickel, as shown in figure 2. This first expansion of the nickel industry was made possible by the development of the deposits of New Caledonia, which in 1875 supplanted Norway as the chief source of nickel. In 1905, Canada's Sudbury ores produced 9,500 short tons of nickel, replacing New Caledonia as the most important producer, and Canada has retained its predominant position ever since. Increased production was required because of the growth of uses developed prior to 1900 and the development of new alloys and uses, including the development of Monel; austenitic stainless steels; low-alloy, high-strength steels; super alloys; and the specialty steels and alloys, such as the magnetic alloys and thermal-expansion alloys, whose importance cannot be adequately expressed by the tonnage involved. The rate of production has increased tremendously since 1900, as shown in figure 2, subject to recessions following World Wars I and II and the 1929 collapse of the stock market. Free world production of nickel in 1955 was about 215,000 short tons, of which 80 percent came from Canadian ores and better than 80 percent of the Canadian production came from the International Nickel Company. In spite of the tremendous increases in production, nickel in recent years has been in very short supply [543], because of defense and stockpiling requirements in addition to industrial needs [773]. It has been estimated [738] that about 40 percent of the free-world's available nickel is currently absorbed by defense and stockpiling requirements. The same authority stated that approximately two-thirds of the 1955 total free-world supply went to the United States.

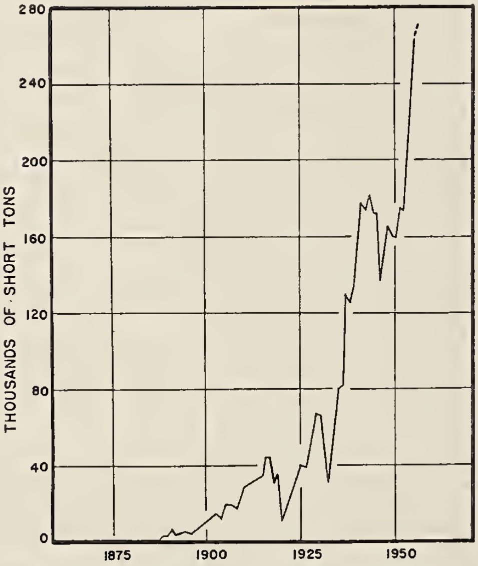

Figure 2. *World production of nickel, 1850 to 1956 [215, 337, 386, 387, 448, 449, 540, 541, 738].*

Table 2 presents data on the principal mine production of nickel for selected years representing the latter part of World War II and the periods during and subsequent to the Korean War, including recently available figures for some of the free-world 1956 production. The data illustrate the dominant position of Canadian production. In 1955, the International Nickel Company supplied 83 percent of the Canadian production, Falconbridge 12 percent, and Sherritt Gordon 5 percent. New Caledonia was second of the free-world producers, followed by Nicaro, Cuba. As explained previously the Nicaro operations were started during World War II, discontinued in 1947, and reopened in 1952. The U. S. A. production for 1955 and 1956 is from operations of the Hanna Nickel Smelting Company at Riddle, Oreg. The United States also

Table 2. *Principal mine production of nickel, short tons, in selected years [541, 660, 700, 738]*

| | 1944 | 1945 | 1950 | 1951 | 1955 | 1956 |
|---|---|---|---|---|---|---|
| Canada | 137, 000 | 122, 000 | 123, 000 | 137, 500 | 175, 000 | 179, 000 |
| New Caledonia | 8, 900 | 4, 750 | 4, 750 | 7, 350 | 17, 500 | 25, 500 |
| Cuba | 5, 140 | 12, 000 | ----- | ----- | 15, 000 | 16, 000 |
| USA | ----- | ----- | ----- | ----- | 4, 400 | 6, 100 |
| USSR (estimated) | 14, 300 | 14, 700 | 27, 500 | 27, 500 | 45, 000 | ----- |
| All others | 7, 660 | 6, 650 | 2, 750 | 2, 650 | 10, 100 | 4, 400 |
| Estimated world production [a] | 173, 000 | 160, 000 | 158, 000 | 175, 000 | 267, 000 | ----- |

[a] Includes 600 or more tons per year of nickel recovered as a by-product of copper refining at Baltimore, Md.; Carteret and Perth Amboy, N. J.; Laurel Hill, N. Y.; and Tacoma, Wash.

has an annual production of about 600 tons of nickel recovered as a by-product of the refining of copper. This is classified by the Bureau of Mines as secondary production in contrast to primary production from ores. Recovery of secondary nickel from ferrous and nonferrous alloys supplied an appreciable tonnage of nickel to U. S. industry in 1955 [700], but this figure is not included in table 2. Detailed data about Russian production have not been available for some time; the estimates in table 2 were made by the U. S. Bureau of Mines. The Union of South Africa has had a growing production, from about 500 tons of nickel per year during World War II to 1,250 tons in 1951, 2,598 tons in 1955, and 3,624 tons in 1956. During World War II, Japan [130], Finland, Sweden, and Norway had annual productions ranging from 300 to 2,000 tons, with minor production from Brazil, French, Morocco, Germany, Greece, Indonesia, and Italy but none in this group was reported to have had measurable production in 1950. Finland was reported to have produced 94 short tons in 1951, and about 400 tons in 1952 and again in 1953 [387, 541]. The same sources report that French Morocco produced less than 100 short tons of nickel in 1951, about 450 tons in 1952, and dropped to 130 tons in 1953. Brazil is reported to have resumed production of nickel ore in 1949, but the amounts reported for 1949 through 1951 were negligible and Brazil is not mentioned in the 1952 and 1953 summaries.

The United States currently consumes two-thirds to three-fourths of the annual production of nickel in the Free World [543, 738] and, consequently, a discussion of U. S. consumption may be indicative of that of the entire Free World. The demand or consumption of five major groups in the United States for the years 1946 through 1955, with an indication of the amounts requested by industry for 1956, is shown in figure 3. Interpretation of figure 3 is complicated by the fact that the total amount of available nickel varies from year to year, as shown in figure 2. Consequently, the data have been replotted in terms of percentage of the available total, in figure 4. It must be borne in mind that nickel has been in short supply and subject to allocation controls. For example, the reduction in the nickel consumed by electroplating in 1951 and 1952 was caused by an increase in the allocation of nickel to other uses, not by a decrease in the demand for electroplating. The data in figures 3 and 4 include demands for defense and nondefense purposes but do not include stockpiling.

Nonferrous alloys were the greatest consumers of nickel during this period, and the consumption by this group was maintained at a fairly constant level by changing the allocations for defense and nondefense uses. The shortage of nonferrous alloys for nondefense uses, and the uncertainty of nickel supplies, have had a serious effect on such industries as the chemical industry. Lack of assurance that maintenance and replacement parts, comparable to the original equipment, will be available, encourages designing away from nickel.

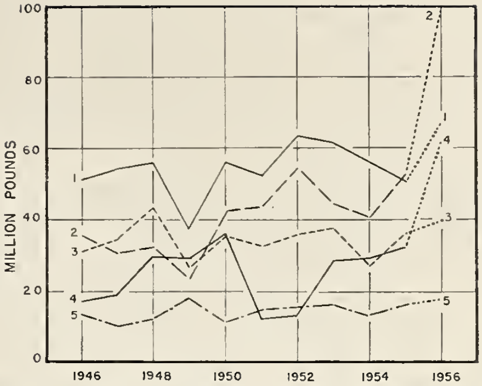

Figure 3. *Nickel consumed in the United States, 1946 to 1955, and "requested by industry" for 1956* [*543*].

Curve 1-nonferrous uses, 2-stainless steels, 3-low-alloy steels, 4-electroplating, and 5-high-temperature and electrical-resistance alloys.

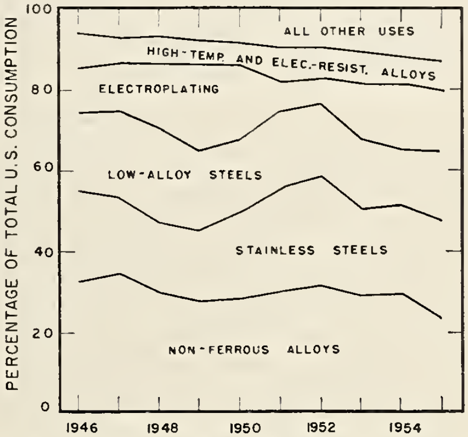

Figure 4. *Nickel consumed by major groups, 1946 to 1955* [*543*].

Nickel consumed in stainless steels reached a peak in 1952, and another in 1955. The shortage of nickel during the Korean conflict resulted in restrictive allocations, for example, in restricting the use of the popular 18:8 stainless steel in the large-consuming food and dairy industries, and in intensive efforts to substitute lower-nickel stainless steels for the standard grades. The scarcity of nickel has been emphasized repeatedly and has resulted in many engineers designing away from nickel stainless steels. Changes in technology, especially in aircraft, were cited as important factors which require an expansion of stainless-steel production. As shown in figure 3, it is estimated that the 1955 consumption of nickel in stainless steel would be doubled in 1956, if the nickel were available.

The low-alloy steels have continued to consume a fairly constant percentage of the available nickel. In spite of the uncertainty of nickel supplies, producers of low-alloy steels are optimistic concerning the prospects for expansion into new markets as well as sustained consumption in established markets.

Nickel consumed in electroplating showed a continued and substantial increase to a maximum in 1950. Application of controls and curtailment of virtually all electroplating except for defense purposes produced a drastic reduction in 1951 and 1952. Restrictions on the amount of nickel for electroplating purposes, and on the thickness of nickel that could be applied were matters of serious concern to the electroplating industry and to the users of nickel-plated products. When the demands of the defense program tapered off and more nickel became available for electroplating, the industry expanded, but great concern has been expressed over the effect of short supplies on the design away from nickel of such products as automobile parts, hardware, and cooking utensils.

The demand for nickel for high-temperature and electrical-resistance alloys reflects the growth of electrical industries and the corresponding growth in electrical equipment and appliance installations. The impact of short nickel supply was especially felt in this industry, which, due to lack of nickel, did not achieve expected levels in keeping with the expansion of the economy [543]. Apparently, in this classification the super alloys, for aircraft and jet engine use, are included in the stainless-steel group.

The demand for nickel for "all other uses", in percentage of the available supply, more than doubled from 1946 to 1955. This category includes cast irons, magnets, ceramics, thermal-expansion alloys, coinage, catalysts, electronic uses, nonmetallic forms or compounds such as oxides, sulfates, chlorides, and many other uses for defense and nondefense purposes.

## 1.5. Available Forms of Nickel

As indicated in the preceding section, approximately 80 percent of the annual consumption of nickel is for the production of ferrous and nonferrous alloys, 10 percent for nickel plating, and 10 percent for high-purity nickel and its modifications that have been developed for improved malleability or to meet requirements of particular applications. The primary forms of nickel that are available to meet these various demands are indicated in table 3. Much of the data in the table was obtained from publications of the International Nickel Company, Inc., and some of the identifications are trade-mark designations.

Carbonyl nickel is unique in that the cobalt content is negligible. The principal impurities are varying amounts of carbon and oxygen, from the decomposition of the carbonyl radical. Cubes, rondelles, and pellets, with their characteristic onion-skin structure, formerly were the major forms available for alloying purposes, but in recent years, carbonyl nickel powder has become an important item for the production of high-purity nickel and alloys. HPM nickel is a powder metallurgy product of Henry Wiggen & Company, in Birmingham, England [619]. It is produced in compacts, weighing about 15 lb., which are hot- and cold-worked to form bars, flats, rods, strip, and wire.

Electrolytic nickel supplies the great bulk 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 0.5 percent, traditionally is counted as nickel, because of the chemical and metallurgical similarities of the two metals. The intensified demand for cobalt in recent years has resulted in a number of proposals for complete separation of nickel and cobalt, by electrochemical or chemical processes other than the carbonyl process, but to date none of these has been incorporated in the commercial refining of nickel.

Electrolytic nickel is available in full-sized cathodes as deposited, approximately 28 by 38 by ⅜ in. and 145 lb in weight, and in smaller sizes, down to 1 by 1 by ⅜ in., prepared by shearing the cathode plates. Electrolytic nickel is melted and sometimes modified to produce anode material for the electroplating industry. Ingots of approximately 10-lb size are prepared by melting cathode material. There is a slight increase in impurities during the melting operation, but the ferrous metal industry prefers to use ingots rather than cathodes for alloy additions to the electric, open-hearth, and cupola furnaces. Nickel shot were used for alloying purposes before the electrolytic refining process was developed, and are still used in small scale alloy production. Shot are produced today by pouring melted electrolytic nickel into water or by high-pressure steam shotting. "XX" shot pass through a 1-in. opening and are 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 grade and 0.071 in. for the high-sulfur grade. Electrolytic nickel powder, for use in powder metallurgy applications, is produced by varying the conditions of electrodeposition from those used in electroplating.

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. Malleable nickels are available in such shapes as plate, bars, sheet, strip, rods, wire, pipes, and tubes. "A" nickel is commercially pure malleable nickel. The low-carbon grade has

TABLE 3. *Nominal composition of commercially available nickels and some alloyed nickels*

| Type | Nickel (plus cobalt) [a] | Carbon | Manganese | Iron | Sulfur | Silicon | Copper | Others |
|---|---|---|---|---|---|---|---|---|
| Carbonyl nickel [a, b] | | | | | | | | |
| | % | % | % | % | % | % | % | % |
| Grade A powder | 99.8 | 0.065 | (c) | 0.02 | 0.002 | 0.005 | (c) | 0.065 $O_2$; 0.005 Mg. |
| Grade B powder | 99.7 | .10 | -------- | .02 | .002 | .005 | ------------ | 0.2 $O_2$; 0.005 Mg. |
| HPM nickel | 99.9+ | .02 | 0.01 | .04 | .005 | .01 | 0.01 | 0.005 Mg; 0.005 Al. |
| Electrolytic nickel | | | | | | | | |
| Cathodes | 99.95 | Trace | -------- | 0.01 to 0.04 | Trace | Trace | 0.01 to 0.03 | |
| Ingots | 99.55 | 0.02 | -------- | 0.15 | 0.03 | -------- | 0.12 | |
| Shot, "XX" | 99.6 | .10 | -------- | .15 | .01 | 0.10 | .04 | |
| Shot, low sulfur | 99.7 | .03 | -------- | .05 | .01 | .10 | .02 | |
| Shot, high sulfur | 99.65 | .03 | -------- | .06 | .045 | .10 | .02 | |
| Powder | 99.+ | -------- | -------- | ------------ | -------- | -------- | ------------ | |
| Wrought nickels | | | | | | | | |
| "A" Nickel | 99.45 | 0.06 | 0.25 | 0.15 | 0.005 | 0.05 | 0.05 | |
| Low-carbon nickel | 99.55 | .01 | .20 | .15 | .005 | .05 | .05 | |
| Electronic grade A nickel | 99.60 | .04 | .15 | .10 | .005 | .05 | .03 | |
| "200" nickel | 99.15 | .06 | .15 | .10 | .005 | .05 | .03 | |
| "201" nickel | 99.05 | .02 | .30 | .10 | .005 | .10 | .05 | |
| "202" nickel | 95.40 | .03 | .07 | .05 | .004 | .02 | .03 | 3.8 W. |
| "220" nickel | 99.65 | .08 | .12 | .05 | .005 | .03 | .03 | 0.03 Mg. |
| "225" nickel | 99.55 | .06 | .12 | .05 | .005 | .20 | .03 | |
| "330" nickel | 99.60 | .09 | .20 | .05 | .005 | .03 | .03 | |
| "D" nickel | 95.0 | .08 | 4.75 | .05 | .005 | .05 | .05 | |
| "E" nickel | 97.8 | .08 | 2.0 | .05 | .005 | .05 | .05 | |
| Duranickel [d] | 93.9 | .15 | 0.25 | .15 | .005 | .55 | .05 | 4.5 Al; 0.45 Ti. |
| Permanickel [d] | 98.65 | .23 | .15 | .10 | .005 | .10 | .05 | 0.35 Mg; 0.45 Ti. |
| Casting nickels | | | | | | | | |
| Nickel | 95.6 | 0.8 | 0.8 | 0.5 | 0.008 | 1.5 | 0.5 | |
| "G" nickel | 94.2 | 1.5 | .8 | .5 | .008 | 1.5 | .5 | |
| "S" nickel | 91.5 | 0.8 | .8 | .5 | .008 | 6.0 | .5 | |

[a] The cobalt content of carbonyl nickel is negligible, within the limits of certainty of available analytical procedures. Electrolytic nickel and products derived from it have contained up to 0.5 percent of cobalt, but in the most modern practice the cobalt content is 0.1 percent or less.

[b] The principal impurities in carbonyl nickel are variable amounts of oxygen and carbon, from decomposition of the carbonyl radical.

[c] Not reported.

[d] Precipitation hardenable.

improved resistance to some types of corrosion but is valued more for its improved workability in such operations as spinning or coining. Electronic grade "A" nickel was developed to meet the requirements of the electronics industry. The nickels numbered from 200 to 330, including the 3.8-percent-tungsten alloy, were subsequently developed for the electronics industry. "D" nickel contains 4.75 percent of manganese for improved resistance to oxidizing sulfurous conditions and improved mechanical properties, but it is less resistant than "A" nickel to sulfur-free oxidizing conditions. "E" nickel contains 2 percent of manganese to reduce its susceptibility to sulfur embrittlement in furnace combustion flames. Duranickel and Permanickel are precipitation hardening or heat-treatable. According to Mudge [153], precipitation hardening of nickel may be produced by additions, separately or in combinations, of aluminum, beryllium, magnesium, molybdenum, silicon, and titanium. The two most widely used to produce precipitation hardening in nickel alloys, such as Inconel "X", are aluminum and titanium.

Casting nickel is commercially pure nickel modified for higher strength and wear resistance, with corrosion-resistance comparable to that of "A" nickel. "G" nickel contains additional carbon for improved resistance to galling. "S" nickel is even more resistant than "G" nickel to galling and wear.

American Society for Testing Materials Specification B 39–22 [513] covers four grades of virgin nickel, that is, nickel from ore or matte and not from remelted metal, for use in the production of alloys, as follows:

| | *Nickel (including cobalt)* | *Sulfur* | *Carbon* | *Iron* |
|---|---|---|---|---|
| | % | % | % | % |
| Electrolytic | 99.5 min | 0.02 max | 0.10 max | 0.25 max |
| "X" shot | 98.9 min | .05 max | .25 max | .50 max |
| "A" shot | 97.75 min | .07 max | .75 max | .75 max |
| Ingot | 98.5 min | -------- | -------- | -------- |

The electrolytic grade is suitable for the manufacture of the highest grades of malleable allows; "X" shot for the manufacture of nonferrous alloys and nickel steel; "A" shot for the manufacture of anodes; and Ingots for the manufacture of open-hearth and electric-furnace nickel steels.

In addition to the metallic forms, nickel is available as compounds, such as oxides, sulfates, chlorides, etc. Nickel oxide or sinter is produced in one of the latter steps in treating nickel ore, when roasting and fluxing have removed sulfur from the separated nickel sulfide, leaving a partially oxidized product. In modern practice the great bulk of the sinter is reduced to metallic nickel, which is electrolytically refined, but, in the early days of the industry, the sinter was the only form of nickel available for making alloys. There is still an appreciable demand for granular sinter in the production of nickel-alloyed steels, because of the price differential as compared to refined nickel.

Nickel oxide is a primary product of processes for leaching nickel from its ores, as practiced by Nicaro, Sherritt Gordon, and others, and nickel oxide is readily obtainable in the new International Nickel Company recovery process that replaced the Orford process. However, information is not yet available about the market demand for nickel oxide from these new sources. There is an appreciable demand for nickel oxide of exceptional purity and uniformity of composition, for the production of ferrites and other special products. In the past this product has been laboriously produced by processes such as the thermal decomposition of purified nickel nitrate, but in modern practice an even better oxide is easily produced by heating grade B carbonyl powder in air at about 1,550° F for 1 hr or so.

The sulfate, chloride and other compounds are used primarily in electroplating but find other uses, for example, in vitreous enameling.

## 1.6. Metallography of Nickel and Its Alloys

The primary object of metallographic examinations 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 is concerned mainly with general practices rather than with specific details.

### 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 specimen depends upon the size and shape of the material, the portion or section of the material that is of interest, and the purpose for which the study is being made. For more detailed discussion of this subject, see ASTM Specification E 3–46T [513].

### b. Preparation of Specimens

The mounted or unmounted specimen is ground on a series of emery papers of increasing fineness, mounted on revolving wheels or backed by a flat surface. The final wet polishing is done with a water suspension of magnesium oxide or levigated alumina. Electrolytic polishing has been suggested as a substitute for the final stages of grind-

TABLE 4. *Recommendations for electrolytic polishing of nickel and some nickel alloys [431, 608]*

| Bath composition | Current density | Voltage | Temperature | Time | Remarks |
|---|---|---|---|---|---|
| | *amp/cm* $^2$ | *v* | ° *C* | *min* | |
| 39 vol. sulfuric acid (conc.)<br>29 vol. distilled water | 0.4 | | 35 max | 4 to 6 | Mix reagents carefully. |
| 1 vol. perchloric acid [a]<br>2 vol. acetic acid | | 50 | 18 | 1 | (a) |
| 1 vol. nitric acid<br>2 vol. methyl alcohol | 0.75 to 1.5 | 40 to 50 | 20 to 30 | Less than 1 | General use, nickel and several alloys. Cooling necessary because of high current density. |
| 144 ml ethyl alcohol<br>10 g anhydrous aluminum chloride<br>45 g anhydrous zinc chloride<br>16 ml *n*-butyl alcohol<br>32 ml water | | 23 to 25 | Room | Successive periods of 1 min. | Satisfactory only for small samples (less than 5 cm² in area). Good polish usually obtained in 5 cycles. |
| 18.5 vol. perchloric acid [a]<br>76.5 vol. acetic anhydride<br>5.0 vol. distilled water | | 50 | Below 30 | | Current density established by experiment. |
| Urea containing:<br>$NH_4Cl$ 5 to 20% by wt<br>$NiCl_2$ 0 to 3.5% by wt | 0.015 to 0.04 | 2.5 to 3 | 120 to 135 | | An induction period, when nickel dissolves normally, is followed by a sudden rise in cell potential when polishing begins. |
| 37 vol. orthophosphoric acid<br>56 vol. glycerol<br>7 vol. distilled water | 0.15 | | 50 to 70 | | For nickel-silver alloys. |

[a] Extreme precautions must be observed in the preparation and use of solutions containing perchloric acid and acetic acid, and particularly if the latter is in the form of acetic anhydride. The ASM Committee on Metallography lists such solutions as DANGEROUS; Dr. Smithells states that "It cannot be too strongly emphasized that explosions have occurred, using perchloric acid mixtures, under *normal* operating conditions in which *every precaution was apparently taken.* Such solutions are thus to be regarded as at all times *potentially explosive.*"

ing and the two wet polishing operations. Many baths and combinations of operating conditions have been investigated, particularly in attempts to avoid the hazards associated with the use of perchloric-acetic acid mixtures. Orthophosphoric acid baths, as was pointed out by Jacquet [283], are not satisfactory for nickel, but are used for some of the nickel alloys. Some of the baths and operating conditions recently suggested for electrolytic polishing of nickel and some of its alloys are listed in table 4.[3]

In general, polished metal does not reveal the crystalline structure, and etching must be used to delineate the structure and to produce optical contrast among 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.

Table 5 lists some of the immersion- or electrolytic-etchants currently in use for nickel and some of its alloys, from the recommendations of ASTM Specification E 3–46T, and the tabulation by Smithells.

### c. Metallographic Examination

The technique of using a microscope is complicated, and the aims of the microscopic examination of metallic specimens are many and varied. Consequently, coverage of this broad field will not be attempted. Instead, the reader is referred to the numerous texts on metallography and the use of a microscope, or to ASTM specifications or recommendations, for example, ASTM Method E 91–51T describes three methods for estimating the average grain size of polished and etched specimens of nonferrous metals, including nickel [513].

TABLE 5. *Etching reagents for nickel and its alloys* [*513, 608*]

| Reagent | Composition [a] | Remarks |
|---|---|---|
| Flat solution | $HNO_3$ 50 ml<br>Glacial acetic acid 50 ml | Make up fresh daily. Etch by 5 to 20 sec immersion at room temperature. For nickel, monel, and nickel-copper alloys. For alloys with less than 25% Ni, dilute with acetone. |
| Electrolytic-contrast | $HNO_3$ 10 ml<br>Glacial acetic acid 5 ml<br>$H_2O$ 85 ml | 20 to 60 sec at 1.5 v. For grain size, grain contrast etching. |
| Electrolytic-sulfuric | $H_2SO_4$ 5 ml<br>$H_2O$ 95 ml | 5 to 15 sec at 3 to 4.5 v. For nickel and Inconel. |
| Aqua regia | $HNO_3$ 5 ml<br>$HCl$ 25 ml<br>$H_2O$ 30 ml | Etch by immersion, 30 sec to 2 min. For Inconel. |
| Nitric-hydrofluoric | $HNO_3$ 20 ml<br>HF (48%) 15 drops | Immerse warm specimen for 15 to 45 sec. For Inconel. |
| Nitric acid | $HNO_3$ 30 ml<br>$H_2O$ 70 ml | Immersion macro-etch. For nickel silver. |
| Potassium cyanide | $KCN$ 5 g<br>$H_2O$ 95 ml<br>$H_2O_2$ Few drops | Immersion etch. For low-zinc nickel silver. |
| Ammonium hydroxide-hydrogen peroxide | $NH_4OH$ 85 ml<br>$H_2O_2$ 15 ml | Immersion etch. For high-zinc nickel silver. |
| Nitric-acetic acid-acetone | $HNO_3$ 10 ml<br>Glacial acetic acid 10 ml<br>Acetone 10 ml | Immersion etch. For pure nickel, cupro-nickel, Monel and nickel silver. |
| Hydrochloric acid-ferric chloride | $HCl$ 30 or 20 ml<br>$FeCl_3$ 10 or 10 g<br>$H_2O$ 120 or 30 ml | Immersion etches. For pure nickel. |
| Sodium hyposulfite-hydroxide-hydrochloric acid | Solution A:<br>$Na_2S_2O_4–2H_2O$ 10 g<br>$H_2O$ 90 ml<br>or<br>$NaOH$ 10 g<br>$H_2O$ 90 ml<br>Solution B:<br>$HCl$ 10 ml<br>$H_2O$ 90 ml | Double electrolytic etch. Specimen is made cathode in solution A for 5 to 10 sec at 10 v and 0.25 amp/cm², then made anode in solution B for 8 to 10 sec at 10 v and 0.1 amp/cm². For nickel-chromium alloys. |
| Ammonium molybdate-hydrochloric-nitric acid | $(NH_4)_2\,MoO_4$ 50 g<br>$HCl$ 100 ml<br>$HNO_3$ 75 ml<br>$H_2O$ 825 ml | Electrolytic etch, 12 v and 0.003 amp/cm². For nickel-rich alloys. |
| Dimethyl-glyoxime | Saturated solution in ethyl alcohol, containing 2 to 3 ml of a 1:9 HCl solution per 100 ml. | Electrolytic etch. Formation of a film promotes uniform etching of anode. For electrodeposited nickel. |

[a] The use of concentrated reagents is intended, unless otherwise indicated.

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[3] In a private communication, R. A. Kozlik states that current practice at the Inco Research Laboratory, Bayonne, N. J. does not use electrolytic procedures for polishing or for etching. The preferred etchant is the Jewett-Wise reagent, a mixture of equal parts of aqueous 10-percent potassium cyanide and 10-percent ammonium persulfate.

# 2. Nickel: Properties and Uses

## 2.1. 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 for most of its corrosion reactions. 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 of nickel but the differences disappear as corrosion proceeds [617].

(1) *Water.* Distilled water and ordinary tap water have neglible effects, and nickel exhibits satisfactory resistance to corrosion by water even at 500° F under pressure of 2,000 psi and at velocities up to 30 fps [447]. In general, salt and brackish waters are more corrosive than fresh waters, but nickel and its alloys find many uses under marine conditions. As long ago as 1928, Friend [37] 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. A report by May and Humble [353] 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 0.005 in./yr in air-free acid to about 0.05 in./yr in air-saturated acid. Nickel is rarely useful in contact with hot sulfuric acid of concentrations greater than about 15 percent [140].

With cold hydrochloric acid the rates vary according to the air content, from 0.01 to 0.04 in./yr in dilute acid to 0.06 to 0.08 in./yr in concentrated acid. Nickel is rarely useful in handling hot HCl of more than 2-percent concentration [140, 774].

Nickel is resistant to pure phosphoric acid at room temperature but is corroded when the acid contains oxidizing impurities such as ferric compounds.

Nickel is corroded strongly by sulfurous acid except for very dilute solutions.

Strongly oxidizing acids, such as nitric acid corrode nickel. The recent work of Berg [630] 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.

Nickel is strongly resistant to alkali solutions, for example, in boiling 50-percent sodium hydroxide the rates of corrosion are less than 0.001 in./yr [140, 249, 677], but nickel is appreciably attacked by ammonium hydroxide in concentrations greater than about 1 percent. The well-known ability of molten NaOH 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 molten sodium hydroxide, as a heat transfer agent in nuclear reactors [327, 595, 670, 732]. These investigations showed that molten sodium hydroxide can be handled in nickel containers at all temperatures up to about 1,000° F, but at 1,200° to 1,500° F the circulating system becomes plugged with deposited nickel. The Development Division of the International Nickel Company reports that, in commercial production of caustic, nickel containers are useful at 1,200° F.

Nickel resists corrosion by neutral and alkaline salt solutions, with rates usually less than 0.005 in./yr. Nonoxidizing acid salts are only moderately corrosive with rates seldom higher than 0.02 in./yr. 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 [140]. Gurovich [460] reported that the magnitude and rate of corrosion in molten alkali chlorides varied with the cation radius; nickel lost 1.3 g/m$^2$ hr in KCl and 4 g/m$^2$ hr in LiCl. Gurovich [672] reported on reactions of nickel with molten nitrates of the alkali metals. Treseder and Wachter [208] 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.

(3) *Organic Acids and Compounds.* Neutral and alkaline organic compounds have virtually no effect on nickel, and organic acids are only mildly corrosive [140]. Nickel is not attacked by fatty acids or soap and is widely used in their processing [137, 184]. The corrosion of nickel by acetic acid is very slight [137]. In the production of low- and medium-priced jewelry, for example, watch bracelets, no single substitute has yet been found with the general usefulness of nickel in resistance to synthetic and natural perspiration [696].

(4) *Atmospheres.* The 20-year atmospheric-exposure tests conducted by the American Society for Testing Materials included exposure of plates of 99+ nickel at industrial locations (Altoona, Pa., and New York City), a marine location receiving 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 [538] and summarized in table 6 and figure 5, showed that nickel is very resistant to corrosion at marine and rural locations, with surface penetration of less than 0.00001 in./yr, based on losses in weight. Even in severe industrial atmospheres the surface loss is less than 0.00025 in./yr. In all cases the corrosion was constant with time, and the corro-

Table 6. *Results of ASTM 20-year atmospheric exposures of 99+ nickel plates [538]*

| 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 | 140.73 | 0.164 | 0.222 |
| New York | 564 | 40.56 | 93.28 | .137 | .144 |
| Sandy Hook | 562 | 9.35 | ------ | .0313 | ------ |
| Key West | 562 | 1.49 | 2.55 | .0050 | .0041 |
| La Jolla | 564 | 1.38 | 3.32 | .0047 | .0058 |
| State College | 565 | 1.95 | 5.44 | .0066 | .0085 |
| Phoenix | 563 | 0.38 | 0.88 | .0013 | .0015 |

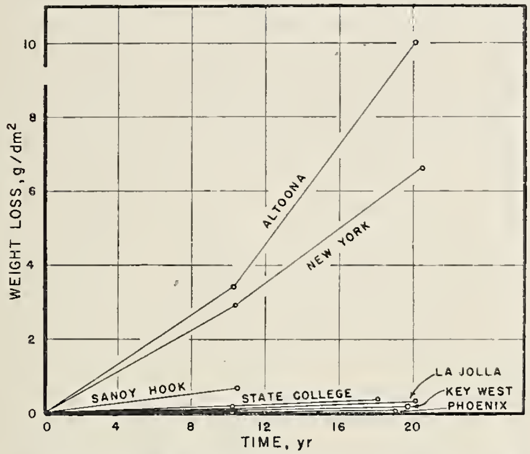

Figure 5. *ASTM 20-year atmospheric exposures of 99+ nickel plate [538].*

sive 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 yr. The corrosion rates corresponded with those of the ASTM industrial locations, but the Bayonne results showed that sheltered specimens corrode more than boldly 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 0.0034 in. for a sheet exposed 12 yr in the exposed vertical position and 0.0014 in. for a sheet exposed for 20 yr 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 [270].

(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 [140]. In wet hydrochloric acid, corrosion begins at isolated points, which increase in number with increasing time [333]. Nickel is resistant to fluorine and fluorides, but this resistance is decreased in the presence of moisture and the consequent formation of hydrofluoric acid [281, 348]. 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 [140]. 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 [600]. The reaction of nickel and molten sulfur follows a parabolic law between 205° and 445° C, forming $Ni_3S_2$ or $Ni_6S_5$ [545].

(6) *Oxidation.* When heated in oxidizing atmospheres, nickel forms a superficial, tightly adherent scale at temperatures below 1,400° F, and its resistance to excessive oxidation makes nickel useful at higher temperatures [140]. The rate of oxidation of nickel in air or oxygen essentially follows a parabolic law, and the purer the nickel the lower the rate [238, 293].

Some data for the oxidation rates of 99.95-percent nickel at temperatures from 550° to 1,260° C and at different oxygen pressures are presented in table 7. The solubility of oxygen in molten nickel, according to Wriedt and Chipman [624], varies from 0.294 weight percent at 1,450° C to 1.63 weight percent at 1,691° C. In a later paper [751], the same authors discuss equilibrium of hydrogen and oxygen with molten nickel, iron, and their alloys.

Table 7. *Rates of oxidation of 99.95-percent nickel [459, 752]*

| Temperature | Oxygen pressure | Parabolic rate law constant |
|---|---|---|
| ° *C* | *cm of* Hg | $g^2\ cm^{-4}\ sec^{-1}$ |
| 550 | 7.6 | $1.08 \times 10^{-14}$ |
| 600 | 7.6 | $5.23 \times 10^{-14}$ |
| 625 | 7.6 | $6.83 \times 10^{-14}$ |
| 650 | 7.6 | $1.46 \times 10^{-13}$ |
| 700 | 7.6 | $5.08 \times 10^{-13}$ |
| 980 | 76 | $1.14 \times 10^{-10}$ |
| 1,096 | 76 | $5.48 \times 10^{-10}$ |
| 1,260 | 76 | $34.1 \times 10^{-10}$ |

### b. Adsorption and Diffusion of Gases

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 particularly important in the use of nickel as a catalyst. In general, the amount of gas taken up by nickel increases markedly with decreasing temperature and mildly with increasing pressure, but the mechanism of the adsorption and absorption reactions has not been completely clarified. Baker, Jenkins, and Rideal [521] 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 [522] 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.

The amounts of hydrogen and other gases adsorbed by nickel are greatly in excess of their true solubilities. Meyerson [237] presented results from numerous sources to show that the solubility of hydrogen in solid nickel varies from about 0.0002 weight percent at 300° C to 0.0008 percent at 900° C.

Some gases, notably hydrogen, can diffuse through solid nickel. It was reported [246] 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 [568] 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.

### 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, and the preparation of edible oils and fats accounts for more than two-thirds of the consumption of nickel as a catalyst, but Fraser [77] in 1937 listed approximately 40 fields in which nickel catalysts were used, and the list is 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, reactions of carbon monoxide with aromatic halogen compounds, and the manufacture of hydrazine from urea.

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 [129], 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 2 weeks before its activity becomes appreciably affected. Ipatieff and Pines [229] 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 [296]. The mechanism 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 [296] and were reviewed by Yasumura [372], who cited some 60 references. Baker, Jenkins, and Rideal [521] believed that chemisorption and energy of activation were important factors and that solution in the lattice was not involved, although lattice spaces or vacancies might be. Smith, Chadwell, and Kirslis [607] 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. Similar conclusions were reported by Sultanov [612], and recent studies of Raney catalysts were reported from Japan [570, 582]. In film catalysts available evidence indicates the presence of a catalytically active nickel-hydrogen layer [725].

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 [296] or by an excess of alkali [582].

### d. Electrolytic Solution Potential: Passivity

Values for the electrolytic solution potential of nickel are −0.227±0.002 v at 20° C [60], and −0.231±0.002 v at 25° C [42]. Values of −0.2508 v at +18° C and −0.2496 at 25° C were reported for powdered nickel in 1*N* solution of nickel sulfate [39].

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 anodes in electroplating.

### 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 [181]. It was shown 30 years ago [31] 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 [213]. 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 [251]. 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 [31].

Some operators of industrial electroplating equipment have suffered from exzematous dermatitis in varying degrees, from contact with nickel-containing solutions and fumes [31, 494], and there have been occasional reports of "nickel poisoning" resulting from the inhalation of dust, for example, in polishing operations [31] or in the production of alkali-cadmium-nickel storage batteries [222]. Modern knowledge of industrial hygiene, improved ventilation, and the use of protective equipment have practically eliminated the danger of "nickel poisoning" in such operations.

The one really dangerous industrial compound of nickel is nickel carbonyl, $Ni(CO)_4$, that is prepared in large quantities in one of the processes for refining nickel and that has industrial uses. The compound is a gas at ordinary temperatures. When nickel carbonyl is present in human lungs, in the presence of moisture the compound dissociates 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 [31, 181, 396]. According to Fairhall [181], the threshold limit of one part of nickel carbonyl per million parts of air in the atmosphere of work rooms was established by the 1949 American Conference of Governmental Industrial Hygienists. In recent years the compound known as BAL (2, 3-dimercaptopropanol) has been found to be an excellent antidote for nickel-carbonyl poisoning [503]. An excellent review of the toxicity of nickel carbonyl is contained in a pamphlet [598] obtainable from the International Nickel Company, Inc.

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 radiations from irradiated nickel (and other metals) are discussed in a recent bulletin issued by the International Nickel Company [749].

## 2.2. Physical Properties

The properties reported here and in subsequent sections are those of 99.95-percent nickel, unless otherwise indicated. See also [775]. Most of the determinations were made on polycrystalline specimens, but monocrystalline specimens have been prepared by slow cooling from the molten state [209], by vacuum-melting [410], and by controlled freezing of the molten metal in a horizontal boat [384]. Crystals 3 mm in diameter and 25 cm in length were prepared [504] by a modified Bridgman method. Monocrystalline "whiskers" of nickel can be grown [635], by condensation of the freshly formed vapor from reduction of halide compounds, but perfect or nearly perfect whiskers are rarely as large as 8 microns, and consequently information in regard to the properties of nickel whiskers is as yet very scarce.

### 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 58.69, representing a composite of the 5 stable isotopes. The natural abundances of the stable isotopes, as reported by White and Cameron [167] and by Brosi [324], 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 molecules, as indicated by the values for packing fraction and nuclear binding energy reported by White and Cameron [167], Duckworth and coworkers [217, 218], and Wapstra [310]. The technique for separating the stable isotopes was developed by Keim [284], 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 [324, 398], 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 of 0.16 sec for $Ni^{54}$, about 6 days for $Ni^{56}$, 36 hr for $Ni^{57}$, approximately 100,000 yr for $Ni^{59}$, about 85 yr for Ni$^{63}$, 2.6 hr for Ni$^{65}$, and 56 hr for Ni$^{66}$. Brosi [324] discussed the decay mechanisms and predicted that Ni$^{63}$ will probably 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 [527], from Atomic Energy Commission publications, as shown in table 8. The reaction cross sections (1 barn= $10^{-24}$ cm$^{2}$) refer to cases in which the neutron is not re-emitted, that is, to (n, γ) 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 an (n, γ) 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. [225], Hildebrand and Leith [227], Grimeland et al. [279], Pomerance [297], Chilton, Cooper, and Harris [442], and Nereson and Darden [481]. Scattering of 1-Mev neutrons was discussed by Walt and Barshall [508] and inelastic scattering of monoenergetic neutrons by Kiehn and Goodman [467].

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 [445].

Table 8. *Thermal neutron cross sections of nickel and its isotopes [527]*

| Element | Isotope | Reaction cross sections (for neutron velocity of 2,200 m/sec)[a] | | Scattering cross sections average |
|---|---|---|---|---|
| | | Absorption | Activation | |
| | | *Barns* | *Barns* | |
| Ni | ---------- | 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$^{64}$ | ---------- | 2.6±0.4 | |
| | Ni$^{65}$ | ---------- | 6±3 | |

[a] In a private communication to F. M. Wise of the International Nickel Company, L. Goldring stated that bombardment of Ni$^{58}$ with fast neutrons produces an absorption reaction cross section of 0.055 barn and yields Co$^{58}$.

(3) *Crystal Form and Lattice Constant.* The normal crystal form of nickel is face-centered-cubic at all temperatures. Jette and Foote's [68] value for the lattice constant, 3.5168 A at 24.8° C, has been generally accepted. Wise [168] expressed this as 3.5238 A at 20° C. Recently Von Batchelder and Raeuchle [507], used Jette and Foote's procedure and found that the lattice constant of nickel was 3.5238±0.0003 A at 25° C, and increased with increasing temperature to 450° C in agreement with established linear-expansion data. Hazlett and Parker [465] determined the lattice constant of nickel at 25° C to be 3.5241 A, and determined the effect on this value of addition of alloying elements in the solid-solution range, as shown in figure 6.

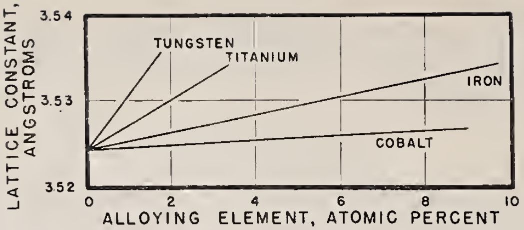

Figure 6. *Effect of some alloying elements on the lattice constant of nickel [465].*

Another crystal form of nickel, hexagonal close-packed, has been observed in thin films of nickel prepared by cathode sputtering or by vacuum distillation [43, 48, 90, 256], in the mixed structure of certain electrodeposits [255], and as a result of the bombardment of cubic nickel with energy of the order of 12 kv [740]. Finch and coworkers [550] 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 unusual crystal forms to revert to the normal face-centered cubic form.

(4) *Density.* The density of nickel, computed from atomic data, is 8.908 g/cm$^{3}$ at 20° C, according to Fraser [337]. Direct determinations of the density of nickel are affected by the composition, physical condition, and prior treatment of the specimen; for example, Jordan and Swanger [45] reported the density of 99.94 nickel as 8.907 g/cm$^{3}$ at 23° C in the cast condition, and 8.900 to 8.903 g/cm$^{3}$ for the same material cold-swaged and annealed. Subsequent investigations [329, 642] showed that discontinuities or vacancies in the lattice structure of nickel may be created by cold deformation and may disappear during annealing at temperatures below the recrystallization temperature.

The effect of composition on the density of nickel is illustrated by data from Metals Handbook (ASM) for some of the commercial forms of nickel. The density of "A" nickel is 8.885 g/cm$^{3}$, of "D" nickel 8.78 g/cm$^{3}$, of Duranickel 8.26 g/cm$^{3}$, and of cast nickel 8.34 g/cm$^{3}$, all at 20° C.

### b. Optical Properties

(1) *Reflection, Transmission, and Absorption.* The ability of polished nickel to reflect a large percentage of the light incident upon it was summarized by Meyerson [237] 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 A to about 90 percent for wavelengths of about 40000 A. Some data presented by the Mond Nickel Co., Ltd., [256] are reflectivities of 41.3 percent for 0.30-micron wavelength (ultraviolet), 64 percent for 0.55 micron (yellow-green), 83.5 percent for 2 microns, and 87 percent for 3 microns, the last two representing wavelengths in the infrared region.

Nickel films thicker than 100 A 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 A, imparting a green color to the film [243].

Values for the refractive index and absorption coefficient of nickel for various wavelengths of light are shown in table 9. The X-ray diffraction patterns obtained from powdered nickel were recorded by Swanson and Tatge [421].

Table 9. *Refractive index (n) and absorption coefficient (k) of nickel for different wavelengths of light [237]*

| Wavelength | $n$ | $k$ | Wavelength | $n$ | $k$ |
|---|---|---|---|---|---|
| *A* | | | *A* | | |
| 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 | | | |

(2) *Emissivity; 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 1,000° C. The emissivity for monochromatic light of 0.65-micron wavelength is 0.355 [256]. Lund and Ward [352] presented data for variations in the emissivity of nickel from 1,000° to 1,300° C.

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 A. Burns and Sullivan [135] measured 230 lines, in the vacuum-arc spectrum, between 1981 and 2991 A, and Gatterer, Junkes, et al. [185] presented charts of the arc and spark spectra of nickel and other metals. A tabulation of the wavelengths, between 2000 and 10000 A, of approximately 500 of the principal lines in the emission spectrum of nickel is presented in the Handbook of Chemistry and Physics [563]. Moore [354] 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 A [101].

### c. Thermal Properties

(1) *Melting Point; Heat of Fusion.* The generally accepted value for the melting or freezing point of pure nickel is based on determinations made at the National Bureau of Standards on 99.94-percent nickel, as reported by Jordan and Swanger [45]. Although they reported 1,455° ± 1° C on the International Temperature Scale of 1927, the value of 1,453° C was assigned to the freezing point of nickel as a secondary fixed point on the International Temperature Scale of 1948 [206], because of slight changes in the constants of the radiation equations. The presence of impurities or alloying elements tends to lower the melting point of nickel and to convert the melting point to a melting range. For example, malleable nickels "A" and "low carbon" both contain 99 percent of nickel and melt at 1,440° ±5° C.

The latent heat of fusion is 73.8 cal/g for 99.95-percent nickel [168]. Smirnova and Ormont [362] reported that the surface tension of nickel at the melting point was 1,756 d/cm.

(2) *Boiling Point.* The boiling point of nickel is too high to permit direct determinations and is estimated by extrapolation of vapor-pressure data. Wise [168] reported 2,730° C for the boiling point of nickel. Some values for the vapor pressure of nickel are $1.2 \times 10^{-6}$ mm of mercury at 1,000° C, $9.4 \times 10^{-3}$ at the melting point, and 213 mm at 2,000° C [256.]

(3) *Specific Heat.* The specific heat of nickel at any temperature represents a combination of lattice vibration, a magnetic effect, and a residual portion. Sykes and Wilkinson [88] determined the specific heat of vacuum-melted Mond pellets from 60° to 600° C. Busey and Giauque [325] 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. Krauss and Warncke [580] used vacuum-melted carbonyl nickel of 99.97 purity and covered the range from 180° to 1,150° C. The work of these authors has been combined in figure 7, and some

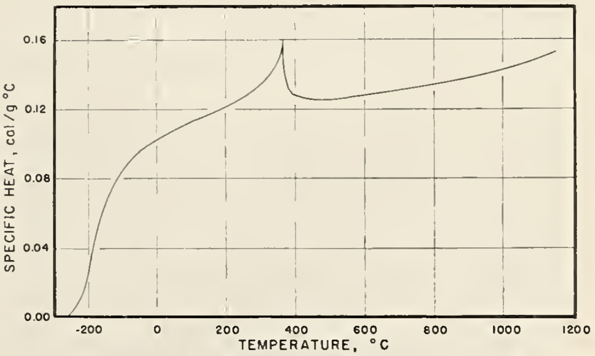

Figure 7. *Specific heat of high-purity nickel [88, 325, 580]*

of the numerical values used in plotting the curve are recorded in table 10. The sharp maximum at the Curie point occurs at 358° C according to Sykes and Wilkinson, and at 357.2° C according to Krauss and Warncke.

Table 10. *Specific heat of high-purity nickel [88, 325, 580]*

| 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 |
| 1,150 | .1525 |

Rayne and Kemp [722] discussed measurements of the heat capacity of nickel and reported that their own determinations on high-purity nickel at liquid-helium temperatures, 1.5° to 4.2° K, agreed with results reported by Busey and Giauque [325].

(4) *Thermal Expansion.* Nickel expands with increasing temperature at a regular rate except 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 the thermal expansion of pure nickel.

Figure 8 records results obtained on 99.9-percent nickel at low temperatures by Nix and MacNair [97], 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 [45] and summarized in table 11, have been the basis for numerous summaries of the average coefficient over specific temperature ranges. Owen and Yates [73] reported higher numerical values as a result of X-ray measurements of the lattice constant of 99.98-percent nickel, but a recent determination [507] of the lattice constant over the range from 24° to 455° C confirmed Hidnert's results.

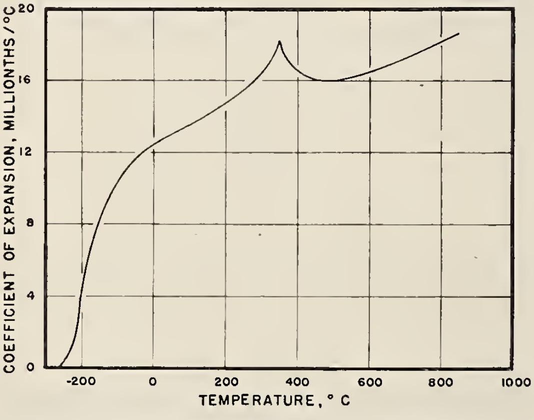

Figure 8. *Thermal expansion of nickel [45, 97].*

Table 11. *Thermal expansion of 99.94-percent nickel [45]*

| 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 | | |

Some values for the spot coefficient at specific temperatures, according to Fraser [337], are

20° C, 12.5 millionths per ° C
100° C, 13.5 millionths per ° C
300° C, 16.3 millionths per ° C
400° C, 16.3 millionths per ° C.

(5) *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 in the varying results obtained recently in measurements at very low temperatures. Kemp, Clemens, and White [686] concluded that, at these low temperatures, thermal conduction in pure nickel is almost completely electronic.

Figure 9 shows results obtained by Van Dusen and Shelton [64] for 99.94-percent nickel over the range 25° to 575° C and by Kemp, Klemens, and White [686] for 99.99+-percent nickel at very low temperatures. The two dashed curves for commercial-purity nickel show that the effect of impurities on the thermal conductivity is most pronounced at extremely low temperatures. The low-temperature curve for commercial-purity nickel represents data from low-carbon nickel obtained by Powers, Schwartz, and Johnston of Ohio State University, according to Powell and Blanpied [492]. The other commercial-purity curve was reported by Van Dusen and Shelton as representing commercial malleable nickel. Some values based on those of Van Dusen and Shelton for 99.94-percent nickel, but expressed [256, 337] in calories per second rather than in watts are

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

According to Geiger [142] and Mudge [153] the thermal conductivity, 0° to 100° C, of "A" nickel is 0.145, and of "D" nickel is 0.115 cal per cm sec ° C.

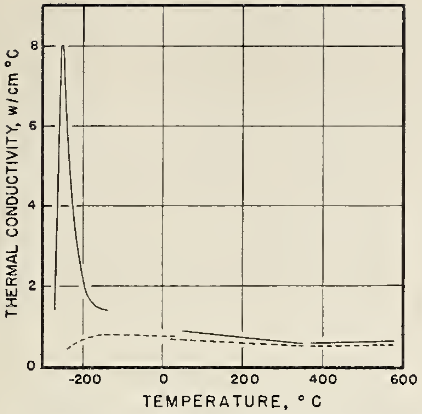

Figure 9. *Thermal conductivity of high-purity (solid lines) and commercial-purity (broken lines) nickel [64, 492, 686].*

Sedles and Danielson [497] computed the thermal diffusivity of 99.95-percent nickel at 25° C as almost 0.23 $cm^2/sec$, of 97.92-percent nickel as 0.12, and of "D" nickel as 0.105. Hoffman, Pikus, and Ward [679] studied the self-diffusion coefficient of high-purity nickel over the range from 870° to 1,248° 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 [287, 590, 735].

(6) *Thermionic Properties.* Thermionic properties of nickel are those properties that make nickel useful for ion emission in vacuum tubes. Nickel sheet is used for anodes in low-power tubes [313]. Cathodes usually are oxide-coated nickel, but cathodes formed by powder metallurgy techniques from sintered nickel powder and alkaline earth oxides [403] or from carbonyl nickel powder, nickel plus about 4 percent of tungsten, or nickel plus 2 percent of titanium [441] have been recommended. Several grades of nickel for electronic use were included in table 3.

Cardwell [178] reported that the thermionic properties of a spectroscopically pure nickel filament became stable only after heat treatment for 1,500 hr at temperatures up to 1,200° C. Wohlfarth [169] 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 [221] and by Blankenfeld [264]. The amount of carbon present and the rate of its diffusion in nickel are of interest in the activation of oxide-coated thermionic cathodes. Lander, Kern, and Beach [349] reported that the solubility of carbon in nickel, between 700° and 1,300° 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 the diffusion rate of carbon by the equation $\log D=0.909-20{,}200/T$, where $D$ is the diffusion coefficient in square centimeters per second.

The thermionic properties of nickel were summarized by Wright [313] as follows:

Work function, $\phi,=5.0$ electron volts,

Temperature, $T_e$, where vapor pressure is $10^{-5}$ mm $=1{,}330°$ K,

$$\frac{\phi}{T_e}\times 10^3=3.78.$$

### d. Electrical Properties

(1) *Electrical Resistivity.* The resistivity of nickel is negligible at extremely low temperatures, but increases with increasing temperature, with a change in the slope of the curve in the vicinity of the Curie temperature, as shown in figure 10. Numerical values for the resistivity at various temperatures are presented in table 12. Somewhat higher values for annealed nickel at low temperatures were reported by Broom [323], and the resistivity of very thin films, for example, vapor-deposited on glass, is 3 to 10 times that of compact metal [414].

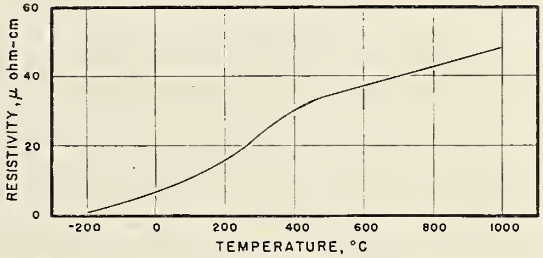

Figure 10. *Electrical resistivity of high-purity nickel [168, 256, 337].*

Table 12. *Electrical resistivity of high-purity nickel [168, 256, 337, 651]*

| Temperature | Resistivity | Relative resistivity | Temperature | Resistivity | Relative resistivity |
|---|---|---|---|---|---|
| *° C* | *Microhm-cm* | $R_t/R°$ | *° C* | *Microhm-cm* | $R_t/R_0$ |
| −200 | 0.49 | 0.08 | 400 | 30.6 | 4.99 |
| −100 | 2.82 | .46 | 500 | 34.2 | 5.57 |
| 0 | 6.141 | 1.00 | 600 | 37.2 | 6.06 |
| 20 | 6.844 | 1.11 | 700 | 39.9 | 6.50 |
| 100 | 10.3 | 1.68 | 800 | 42.8 | 6.97 |
| 200 | 15.8 | 2.57 | 900 | 45.5 | 7.41 |
| 300 | 23.0 | 3.75 | 1,000 | 48.3 | 7.86 |

The resistivity of nickel is increased by other factors than increasing temperature. The effect of impurities and relatively small amounts of alloying elements is illustrated by the values of 6.844, 9.5, and 14 microhm-cm for the resistivities at 20° C of high-purity nickel, "A" nickel, and the nickel-manganese "D" alloy, respectively, [142]. Bridgman [320] found that the resistivity of a single crystal of high-purity nickel decreased with increasing pressure, as follows:

| Pressure *kg/cm²* | Relative resistivity $R/R_0$ |
|---|---|
| 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 Poissons ratio [271], and the strain coefficient of resistivity of nickel can be qualitatively explained by the free-electron theory [469]. Broom [322] found that the longitudinal and transverse resistivities in cold-rolled nickel are equal. According to Potter [50] and Matuyama [62], 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 room temperature. Smit [303] 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 [499].

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 [337] and of "A" nickel from 0.004 to 0.006 [256]. The temperature coefficient of resistance of very thin films of nickel is negative, passing through zero and becoming positive as the thickness of the film increases [407, 418, 721].

(2) *Thermal Electromotive Force.* Nickel is thermoelectrically negative to platinum, i. e., in a simple thermoelectric circuit of these two metals the current at the cold junction flows from the platinum to the nickel. Iron, copper, gold, silver, and numerous other metals, which are positive to platinum, develop higher emf with nickel than they do with platinum, but, in spite of this, nickel is not one of the most common thermocouple materials.

Values for the thermal emf of nickel with several metals at various temperatures are shown in figure 11. Values for nickel-copper thermocouples, reported by Pecheux [16] are very similar to the values shown for nickel-silver. In a recent study, Mortlock [406] observed the effect of elastic tensile strain on the thermoelectric power of high-purity nickel from 20° to 400° C. Bridgman [439] showed that pressures up to 12,000 kg/cm² had a slight but consistent effect on the thermal emf of nickel. The effect of magnetic fields of different intensities was studied by Yamanaka [82]. The effect of magnetization on the thermoelectric power of a single crystal of 99.2-percent nickel is always positive except near the Curie point, but varies with different orientations within the crystal [478].

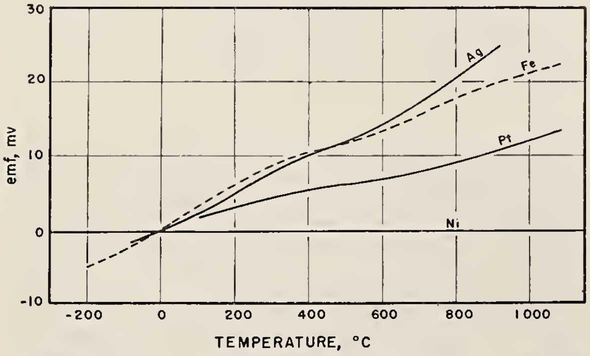

FIGURE 11. *Thermal electromotive force of nickel against platinum [44], silver [17], and iron [136].*

Effects associated with the development of thermal emf in nickel and other metals, i. e., the Peltier and Thomson effects, are discussed in the Smithsonian Physical Tables [499].

### e. Magnetic Properties

(1) *General.* Nickel is ferromagnetic at ordinary temperatures, but at moderately elevated temperatures it becomes paramagnetic. The magnetic properties of nickel and other ferromagnetic metals are affected by atomic factors and by the chemical and physical condition, and much of the recent work on nickel has been concerned with the theory of magnetic behavior. Bozorth discussed theories of magnetization in his book [266] and in a subsequent paper [526]. Forrer [336] showed that, under certain conditions, the magnetic properties of nickel and its alloys were functions of the distance between atoms having magnetic moments. Hunt [394] found a high degree of coordination of the magnetic properties of nickel with the collective-electron theory. The formation of ferromagnetic domains in single crystals of nickel, their identification through Bitter patterns, and the effect of grain boundaries have been reported by several investigators [290, 378, 659, 684]. Unterwiser [741] reported that the structure of a magnetic domain may be altered by mechanical stress, with accompanying dissipation of energy and even an alteration in the direction of magnetization. Dietrich and Kneller [653] discussed the effect of plastic deformation on the magnetic properties of nickel single crystals Tebble and Newhouse [423] reported that the Barkhausen effect is associated with movements of 180° rather than 90° boundaries. Went [312] associated the spontaneous magnetization of nickel with an order-disorder phenomenon of magnetic moments. Huzimura [681] discussed the magnetic after effect in terms of the retardation of irreversible magnetic wall displacement.

(2) *Curie Point.* The Curie point for nickel, the temperature at which the change from ferromagnetism to paramagnetism occurs, is affected by numerous factors including the prior mechanical and thermal treatment of the specimen, the nature and amount of impurities present, and the method of determination.

The Curie point for high-purity nickel occurs between 350° and 360° C. A value of 353° C was reported for 99.94-percent of nickel, 360° C for "A" nickel [256, 337, 651], and 357° or 358° C for high-purity nickel [88, 580]. The Curie point is lowered slightly by tensile stresses [172] and is raised by pressure at the rate of 0.35° per 1,000 atmospheres [484]. Bader [377] 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 12. Small heat changes accompany the magnetic transition [132] and this effect for nickel has been reported by various observers as 0.65, 1.33, and 2.01 cal/g [76]. At relatively high field intensities the magneto-caloric effect is mainly reversible; in low positive fields there is a marked cooling effect, which is associated with large irreversible changes in magnetization [365].

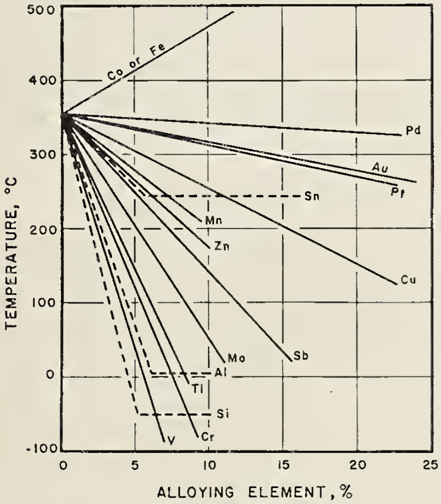

FIGURE 12. *Effect of single alloying elements on the Curie point of nickel [100].*

(3) *Saturation.* The magnetic saturation value for high-purity nickel is approximately 6,500 gauss and for "A" nickel approximately 6,000 gauss [256, 337]. The effect of tension in decreasing the magnetic saturation of nickel was explained by Buhl [177] 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 $H=1$ oersted. For "A" nickel the initial permeability is approximately 200 and the maximum permeability, $H=20$ oersteds, is approximately 1,000 [256, 337]. The theoretical effect of temperature on the permeability of nickel was compared, by Kersten [687], with the vaulting of the Bloch walls.

(5) *Coercive Force.* The coercive force, $H_c$, of nickel is 2.73 oersteds when $B=5{,}000$ [337]. The effect of plastic deformation on the temperature dependence of the coercive force, through the range −195° to +360° C, is reversible on annealing [204]. Nickel rods sintered above 1,000° C show an increase in coercive force with decreasing temperature, and the increase is proportional to the square root of the crystal energy or the anisotrophy constant [340].

(6) *Magnetostriction.* Magnetostriction is the change in dimensions of a ferromagnetic material when it is placed in a magnetic field, or the change in magnetization when the dimensions are changed by an external force. Magnetostriction is exhibited by the ferromagnetic metals iron, nickel, and cobalt and many of their alloys, and by other ferromagnetic alloys such as the Heusler alloys. If an alternating field is used, the resultant vibrations of the metal produce sound waves within or above the audible range.

According to the domain theory of magnetiziation, 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 an external field, the random orientation of the 100,000 domains in a crystal of average size results in a net magnetic field 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 in figure 13. The nickel-iron alloy system is interesting in the wide range of magnetostrictive properties available, as shown

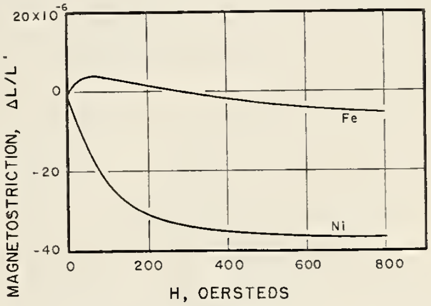

FIGURE 13. *Effect of field strength on the magnetostriction of nickel and iron [652].*

in figure 14. A few percent of nickel makes iron exhibit positive magnetostriction at all 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 treatments. 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 type 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.

The actual change in length that accompanies magnetostriction is small; even in nickel the maximum change in length is only about 30 ppm. As recently as 1926, it was said that no important use had been made of this laboratory curiosity, magnetostriction, but today it is of vital importance in equipment used in many and diverse fields, including Sonar and related devices for detecting marine craft (or schools of fish) and for determining the depth of uncharted waters; electrical filters, e. g., a band pass filter for use in commercial receiving sets; homogenization and sterilization of milk; acceleration of chemical reactions and cavitation effects; strain gages; vibration and engine detonation; phonograph pickups; frequency control of oscillators operating below 100,000 cycles; and dust precipitation.

An extended discussion of the theory and practice of magnetostrictive effects, with an appendix of pertinent references, is contained in two booklets issued recently by the Development and Research Division of the International Nickel Company [652, 748].

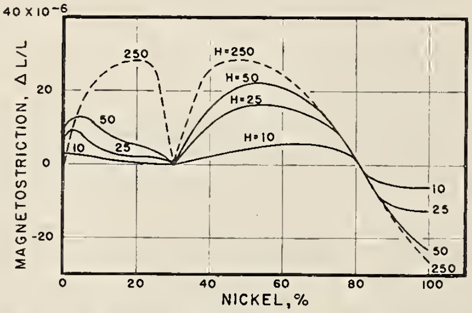

FIGURE 14. *Magnetostriction in iron-nickel alloys at different field strengths [652].*

## 2.3. Mechanical Properties

The mechanical properties of nickel are greatly influenced by the purity, temperature, and the previous thermal and mechanical history of the specimen. As is 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 impact values, less pronounced increases in yield strength, hardness, modulus of elasticity, elongation, and fatigue resistance, with inconsistent effects on the reduction in area and compressibility. Nickel does not show the embrittlement and abrupt change from ductile to brittle behavior with decreasing temperature that is encountered in many ferritic materials. 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 indicative rather than an attempt at complete coverage.

### a. Tensile Properties

The tensile strength of annealed nickel of high purity, 99.99 percent [100] and 99.94 percent [45], was reported as 46,000 psi. For commercial grades of nickel containing more cobalt than is present in current production, Wise and Schaefer [100] summarized the tensile strengths 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 in wire, whereas over 200,000 psi can be had in heat-treated, aged "Duranickel" wire. ASTM Specifications B 160–49T for Nickel Rods and Bars, B 161–49T for Seamless Pipe and Tubing, and B 162–49T for Plate, Sheet, and Strip [513] require minimum tensile strengths of 55,000 psi for annealed "A" nickel and 50,000 psi for annealed "low-carbon" nickel, with higher values for worked material, for example, 60,000 psi minimum for hot-finished rods and bars, and 90,000 psi minimum for hard, cold-rolled strip and sheet. Figure 15, from the data of Jenkins and Digges [345], shows that the tensile strength of 99.85 percent nickel decreases smoothly and quite rapidly with increasing temperature. Small irregularities in the vicinity of the Curie temperature were reported by Zackey and Hazlett [428]. Foley [388] 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. Ancker and Parker [432] reported that the tensile strength of nickel increased

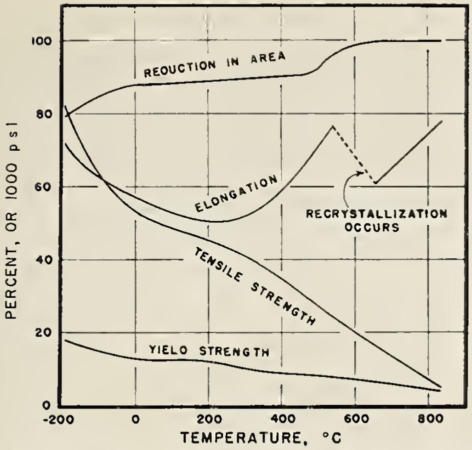

Figure 15. *Effect of temperature, from —196° to 834° C, on the mechanical properties of annealed 99.85-percent nickel* [*345*].

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. In pile irradiation, doses up to $3\times10^{20}$ thermal neutrons at 20° to 250° C increased the tensile strength of nickel by 45,000 psi [697].

The yield strength of annealed 99.95 percent nickel, according to Wise [168], is 8,500 psi. Jenkins and Digges [345] reported the yield strength of annealed 99.85-percent nickel as 12,500 psi at room temperature, 18,000 psi at —196° C, and 4,000 psi at 800° C, as shown in figure 15. ASTM Specifications B 160, B 161, and B 162 [513] require minimum yield strengths of 15,000 psi for annealed "A" nickel and 12,000 for annealed "low-carbon" nickel, 50,000 psi for cold-drawn rounds 1 to 4 in. in diameter and 60,000 psi for diameters less than 1 in., 40,000 psi for pipe and tubing stress-relieved and 50,000 for the same materials stress-equalized, and 70,000 psi minimum for cold-rolled hard sheet and strip. Rosenberg [93] reported that the yield strength of cold-drawn commercial nickel (about 99.4 percent) was 97,000 psi at room temperature and 112,000 psi at —76° C. Meyerson [237] quoted values for yield strength in compression, for 0.2 percent offset, as follows: for "A" nickel, 23,000 psi for hot-rolled material, 58,000 psi cold-drawn and stress-relieved, 26,000 psi cold-drawn and annealed, and for age-hardening "Permanickel" 51,000 psi for hot-rolled, 103,000 for cold-drawn, 148,000 for hot-rolled and aged, and 166,000 psi for cold-drawn and aged. The yield point in stress-strain curves of single crystals of nickel was discussed by Haasen and Kelly [776].

Pile irradiation had a greater effect on the yield strength than on the tensile strength of nickel. The increase in yield strength, by irradiation with $5\times10^{19}$ nvt at about 100° C, was removed by annealing between 340° and 400° C [697].

Jenkins and Digges [345] reported the elongation of 99.85 percent nickel as 73 percent at —196° C, decreasing to a minimum of 31 percent at about 250° C, and thereafter rising to about 75 percent at 800° C with pronounced irregularities between 550° and 650° C because of recrystallization. According to Meyerson [237] the elongation of "A" nickel, and commercial wrought nickels in general, is between 30 and 50 percent for annealed material. Cold working reduces elongation as it increases tensile and yield values, for example, spring-temper cold-drawn wire has a yield strength of 130,000 psi and elongation of 10 percent in 2 in.

### b. Elastic Properties

Studies of single crystals revealed pronounced anisotropy in the elastic properties of nickel [174, 191, 254, 371]. For example, the anisotropy factor is $2\ C_{44}/(C_{11}-C_{12})=2.63$, according to Bozorth [174], and values for Young's moduli, according to Yamamoto [371], are $E_{(100)}=1.198$, $E_{(110)}=2.008$, and $E_{(111)}=2.592\times10^{12}$ d/cm$^2$. Measurements made on polycrystalline specimens with random orientation represent a balance between anisotropic values; computations made by Yamamoto [254] 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 about 30,000,000 psi for electrolytic nickel [168]; 21,500,000 psi for sandcast and 30,000,000 psi for annealed "A" nickel [142]; 31,200,000 psi for cold-drawn nickel wire and 30,000,000 for "Permanickel" [237, 763]. Bennett and Davies [173] concluded, from a comparison of their own results with those of other investigators, that purity had less 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 magnetic fields on Young's modulus for 99.7-percent nickel, according to Siegel and Quimby [75] is summarized in figure 16.

The modulus of elasticity in compression is the same as in tension, about 30,000,000 psi, for all commercial forms of nickel [237].

The modulus of elasticity in torsion, also known as the modulus of rigidity and modulus of shear, was reported as 11,000,000 psi for "A" nickel [256]; 12,000,000 psi for annealed 99.2 percent nickel and 11,600,000 psi for the same material before annealing [85]; 11,270,000 psi for hot-rolled nickel and 11,340,000 psi for hot-rolled "D" nickel [38].

Poisson's ratio, i. e., the ratio of transverse con-

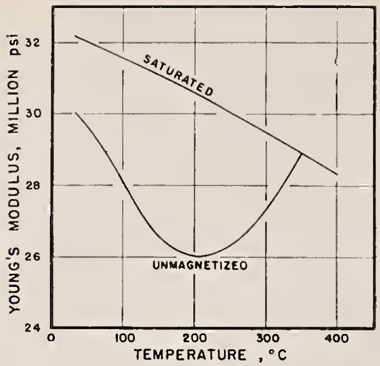

Figure 16. *Effect of magnetic conditions on the modulus of elasticity of 99.7-percent nickel* [75].

traction to longitudinal extension under tensile stress, is 0.31 for nickel [499].

### c. Hardness

Values as low as 35 Rockwell B, and 64 Vickers have been reported for the indentation hardness of annealed high-purity nickel [237]. Cold work and the presence of impurities increase the hardness, for example, the discussion of strip in ASTM Specification B 162–49T [513] for Nickel Plate, Sheet and Strip lists Rockwell B numbers ranging from 64 maximum for annealed "A" nickel and 55 maximum for annealed "low-carbon" nickel to 90 minimum for hard cold-rolled and 95 minimum for spring-temper cold-rolled strip. Some data for the effect of cold work on the hardness of several grades of nickel are shown in figure 17. The hardness of electrolytic nickel as deposited ranged from 100 to 425 Vickers [391], and the effect of annealing temperature on the Vickers hardness of electrolytic nickel was slight up to about 300° C. With further increase in annealing temperature, the Vickers hardness drops sharply to about one-third of the room-temperature value.

Pile irradiation of $10^{19}$nvt increased the Brinell hardness of annealed nickel by 110 numbers. The increase in BHN was smaller for partially hardened material [697].

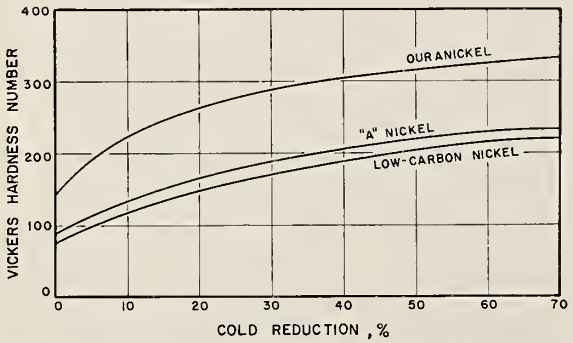

Figure 17. *Effect of cold work on the Vickers hardness of nickel* [766].

### d. Impact

For "A" nickel at room temperature, Charpy values were reported as 222 ft-lb annealed, 197 hot-rolled, 195 cold-drawn, and 85 as sand-cast; Izod values were 120 ft-lb for annealed, hot-rolled, or cold-drawn material, and 85 ft-lb for sand-cast [142]. Some low-temperature Charpy impact values for "A" nickel are recorded in table 13. Rosenberg [93] reported similar values for cold-drawn commercial nickel, 204 ft-lb at room temperature and 216 at −78° C. Izod values for a "D" nickel rod were 110 ft-lb hot-rolled and 69 ft-lb after annealing [113], and Izod values for Duranickel and Permanickel were 120 ft-lb hot-rolled or cold-drawn and stress-relieved, and 25 ft-lb for material annealed after hot-rolling or cold-drawing [237].

Table 13. *Charpy impact values of 99.51-percent nickel at low temperatures* [256]

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

### e. Endurance Limit

Results for the endurance limit for 100,000,000 cycles were compiled by Meyerson [237] as follows: for "A" nickel annealed 24,000 psi, hot-rolled 30,000 psi, cold-drawn 42,500 psi; for Permanickel and Duranickel annealed 55,000 psi, hot-rolled 53,500 psi, cold-drawn 55,000 psi, cold-drawn and aged 59,000 psi.

Greenall and Gohn [78] found that rolling 24-gage "A" nickel sheet to reductions of 4 or 8 B&S numbers raised the endurance limit from 25,000 to 40,000 psi. Betty [102] 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 [490].

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 [36] 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.

### 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.

Jenkins, Digges, and Johnson [466] conducted an exhaustive study of the creep behavior of annealed 99.85-percent nickel in tension at temperatures up to 650° C (1,200° 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. Some of Jenkins and Digges 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 700° F fracture occurred in 21,000 hr at 21,330 psi and in 22 hr at 32,000 psi; at 900° F fracture occurred in 153 hr at 18,670 psi and in 57 hr at 20,000 psi; and at 1,200° F fracture occurred in 6,800 hr at 4,010 psi, 224 hr at 6,670 psi, and 32 hr at 9,330 psi.

Hazlett and Parker [465] made constant-stress creep studies of 99.94-percent nickel alloyed with solid-solution amounts of tungsten, titanium, iron, and cobalt, and discussed their results in terms of the three parameters in the equation $e-e_0=At^b$, where $e$=total true strain; $e_0$=instantaneous strain at moment of loading; $t$=time; and $A$, $b$=constants.

The stress required to extend a hot-rolled nickel rod 0.25 percent in 1,000 hr at 427° C was reported to be 20,000 psi; at 538° C, a stress of 10,000 psi produced 0.28-percent extension in 1,000 hr [103]. For "A" nickel Geiger [142] reported that a stress of 10,000 psi produced a creep rate of 1 percent in 10,000 hr for hot-rolled material at 400° C, whereas cold-drawn material required 24,000 psi at 425° C to develop the same creep rate.

### g. Ductility

Values for elongation and reduction in area are the usual indications of ductility, with certain other determinations designed to show ductility or deformability under particular conditions. The amount of cold-work that may be done without annealing is indicated by the Olsen (Erickson) test. The depth of cup in 0.062-in. nickel sheet at fracture is 0.60 in. when a ⅞-in. ball is used with a 1⅝-in. die [95].

Ellis [61] 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, thereafter, rapidly up to 1,100° C, with irregularities at about 850° C. In the practice of the International Nickel Company [133, 134] the temperature range for hot-rolling and hot-forging is usually 650° to 1,250° C.

Bridgman [381] reported that nickel remained ductile under pressures up to 30,000 kg/cm$^2$.

The flexure of nickel wire was determined by MacBride [79], by cantilever bend 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 of nickel in rubbing contact was reported by Tichvinsky [92] 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.

Simon and coworkers [301] 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.

### i. Transmission of Sound

The speed of sound in a longitudinal bar of commercial nickel (99.51%) was reported as $4.7\times10^5$ cm/sec [256]. For ultrasonic frequencies of 3.5 Mc, the transmission rate in electrolytic nickel is 5,660 m/sec [355].

## 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 Kurnakov [232], 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 the high-sulfur shot in table 3.

The effect of individual impurities commonly present in commercial nickel is reviewed as follows:

### a. Carbon

Carbon exists in nickel in solid solution or as graphite formed by decomposition of the carbide, $Ni_3C$, which exists at temperatures above 1,500° C but is exothermic and unstable. The solubility of carbon in solid nickel is about 0.03 weight percent at 500° C, 0.41 at 780° C, 0.245 at 1,030° C, and 0.65 at the eutectic temperature, 1,318° C [149, 349]. The diffusion coefficient of carbon in nickel ranges from $4.0\times10^{-9}$ cm$^2$/sec at 727° C to $4.1\times10^{-7}$ at 1,020° C [349].

Carbon in solid solution in nickel increases the ease of hotworking, 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 listed in table 3 was developed to facilitate spinning and deep drawing operations.

Small amounts of carbon do not appreciably affect the Curie temperature [149], but the diffusion of even small amounts of carbon in nickel is of interest in the activation of thermionic oxide-coated cathodes [349]. 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 Mond 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 recent development of improved processes for recovering nickel from its ores, have resulted in lowering the average content of cobalt to about 0.1 percent, from the 0.5 percent which previously represented the practical economic limit of separation of nickel and cobalt in commercial production.

It has been reported [558] 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 tools 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, and is still an important metal used to control the harmful effects of sulfur. Practically all of the added magnesium is slagged off, as sulfide or oxide, and the residue is too small to be detected in ordinary analyses or to have any effect on the properties.

### f. Manganese

The equilibrium diagram of the nickel-manganese system according to Lacy [150] 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 of 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 in hot-working and heat-treating operations.

Additions of 10 to 20 percent of manganese markedly increased the electrical resistance of annealed nickel [22]. Ten percent of manganese lowers the Curie temperature to about 200° C, as shown in figure 12. In the common commercial alloys, each percent of manganese up to 15 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 [624], the solubility is 0.294 weight percent of oxygen at 1,450° C and 1.63 percent at 1,691° C. The presence of oxygen lowers the melting point of nickel progressively until the eutectic composition (0.22 percent of oxygen) is reached, with a melting point 20° C lower than that of pure nickel [161]. According to Seybolt [74], the solubility of oxygen in solid nickel is exceptional since it increases with decreasing temperature, from 0.012 percent at 1,200° C to 0.020 percent at 600° C.

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 [32] showed that nickel may contain up to 1.1 percent of nickel oxide and still be malleable hot or cold. Nickel oxide is readily detectible microscopically and 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 percent of Si) 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 [161].

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 nickel 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 Iwasé [72], 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 percent of sulfur) melts at 644° C [144]. The solubility of sulfur in solid nickel is about 0.005 percent [32], and amounts in excess of the solid solubility exist as sulfides, which can be identified by microscopic procedures [104].

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 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 [32]. 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 nickel-nickel sulfide eutectic, but additions of manganese and magnesium converted the films of nickel sulfide to globules or particles of manganese or magnesium sulfide, thereby greatly increasing the hot and cold malleability. In modern practice manganese is added to nickel that has been treated with magnesium, to enchance hot workability and to extend the hot-working range, and agents such as titanium and boron may be added to correct the minor effects, on the malleability, of oxides and of gases such as CO, $N_2$, and $H_2$.

In addition 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. Industrial Melting, Casting and Fabrication of Malleable Nickel

Much of the industrial manipulation 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 [143].

Large melts, in the range from 9,000 to 23,000 lb, are usually made in acid-lined openhearth furnaces of the reverberatory type. No slag is added intentionally but some is formed from the silica-alumina refractories. 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. square 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 foregoing procedure [133, 777].

#### 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 [134].

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 [133].

Extrusion of nickel and high-nickel alloys is difficult because of the high strength and resistance to deformation, and the narrow range of temperature in which plastic deformation can be accomplished. Barclay [66] 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 [525] reported that the extrusion of bars of nickel, Monel, 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 B 161–49T [513], 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. outside diameter 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, dies of hard bronze, heat-treated alloy cast iron, or chromium-plated steel are used in quantity production operations and tungsten carbide dies for small work, with beef tallow, castor oil, and water- or oil-soluble lubricants [106, 171].

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. 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 prior to drawing. Mineral oil is a satisfactory lubricant for fine sizes, and water-soluble oil for superfine sizes [525].

Shearing of nickel requires a shear load double that needed for mild steel of equal gage. For punching operations, the use of alloy steel punches and dies with Rockwell C hardness of 58 to 61 is recommended, with a sulfur-base oil as a lubricant. The minimum permissible diameter of punch hole for nickel varies with the sheet thickness [95, 98].

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 heat treatment [95].

### d. Welding, Brazing, and Soldering

Nickel may be welded to itself or to other suitable metals by inert-gas-shielded metal-arc, oxyacetylene, atomic hydrogen, and resistance processes, and in special cases by submerged arc, and carbon-arc processes, but not by forge-welding. Metal-arc welding is most widely used. When properly made, the as-welded joints are equal to the parent metal in strength and resistance to corrosion. 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 [162]. See also Pease [778].

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

Nickel may be brazed using any of the commercially available silver brazing alloys except those that contain phosphorus. The parts should be clean prior to brazing and a proprietary flux produced by a reputable manufacturer should be used.

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.

### e. Annealing

In all annealing treatments of nickel, the furnace atmosphere should be free from sulfur compounds, and should not fluctuate between oxidizing and reducing conditions. 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. Full annealing (soft annealing) of nickel is accomplished in 6 min or less at 1,500° to 1,700° F for open annealing. In special cases nickel may be soft annealed in sulfur-free salt baths or by electrical-resistance annealing. Dead-soft annealing results from the use of higher temperatures or longer times than for soft annealing, and is usually accompanied by appreciable increases in grain size. Stress-relief annealing may be done in 3 hr or less at 1,000° to 1,100° F, and stress-equalizing in 3 hr or less at 525° to 650° F [106, 153, 779].

The recrystallization temperature of highly purified nickel was reported by Ransley and Smithells [55] as 480° C, and by Fetz [84] as between 300° and 400° C. Both investigators found that small amounts of impurities raised the recrystallization temperature appreciably, so that the value for commercial nickel exceeds 600° C. Hirata and Yanagisawa [189] reported that annealing rolled nickel foil 0.5 mm thick at 470° C, far below the recrystallization temperature, changed the common axis of the fibrous structure from [*111*] to [*110*].

#### f. Pickling

The resistance of nickel to corrosion makes its pickling more difficult than that of iron, steel, 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. A bath containing sulfuric acid, nitric acid, and sodium chloride is generally used to remove tarnish or light oxide films, or for brightening after more drastic pickling, for example, in the hydrochloric acid-cupric chloride bath used to remove heavy oxides [134].

#### 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 machining operations, turning, boring, drilling, reaming, threading, planing, broaching, milling, etc., were discussed by Fowler [139].

#### h. Grinding, Polishing, and Buffing

For heavy grinding, where the finish is not important, grinding wheels of No. 14 or 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 fining, 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 alumina or green chromic acid for color buffing. For the highest mirror finish, chromic oxide is used. Lime compounds may be used for buffing nickel plate.

Detailed information about the grinding, polishing, and buffing of nickel and its alloys was presented by Burchfield [134] and by Spencer [780].

## 2.6. 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. Plating

(1) *Electroplating.* According to Gray [391], the history of electroplating goes back to the production of the first good nickel plate by Boettger in 1843. Adams [13] in 1869 was probably the first to do nickel plating on a commercial basis, thereby establishing electroplating as one of the major consumers of nickel. (According to McEnally and Brune [701], and as indicated in figure 3, about 62 million lb of nickel will be used in electroplating in 1956.) Developments in nickel electroplating led to the installation 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 automatic equipment for conducting the operations [291]. Surface improvement and corrosion resistance are the principal objectives of nickel electroplating, but it is also used for building up worn parts and for electroforming of printing plates, tubes, and many other articles [201, 640]. Williams [622] 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 orginally was used on iron, steel, and copper alloys but has been extended to zinc-base die castings and, recently, to aluminum and magnesium alloys, and to other metals. 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 chromium or other metals, including gold.

Steps in the improvement of the nickel-ammonium sulfate bath used by Boettger included the addition by Adams of nickel chloride, the introduction [6] of boric acid to decrease pitting and porosity in the deposit, the explanation by Bancroft [14] that the use of chlorides decreased polarization and promoted anodic corrosion, and development of the Watts bath [20], which is the basis of most modern baths for the production of protective, decorative coatings and for some of the engineering applications. According to Gray [391] the composition of the modern Watts bath is approximately

| | |
|---|---|
| Nickel sulfate, $NiSO_4 \cdot 7H_2O$ | 40 oz/gal. |
| Nickel chloride, $NiCl_2 \cdot 6H_2O$ | 8 oz/gal. |
| Boric acid | 5 oz/gal. |

An all-chloride bath was developed by Blum and Kasper [67]. The better-buffered, half-chloride, half-sulfate bath of Pinner and Kinnaman [115] has advantages of both the Watts and the high-chloride baths and has been found to be especially suitable for high-speed plating.

Improvements in the nickel anode material kept pace with improvements in the bath and in the operating procedure. Nickel containing up to 10 percent of impurities was acceptable in the early low-speed baths. The more drastic requirements of plating in the Watts bath led to the development 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 anodes, which under some conditions form 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 example [158], for introducing corrosion-promoting sulfur into nickel anodes.

In addition to the special baths cited by Gray [391], references to the use of fluoborate [242, 625] and pyrophosphate [597] baths, and to the electrodeposition of nickel from molten salt baths [409] have been noted. The brightening action of cadmium salts has been long 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 [391, 611, 711]. A black nickel deposit, containing nickel sulfide, can be obtained [360]. Wesley [745] 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 and aluminum alloys [383, 434, 673]. Nickel can be plated on beryllium [379], on magnesium [542], on molybdenum [426, 634], and on zirconium [417].

Examples of industrial nickel-plating baths and operating conditions are shown in table 14, 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. The requirements of ASTM Specifications A 142–55, A 166–55T, and B 141–55, for minimum thickness of coating for service conditions of varying severity, are summarized in table 15. (The requirements of British Standard 1224 [382] are similar to those of the ASTM specifications). Acceptance tests usually are based on determinations of the thickness of coating, according to ASTM Specification A 219–54 [513], and on freedom from porosity as indicated by exposure to the salt-spray test.

The physical and mechanical properties of electroplated nickel are affected by the composition of the bath, by all of the variables in bath operation, and by the presence of metallic and gaseous impurities. These effects were reviewed in detail by Zentner, Brenner, and Jennings [373]. The mechanical properties of nickel deposits for engineering uses may be summarized [257] as shown in table 16.

In addition to electroplates of nickel alone, baths and operating conditions have been developed for the deposition of nickel alloys. For

Table 15. *ASTM Standards for nickel coatings on steel, copper, and its alloys, and zinc and its alloys* [513]

| Type of coating | D | F | K | Q |
|---|---|---|---|---|
| On steel. ASTM A 166–55T: | *in., min* | *in., min* | *in., min* | *in., min* |
| Copper plus nickel | 0.002 | 0.0012 | 0.00075 | 0.0004 |
| Final nickel | .001 | .0006 | .0004 | .0002 |
| Chromium, if required | .00001 | .00001 | .00001 | .00001 |
| On copper and its alloys. ASTM B 141–55: | | | | |
| Nickel | ------ | 0.0005 | 0.0003 | 0.0001 |
| Chromium, if required | ------ | .00001 | .00001 | .00001 |
| On zinc and its alloys. ASTM B 142-55: | | | | |
| Copper plus nickel | ------ | 0.0012 | 0.00075 | 0.0005 |
| Copper | ------ | .0002 | .0002 | .0002 |
| Final nickel | ------ | .0005 | .0003 | .0003 |
| Chromium, if required | ------ | .00001 | .00001 | .00001 |

Table 16. *Mechanical properties of nickel deposits for engineering uses* [257]

| Type of bath | Watts, low $pH$ | | Chloride | | Hard, as plated |
|---|---|---|---|---|---|
| | As plated | Annealed | As plated | Annealed | |
| Tensile strength—psi | 63,000 | 50,000 | 100,000 | 58,000 | 156,000 |
| Elongation—% in 1 in. | 31 | 50 | 21 | 48 | 6 |
| Rockwell hardness | 75 B | 17 B | 99 B | 36 B | 42 C |

Table 14. *Examples of industrial nickel-plating baths and operating conditions*

| | Watts | | All-chloride | Intermediate | Hard-plating | Special-purpose |
|---|---|---|---|---|---|---|
| | (high $pH$) | (low $pH$) | | | | |
| Nickel sulfate, oz/gal | 32 | 44 | ------------ | 26 | 24 | 16 |
| Nickel chloride, oz/gal | 6 | 6 | 40 | 23 | ------------ | ------------ |
| Ammonium chloride, oz/gal | ------------ | ------------ | ------------ | ------------ | 3.3 | 2 |
| Boric acid, oz/gal | 4 | 5 | 4 | 5.3 | 4.0 | 2 |
| $pH$ | 4.5 to 6.0 | 1.5 to 4.5 | 2.0 | 1.5 | 5.6 to 5.9 | 5.0 to 5.5 |
| Temperature, ° F | 115 to 160 | 115 to 140 | 140 | 115 | 110 to 140 | Room |
| Current density, amp/ft $^2$ | 20 to 100 | 25 to 100 | 25 to 100 | 100 | 25 to 50 | 5 to 10 |

example, white gold may be electrodeposited from a cyanide bath [166], electrodeposited cobalt-nickel alloys for tape recorders have high remanence and low coercivity [706], black deposits of chromium-nickel and chromium-nickel-vanadium alloys from a modified chloride bath, have high thermal emissivity and good adherence to copper, nickel, etc. [719], nickel-rhenium alloys resist tarnishing and may be deposited from a bath that contains ammonium citrate and potassium perrhenate [295], tin-nickel coatings approximately 65 Sn–35 Ni can be obtained up to 0.01 in. thick and are hard, pleasing in appearance, as tarnish-resistant as chromium, and as resistant as pure nickel to mineral acids and to corrosion in general [559, 720].

The recent and current short supply of nickel led to investigation of the possible use of substitutes, such as combinations of copper, chromium, tin, lead, antimony and brass plating. The possibilities of these emergency substitutes were reviewed by Graham [666].

(2) *Electroless Plating.* Brenner and Riddell [117], in 1946 at the National Bureau of Standards, described a process for the deposition of nickel from an ammoniacal solution containing hypophosphite, by chemical reduction in the absence of an electric current. The following year the process was expanded to include deposition of nickel from acid solutions and the deposition of cobalt from both alkaline and acid solutions. Reduction of nickel salts by hypophosphite had been long known as a chemical reaction, but Brenner and Riddell were the first to develop a controlled, autocatalytic reaction, to produce a sound, coherent metallic coating that can be built up to appreciable thicknesses. The coatings contain up to 6 or 7 percent of phosphorus, probably in the form of finely dispersed phosphides. As deposited the coatings have a Vickers hardness number as high as 700, but heating at elevated temperatures reduces the hardness, and heating for at least 4 hr at 725° to 800° C converts the plated coating into an iron-nickel alloy [200, 438]. The deposits are somewhat less magnetic, but are similar to electrodeposited nickel 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 build-up 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. 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 adsorbed 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 [483].

Three baths recommended [547] for electroless nickel plating are

ALKALINE BATH

| | *oz/gal* |
|---|---|
| Nickel chloride, $NiCl_2 \cdot 6H_2O$ | 4 |
| Ammonium chloride, $NH_4Cl$ | 6.7 |
| Sodium citrate, $Na_3C_6H_5O_7 \cdot 2H_2O$ | 13.4 |
| Sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$ | 1.3 |

*p*H 8 to 10.

ACID BATH A

| | |
|---|---|
| Nickel chloride | 4 |
| Sodium hydroxyacetate, $NaC_2H_3O_3$ | 6.7 |
| Sodium hypophosphite | 1.3 |

*p*H 4 to 4.5.

ACID BATH B

| | |
|---|---|
| Nickel chloride | 4 |
| Sodium citrate | 2 |
| Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$ | 0.7 |
| Sodium hypophosphite | 1.3 |

*p*H 4 to 4.5.

All baths are operated at 95° to 100° C. If the operating conditions are maintained as indicated, and the bath composition is kept constant, each bath will deposit nickel at a rate of approximately 0.0003 in./hr.

Development of the process, in custom plating shops and in large industrial plants, during the period of the Korean War produced more patents than technical papers, according to the reviews by Brenner [438, 547]. MacLean and Karten [475] reported that small fuse parts with deep blind holes could be plated with 0.1 mil of nickel. Rich [599] reported that the use of ultrasonic vibrations from stainless-steel transducers increased the rate of electroless nickel plating. Gutzeit and Landon [461] described operations of a large-scale, electroless, custom plating shop. Chinn [536] reviewed the subject of electroless plating and cited numerous examples of its practical uses.

(3) *Nickel Cladding.*—Nickel cladding, like electroplating, supplies corrosion resistant, nickel-surface material that is cheaper than solid metal. In this process the cladding metal is pressure welded to one or both sides of an open-hearth steel slab in a rolling mill at about 1,200° C. If the bonding surfaces have been properly cleaned and protected during heating, excellent bonding through the formation of an iron-nickel solid solution is accomplished during hot reduction to between one-eighth and one-sixteenth of the original thickness.

The ratio of cladding material to the base plate is usually expressed as a percentage of the total thickness of the composite plate. For example, a ½-in. plate clad 10 percent on one side only, consists of about 0.45 in. of steel and 0.05 in. of nickel; clad 10 percent on both sides, it would be 0.40 in. of steel and 0.05 in. of nickel on each side.

When both sides are clad, the same thickness of nickel usually is applied to each side, but different thicknesses on the two sides may be developed if desired. Nickel-clad steels are regularly supplied with 5-, 10-, 15-, or 20-percent cladding on a 55,000-psi minimum tensile strength steel as base material. According to Theisinger and Huston [165], nickel cladding does not effect the mechanical properties of the clad material, as illustrated by the following data of ½-in. steel with and without 10-percent nickel cladding.

| | Tensile strength | Yield point | Elongation | Reduction in area |
|---|---|---|---|---|
| | *psi* | *psi* | *% in 8 in.* | *%* |
| Clad | 60, 600 | 40, 400 | 30. 0 | 57. 2 |
| Plate | 60, 800 | 40, 200 | 30. 5 | 59. 0 |

The composition, thickness, and properties of steel plate nickel-clad on one or both sides are described in British Standard 1822 [321]. Nickel alloys, including Monel and stainless steel, are also used for cladding, as indicated in ASTM Specification A 265–43T for nickel and nickel-base alloy-clad steel plate [512].

(4) *Sprayed and Vapor-Deposited Coatings.* Protective coatings of nickel may be applied by metal-spray processes, which are particularly adapted for coating large objects of irregular shape [197].

Nickel can be deposited on fluidized beds of silica sand, alumina, and silicon carbide, by the decomposition of nickel carbonyl at 235° C in a carrier gas such as hydrogen [268]. Adherent coatings up to 3 mils thick, from the decomposition of nickel carbonyl, may be applied to steel strip or to the interior of gun barrels, according to a recent patent [709].

### b. Nickel Powders

By varying the conditions of electrodeposition, nickel may be deposited as a powder rather than as a continuous plate [236, 253, 400, 546]. Nickel powder has been produced by electrolysis of fused salts [131], and in the ammonia-leach process for the recovery of nickel from its ores [454], but the principal production of nickel powder for powder metallurgy uses is by electrodeposition from aqueous solutions or by decomposition of nickel carbonyl. Electrolytic powder of 99-percent, or higher, purity is available in 5 grades or sizes ranging from minus 60 to minus 325 mesh [519]. In addition to grades A and B of table 3, high-purity carbonyl powder is also available with an average particle size of 4.5 microns [517].

Nickel powder may be used by itself, to form all-nickel parts, or in combination with other metal powders to produce alloys or compounds [619, 665]. Storage battery plates of nickel may be formed by powder metallurgy techniques [344]. 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 [517]. Nickel alloyed with up to 40 percent of tungsten is useful for thermionic valve construction [651]. Nickel-chromium alloy powders added to iron powder produce compacted parts with tensile strengths between 80,000 and 120,000 psi [457]. Nickel or nickel-alloy objects infiltrated with silver or a silver alloy have effective resistance to wear at elevated temperatures [637]. 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 [705]. Forming of stainless-steel powders by slip-casting instead of pressing has been reported [693], and this technique should be applicable to other alloys and to nickel itself, particularly for the production of thin-walled and special shapes.

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 [220, 440].

### c. End Uses of Nickel and Nickel-Surfaced Material

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, plastic, and automotive industries [203, 592, 701]. These properties plus electrical and magnetic properties make nickel useful in the electrical and electronic industries. The following list of ASTM Specifications and British Standards indicate the forms and shapes of nickel that are available for the construction of equipment or parts for these conditions of use:

ASTM B 160–49T, Nickel Rods and Bars.
B 161–49T, Nickel Seamless Pipe and Tubing.
B 162–49T, Nickel Plate, Sheet, and Strip.
B 163–49T, Seamless Nickel and High-Nickel Alloy Condenser, Evaporator, and Heat-Exchanger Tubes.
B 295–54T, Nickel and Nickel-Alloy Covered Welding Electrodes.
British Standards 1531–33, Nickel and Nickel-Alloy Tubes.
ASTM B 141–55, Electrodeposited Coatings of Nickel and Chromium on Copper and Copper-Base Alloys.
B 142–55, Electrodeposited Coatings of Nickel and Chromium on Zinc and Zinc-Base Alloys.
A 166–55T, Electrodeposited Coatings of Nickel and Chromium on Steel.
British Standard 1822, Nickel-Clad Steel Plate.

The ensuing paragraphs record some recent discussions of the applications of nickel and nickel coatings.

Nickel finds a variety of uses in the electrical industry [572, 762], including the use of very thin films, sputtered or vapor deposited, as resistance thermometers at very low temperatures [414]. A thin film of nickel, which transmits 30 percent of the incident light to the germanium semiconductor, improves the performance of a photoelectric cell [412].

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 [762]. 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, as indicated in references [313, 437, 505, 569, 609, 643].

The use of nickel in nuclear power plants and reactors was discussed by Koenig [397], Convey [445], and Dalzell [781]. Fuller [662] 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 parts, have 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 [201, 502].

Nickel combustion boats and crucibles for laboratory use may be made from sheet metal [207]. Nickel tubes with walls 0.1 mm thick were used for diffusion-purification of hydrogen [419]. Nickel is an activator of phosphors [427]. Nickel powder is pyrophoric under some conditions and finds use in incendiaries, tracer ammunition, igniters, primers, etc. [280]. Nickel-plated silk was used in England as a war-time substitute for fine copper gauze, for straining gasoline [199], and nickel-plated wires produced a superior Fourdrinier cloth [731]. Nickel and some of its alloys are included in a tabulation of commonly used spring materials [330]. Nickel was recommended as a container for bromine [187], and for use as a spinneret in the production of acetate and cupro-ammonium fibers [300]. According to Atkinson [782], about 500,000 pounds 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 than Raney catalysts. The use of nickel compounds in applying vitreous enamel to steel, as a dip bath and in ground coats, is reviewed in two papers from the National Bureau of Standards [479, 708].

## 3. Ferrous Alloys

### 3.1. General

The history of manmade alloys of iron and nickel appears to date from 1754, when Cronstedt (according to Benedicks [34]) announced that "among the metals proper, iron has the greatest friendship for nickel." The discovery that nickel was a constituent of meteoric iron encouraged attempts to produce manmade alloys with the strength, toughness, and generally desirable properties of meteoric iron. According to Marsh [86], Stodart and Faraday about 1820 attempted to prepare synthetic meteoric iron by fusing horseshoe nails with 3 and 10 percent of nickel, and thereby produced nickel steel. In 1827, Berthier called attention to the strength and ductility of a meteoric iron that contained 8.6 percent of nickel, and suggested the artificial production of such materials. However, the development of nickel steels was retarded by the scarcity, costliness, and low quality of the nickel then available, and the modern history of nickel steels dates from 1889, when Riley [7] demonstrated the value, versatility, and usefulness of nickel as an alloying element. The original nickel steels, usually containing either 3.5 or 5.0 percent of nickel, were soon followed by nickel-chromium, nickel-molybdenum, and complex compositions for engineering uses involving resistence to atmospheric corrosion and to oxidation at temperatures in the vicinity of room temperature; by the austenitic stainless steels for improved physical and mechanical properties and improved corrosion resistance over a wide range of temperatures; and by the development in recent years of the "super" steels and alloys for use in jet engines and in supersonic aircraft. Nickel is also an important constituent of alloy cast irons, of a series of ferrous alloys having coefficients of thermal expansion ranging from the negligible to the highest values found in ferrous metals, of alloys having the two extremes of magnetic permeability, of alloys having superior resistance to corrosion and oxidation, of electrical resistance alloys, and others.

The literature on the subject of the simple and complex alloys of iron and nickel is tremendous. In the Alloys of Iron Monograph Series, two volumes are devoted to nickel [86, 463], and Marsh commented in the first volume that adequate treatment of the single topic of nickel-magnetic alloys would require another volume. Within the limitations of the present publication, it will be possible only to discuss briefly some of the topics and to indicate sources of more detailed information.

### 3.2. Nickel Steels

At high temperatures, nickel forms a continuous series of solid solutions with iron, as indicated in the phase diagram according to Sachs [159], figure 18. Both the alpha and delta solid solutions have a body-centered cubic lattice, whereas the gamma phase is face-centered cubic. Nickel lowers the temperature of the $A_3$ transformation, and produces an extensive mixed alpha-gamma field between $Ac_3$ and $Ar_3$. The transformation is sluggish, and the boundaries are doubtful below about 600° C. When carbon is present, nickel also lowers the $A_1$ temperature and reduces the carbon content of the eutectoid. In complex alloy steels the effect of nickel may be complicated by the tendency of elements such as chromium and molybdenum to raise the transformations on heating, and of manganese to retard the gamma-alpha transformation. For nickel-steel bars cooled slowly in an attempt to approximate equilibrium, Eash and Pilling [99] found that up to about 5 percent of nickel the structure was ferrite plus pearlite; above 5 percent of nickel a bainite structure formed and blended into martensite as nickel or carbon increased; with further increases in nickel, stable austenite appeared in quantities that increased with increasing nickel content.

The density of nickel steels is essentially the same as for unalloyed steels of comparable carbon content. The thermal conductivity of iron is reduced by nickel and other elements, and is further reduced by increasing temperature; Shelton and Swanger [59] reported that the thermal conductivity of an 0.35 C, 1.37 Ni, 0.46 Cr steel decreased in a linear manner from 0.11 cal/sec cm$^2$ °C at 0° C to 0.085 at 600° C. Electrical resistivity depends upon the carbon content, as well as on the alloy content, and invariably is greater for quenched than for annealed material. Figure 19 compares the resistivity of annealed carbon steel and 3.5-percent-nickel steel, from data of Campbell and Mohr [35], with added points from the data of Powell and Hickman [91] to show the effect of 0.8 percent of chromium alone and with 0.4 percent of molybdenum, on the resistivity of a 3.5-percent-nickel steel containing 0.33 percent of carbon.

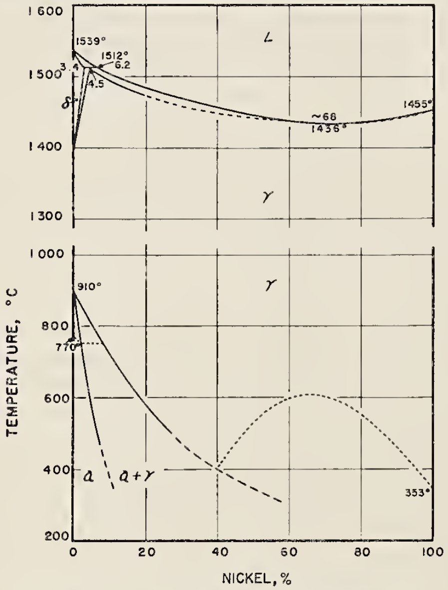

Figure 18. *The iron-nickel diagram [159].*

On the International Temperature Scale of 1948, the freezing point of nickel is 1,453° C and that of iron 1,536° C.

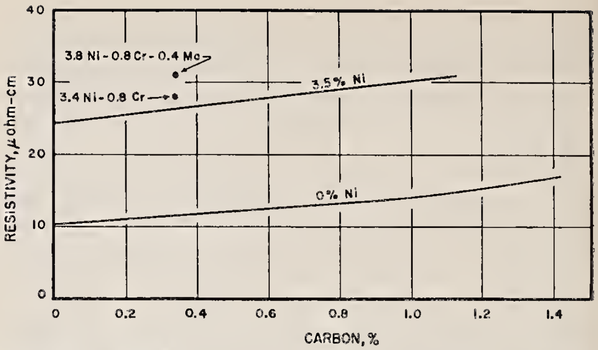

Figure 19. *Effect of carbon and alloy content on the electrical resistivity of annealed low-alloy steels [35, 91].*

Nickel benefits the mechanical properties of steels in various ways. It is a ferrite strengthener, as shown in figure 20, and thus increases the tensile and yield strength in high-purity alloys [493], as well as in commercial steels. In austenitic steels, nickel strengthens and stabilizes the austenite. Nickel toughens and strengthens iron, and appreciably improves the impact toughness of carburizing steels [579]. In normalized low-carbon steels, nickel lowers the temperature of the ductile-brittle transition and makes it more gradual, as shown in figure 21. Nickel mildly improves the hardenability and thus permits the hardening of larger sections. Nickel does not combine with carbon or oxygen and does not form intermetallic compounds in simple steels. However, carbides of other elements and intermetallic compounds involving nickel are formed in complex nickel-bearing steels, particularly the age-hardening stainless steels and super alloys, and help to develop the strength and resistance to deformation of these materials at high temperatures. Marsh [86] reviewed the work of many investigators of the effect of nickel on the modulus of elas-

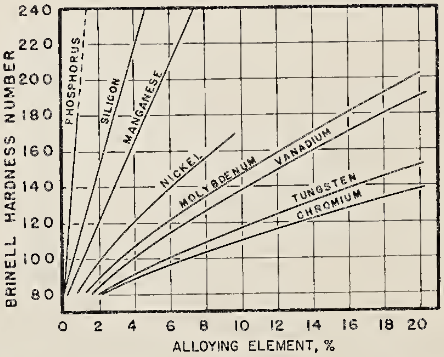

Figure 20. *Relative effectiveness of alloying elements as ferrite strengtheners [267].*

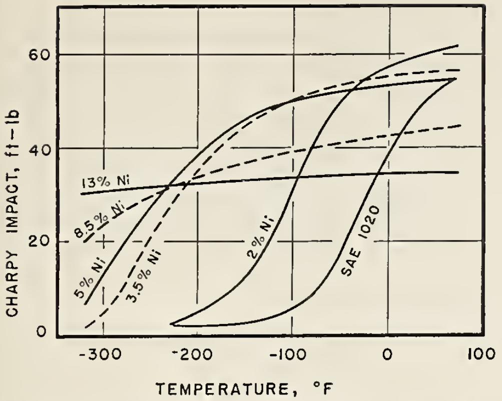

Figure 21. *Effect of nickel on the low-temperature embrittlement of normalized low-carbon steels (0.20 C in SAE 1020, 0.15 C in 2-percent nickel steel, 0.10 C in all others)* [*123*].

ticity of iron and concluded that, as shown in figure 22, the modulus of both ferritic and austenitic alloys decreases with increasing nickel to about 22 million psi at 30 percent of nickel; with increasing nickel above 35 percent, the modulus rises to about 30 million psi for nickel.

Nickel improves the resistance to corrosion in the atmosphere and in other environments. It supplements and intensifies the effects of other alloying elements on various properties, including resistance to corrosion.

The low-nickel steels usually are melted in openhearth or electric furnaces, with melting practice the same as that used to produce unalloyed steel of high quality and of corresponding carbon content. Hot- and cold-working of the low-alloy steels are, in general, accomplished with the same practices and equipment as for carbon steel, with allowances for increased resistance to deformation resulting from the presence of alloying elements. Steels with higher alloy contents, stainless steels, for example, are melted in electric furnaces, and the subsequent fabrication operations differ appreciably from those used for simple carbon steels. For further details on melting and fabrication, the reader is referred to Hall [463], to appropriate sections of Metals Handbook, and to publications issued by The International Nickel Company.

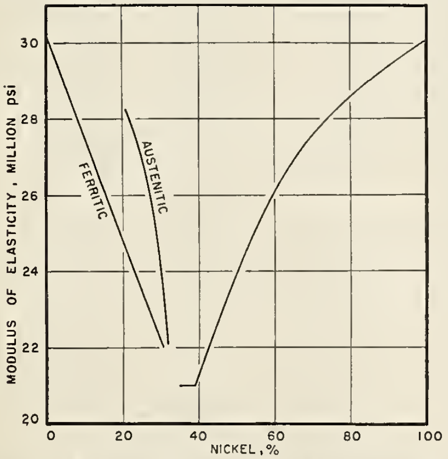

Figure 22. *Modulus of elasticity of nickel-iron alloys* [*86*].

### a. Low-Alloy Steels

The first interest in nickel steels was shown by the ordnance and armor makers, who sponsored Riley's report to the Iron and Steel Institute in 1889. 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, with and without heat treatment. When the Society of Automotive Engineers early in the 20th century began the systematic classification of steels, the first series or class (SAE 10XX) was assigned to plain carbon steels and the second series (SAE 2XXX) to nickel steels. The third series to be adopted in the SAE classification was the low-nickel low-chromium series, SAE 3XXX. In the 1920's a series of nickel-chromium-molybdenum steels, SAE 43XX, and two series of nickel-molybdenum steels, SAE 46XX and 48XX, were added primarily for use in the heat-treated or carburized condition. During World War II, when alloying elements were in extremely short supply, the design of the National Emergency steels was made possible by the accumulated knowledge of the reasons for and mechanism of the beneficial effects of individual alloying elements, and of the interrelation of the effects of nickel and of other alloying elements. The modern concept of the functions of nickel in the low-alloy ferritic engineering steels may be summarized as follows:

Nickel is a ferrite strengthener, increasing the tensile strength of unhardened or partially hardened steels about 4,000 psi for each 1 percent of nickel [112]. Nickel lowers the temperatures and slows the rate of the gamma-alpha transformation. It lowers the temperature at which pearlite forms. It reduces the eutectoid carbon value approximately 0.04 percent for each 1 percent of nickel [160].

The strengthening and refining of both ferrite and pearlite combine to permit a desired level of strength and hardness to be obtained, in normalized or annealed nickel steels, with a lower carbon content than would be required in a plain carbon steel.

Nickel increases the hardenability and lowers the cooling rate for attainment of desired hardness. These combined effects decrease the danger of distortion and quench cracking in through-hardened sections and, of greater importance, increase the size of section that can be through-hardened under prescribed cooling conditions.

In complex steels the effects of nickel and other alloying elements are complementary in a balanced composition and frequently are mutually intensifying. For example, the 1.25-percent-nickel plus 0.65-percent-chromium steels, with a combined alloy content of less than 2 percent, responded to heat treatment as did the 3.5-percent-nickel steel; 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 [118]; in carburizing steels 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 successive development of new alloy combinations, particularly under the stimulus of National Emergency demands and the unavailability of nickel for civilian uses, led to successive reductions in the number and variety of the early engineering steels. A 1954 bulletin issued by the American Iron and Steel Institute [430] includes, in the listing of Standard Constructional Alloy Steels, the nickel steels, nickel-chromium, nickel-molybdenum, and nickel-chromium-molybdenum steels listed in table 17.[4]

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[4] Further changes in the listing of AISI Standard Steels are evident in the bulletin "Supplementary Information March 1957, Alloy Steel; Semifinished; Hot Rolled and Cold Finished Bars, July 1955," which was not available when this section of the Circular was prepared.

Table 17. *Nickel steels and nickel-containing steels in the 1954 AISI listing of Standard Constructional Alloy Steels* [*430*]

| AISI number [a] | Chemical composition ranges and limits, percent | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | Mn | P max | S max | Si | Ni | Cr | Mo |
| 2317 | 0.15/0.20 | 0.40/0.60 | 0.040 | 0.040 | 0.20/0.35 | 3.25/3.75 | ---------- | ---------- |
| 2515 | 0.12/0.17 | 0.40/0.60 | 0.040 | 0.040 | 0.20/0.35 | 4.75/5.25 | ---------- | ---------- |
| E2517 | 0.15/0.20 | 0.45/0.60 | 0.025 | 0.025 | 0.20/0.35 | 4.75/5.25 | ---------- | ---------- |
| 3120 | 0.17/0.22 | 0.60/0.80 | 0.040 | 0.040 | 0.20/0.35 | 1.10/1.40 | 0.55/0.75 | ---------- |
| 3130 | 0.28/0.33 | 0.60/0.80 | 0.040 | 0.040 | 0.20/0.35 | 1.10/1.40 | 0.55/0.75 | ---------- |
| 3135 | 0.33/0.38 | 0.60/0.80 | 0.040 | 0.040 | 0.20/0.35 | 1.10/1.40 | 0.55/0.75 | ---------- |
| 3140 | 0.38/0.43 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 1.10/1.40 | 0.55/0.75 | ---------- |
| E3310 | 0.08/0.13 | 0.45/0.60 | 0.025 | 0.025 | 0.20/0.35 | 3.25/3.75 | 1.40/1.75 | ---------- |
| E3316 | 0.14/0.19 | 0.45/0.60 | 0.025 | 0.025 | 0.20/0.35 | 3.25/3.75 | 1.40/1.75 | ---------- |
| 4320 | 0.17/0.22 | 0.45/0.65 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | 0.40/0.60 | 0.20/0.30 |
| 4337 | 0.35/0.40 | 0.60/0.80 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | 0.40/0.60 | 0.20/0.30 |
| 4340 | 0.38/0.43 | 0.60/0.80 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | 0.49/0.60 | 0.20/0.30 |
| E4340 | 0.38/0.43 | 0.65/0.85 | 0.025 | 0.025 | 0.20/0.35 | 1.65/2.00 | 0.40/0.60 | 0.20/0.30 |
| 4608 | 0.06/0.11 | 0.25/0.45 | 0.040 | 0.040 | 0.25 max | 1.40/1.75 | ---------- | 0.15/0.25 |
| 4615 | 0.13/0.18 | 0.45/0.65 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | ---------- | 0.20/0.30 |
| 4617 | 0.15/0.20 | 0.45/0.65 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | ---------- | 0.20/0.30 |
| 4620 | 0.17/0.22 | 0.45/0.65 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | ---------- | 0.20/0.30 |
| X4620 | 0.18/0.23 | 0.50/0.70 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | ---------- | 0.20/0.30 |
| 4621 | 0.18/0.23 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | ---------- | 0.20/0.30 |
| 4640 | 0.38/0.43 | 0.60/0.80 | 0.040 | 0.040 | 0.20/0.35 | 1.65/2.00 | ---------- | 0.20/0.30 |
| 4812 | 0.10/0.15 | 0.40/0.60 | 0.040 | 0.040 | 0.20/0.35 | 3.25/3.75 | ---------- | 0.20/0.30 |
| 4815 | 0.13/0.18 | 0.40/0.60 | 0.040 | 0.040 | 0.20/0.35 | 3.25/3.75 | ---------- | 0.20/0.30 |
| 4817 | 0.15/0.20 | 0.40/0.60 | 0.040 | 0.040 | 0.20/0.35 | 3.25/3.75 | ---------- | 0.20/0.30 |
| 4820 | 0.18/0.23 | 0.50/0.70 | 0.040 | 0.040 | 0.20/0.35 | 3.25/3.75 | ---------- | 0.20/0.30 |
| 8615 | 0.13/0.18 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8617 | 0.15/0.20 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8620 | 0.18/0.23 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8622 | 0.20/0.25 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8625 | 0.23/0.28 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8627 | 0.25/0.30 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8630 | 0.28/0.33 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8635 | 0.33/0.38 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8637 | 0.35/0.40 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8640 | 0.38/0.43 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8641 | 0.38/0.43 | 0.75/1.00 | 0.040 | 0.040/0.60 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8642 | 0.40/0.45 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8645 | 0.43/0.48 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 86B45 [b] | 0.43/0.48 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8650 | 0.48/0.53 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8653 | 0.50/0.56 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.50/0.80 | 0.15/0.25 |
| 8655 | 0.50/0.60 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8660 | 0.55/0.65 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.15/0.25 |
| 8715 | 0.13/0.18 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| 8717 | 0.15/0.20 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| 8720 | 0.18/0.23 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| 8735 | 0.33/0.38 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| 8740 | 0.38/0.43 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| 8742 | 0.40/0.45 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| 8750 | 0.48/0.53 | 0.75/1.00 | 0.040 | 0.040 | 0.20/0.35 | 0.40/0.70 | 0.40/0.60 | 0.20/0.30 |
| E9310 | 0.08/0.13 | 0.45/0.65 | 0.025 | 0.025 | 0.20/0.35 | 3.00/3.50 | 1.00/1.40 | 0.08/0.15 |
| E9314 | 0.11/0.17 | 0.40/0.70 | 0.025 | 0.025 | 0.20/0.35 | 3.00/3.50 | 1.00/1.40 | 0.08/0.15 |
| 9840 | 0.38/0.43 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.85/1.15 | 0.70/0.90 | 0.20/0.30 |
| 9845 | 0.43/0.48 | 0.70/0.90 | 0.010 | 0.040 | 0.20/0.35 | 0.85/1.15 | 0.70/0.90 | 0.20/0.30 |
| 9850 | 0.48/0.53 | 0.70/0.90 | 0.040 | 0.040 | 0.20/0.35 | 0.85/1.15 | 0.70/0.90 | 0.20/0.30 |

[a] AISI and SAE numbers are identical for these steels.
The prefix E denotes production in a basic electric furnace. All others are normally manufactured by the basic open-hearth process, but may be made by the basic electric furnace process with adjustments in phosphorus and sulfur. The prefix X denotes a modification.
[b] 86B45 is 8645, plus a minimum of 0.0005 percent of boron.

The mechanical properties of these steels are affected by the carbon content, the alloy content, and particularly by the thermal treatment. The tensile properties of 3.5- and 5-percent nickel steels are shown at the left in figure 23; the right side of the figure shows the properties of the same steels, at the 0.15-percent carbon level, in the oil-quenched and tempered condition. Figure 24 shows the tensile and impact properties of nickel, nickel-chromium, nickel-molybdenum, and nickel-chromium-molybdenum steels, of the same carbon content and section size, in the oil-quenched and tempered condition. Janitsky and Baeyertz [89] in 1939 called attention to the apparent interchangeability of these steels because of the marked similarity in their properties in the quenched and tempered condition. Their conclusions were confirmed and extended by Patton [107], whose results are shown in figure 25. Hodge and Bain [146]

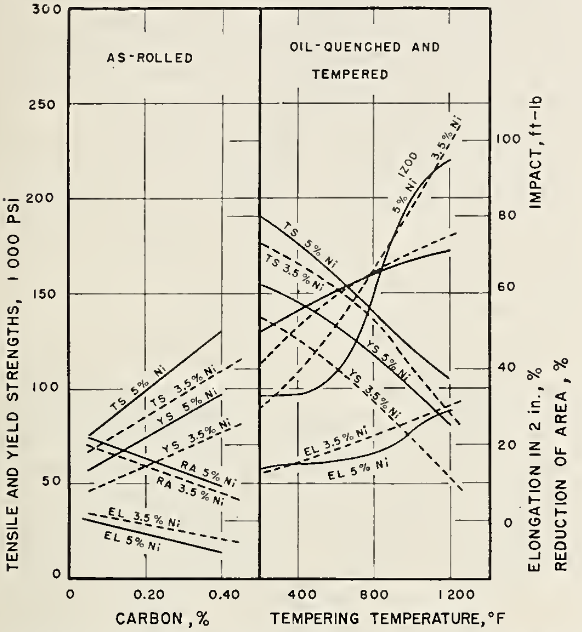

Figure 23. *Tensile properties of 3.5- and 5-percent nickel steels as-rolled and (SAE 2317 and 2515) quenched-and-tempered [124, 126].*

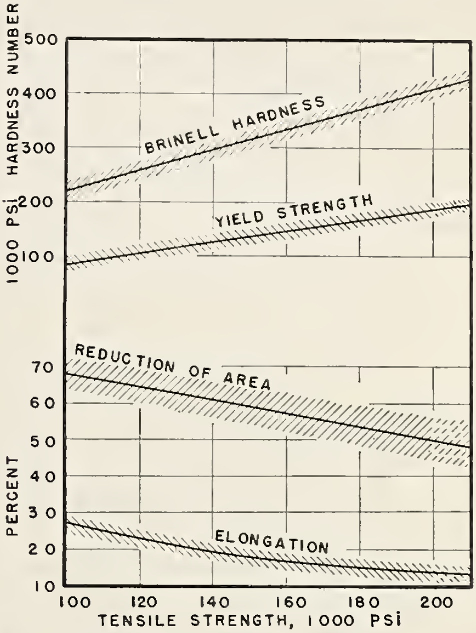

Figure 25. *Normally expected mechanical properties (heavy line) and average variation (hatched band) of quenched and tempered low-alloy steels containing 0.30- to 0.50-percent carbon [107, 146].*

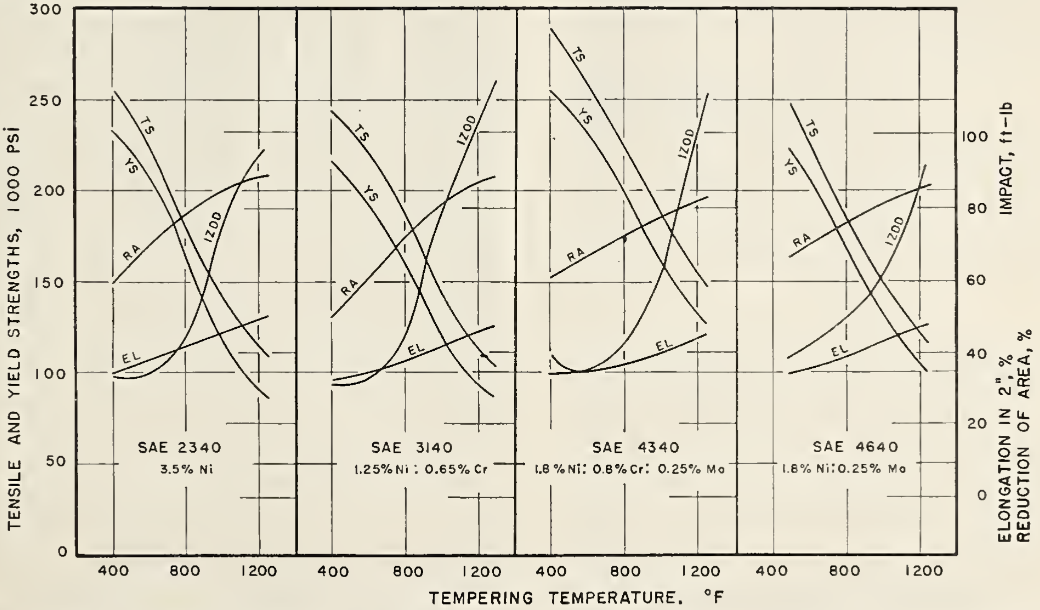

Figure 24. *Tensile and impact properties of oil-quenched and tempered 1-in. sections of* Ni, Ni–Cr, Ni–Mo, *and* Ni–Cr–Mo *steels at the same carbon level [124].*

stated that these curves can be used to predict the properties of any of the common alloy steels within ±10 percent, if the hardenability and heat treatment are such as to obtain a microstructure consisting essentially of tempered martensite.

The low-alloy engineering steels as a class retain their room-temperature properties up to about 300° C, but thereafter the tensile and yield strengths begin to fall off rapidly with further increases in temperature. The limitation on the use of these steels at low temperatures is their low-temperature brittleness, which, as shown in figure 21, is reduced by nickel, but is not eliminated until the nickel content is raised above the normal content of these steels. Brophy and Miller [175] described a low-carbon nickel steel containing 0.12 C max, 0.35 to 1.00 Mn, 0.15 to 0.30 Si, and 8.0 to 10 Ni that was developed for use at temperatures down to −195° C. Armstrong and Miller [258] showed that the Charpy impact values for this type of steel, annealed, were not affected by continuous exposure in liquid nitrogen (−195° C) for periods up to 2 months. According to Armstrong,[5] restrictions on nickel during the last several years retarded the development of this steel, and it is only recently that the steel industry has been interested in again promoting it. The 9-percent-nickel steel is included in ASTM Specifications A 353–56 and A 300–56, and has been accepted by the ASME Boiler and Pressure Vessel Code under case No. 1175.

According to Hall [463], bridge designers were among the first to specify nickel steels, and the 1906 specifications of the 3.5-percent nickel steel, 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 A 8–54 [512], for structural nickel steel for use in main stress-carrying structural members, as follows:

| | Tensile strength | Yield strength, min | Elongation in 8 in. min | Reduction of area, min |
|---|---|---|---|---|
| | *psi* | *psi* | *%* | *%* |
| 1906. Manhattan Bridge | 85,000 to 95,000 | 55,000 | 19 to 17 | 40 |
| 1956. ASTM A 8–54 | 90,000 to 115,000 | 55,000 | 14 | 30 |

Industries other than bridge building and armament made wide use of the nickel steels for parts such as crankshafts, connecting rods, axles, gears, pinions, etc., which must withstand high stresses and be resistant to fatigue and to shock loads. In general, when size permitted, the parts were used in the quenched and tempered conditions, to obtain maximum benefits of the alloy content. For uses that required a hard, wear-resistant surface, the nickel steels were case-hardened by carburization. Forgings have always constituted an important use of nickel steels, particularly when, because of their size or shape, the forgings cannot be liquid quenched, for example, large crankshafts or the shafting for generator and turbine rotors. Because of the mass effect that exists even in nickel steels, The International Nickel Company recommends, as a general rule, that solid forgings over 10 in. in diameter and bored forgings with more than 8-in. wall thickness should not be quenched but, instead, should be annealed or normalized and tempered. According to Hall [463], examples of large forgings made from nickel steels included a 43-in. diameter shaft forged from a 2.68-percent nickel, 0.33-percent-carbon steel, that contained 0.05 percent of vanadium for grain refinement. When double normalized and tempered, this shaft exhibited 86,200-psi tensile strength, 55,800-psi yield strength, and 27-percent elongation in 2 in. In forgings of smaller size, a 2.75-percent nickel, 0.20- to 0.30-percent-carbon steel has been widely used for railroad forgings, including axles, side and main rods, crank pins, and radius bars.

When nickel-alloy steels (containing other alloying elements) became available, they too found important uses as forgings, particularly when vanadium-treated for fine grain size. Nickel-chromium forgings of AISI types 3135 and 3140 have been used for breech mechanisms and for armor, for pinions, gears, shafting, and for drill collars, tool joints, and other applications in the petroleum industry. Nickel-molybdenum forgings have been used for reduction-gear pinions, large-diameter shafting, and turbine and generator rotors. Nickel-chromium-molybdenum steels are exceptionally deep hardening and are used for heavy forgings where high tensile strength is required, for example, in large-diameter shaftings for turbine or generator rotors and shafts. Specifications for different classes of Ni–Cr–Mo–V forgings for generator rotors and for turbine rotors and shafts are found, respectively, in ASTM Specifications A 292–55 and A 293–55T [512]. An example of the tendency to specify only the properties, leaving it up to the producer to select the alloy combination, is supplied by ASTM Specification A 294–55 for carbon and alloy steel forgings for turbine bucket wheels. Properties are defined for six classes of forgings, and the maximum limits for carbon, manganese, phosphorus, sulfur, and silicon are stated, but the only mention of alloy content is a supplementary requirement that when the forgings for turbine wheels are to be used at high operating temperatures, the steel shall contain 0.40 to 0.60 percent of molybdenum.

The AISI bulletins [430, 753] that described the constructional steels shown in table 17 also show in graphic form the deep-hardening characteristics of most of these steels and of some boron-treated steels. The examples of hardenability curves shown in figure 26 illustrate that maximum hardness depends primarily upon the carbon content;

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[5] T. N. Armstrong, letter June 12, 1957.

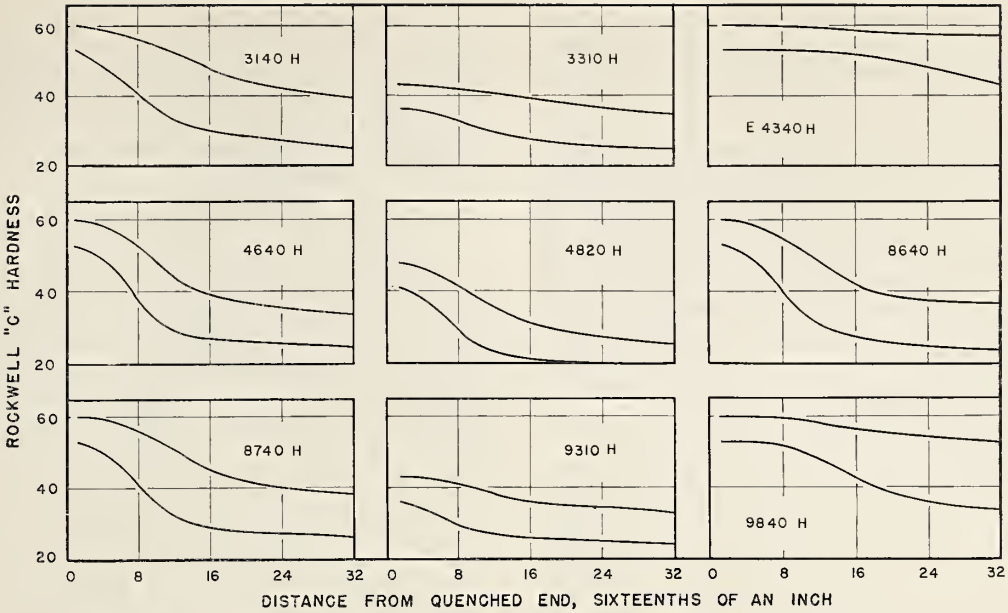

Figure 26. *Hardenability bands for some of the steels listed in table 17* [*430, 753*].

that the steels show a wide range in depth-hardenability as indicated by departures of the curves from flatness; and that, for any steel, there is an appreciable range of hardenability between the upper curve, where carbon, manganese, silicon, and alloying elements all are near the maximum permissible amounts, and the lower curve where all these elements approach the minimum permissible values.

In the early days of the 20th century a large share of the total annual consumption of nickel was required for the production of steel containing up to about 6 percent of nickel. Nickel has never been a cheap and abundant alloying element, and recent restrictions on civilian uses have supplied additional stimuli to design away from nickel and to search for low-nickel or nickel-free substitutes for the nickel steels. For example, the automobile industry formerly was one of the largest users of nickel steels, but today, according to Boegehold [632], most of the nickel used in automobile construction, excluding valve steels, is in the form of SAE 4615 (1.75% Ni) or 8620 and 8640 (0.65% Ni), and in the future these probably will be supplanted by steels with still lower nickel contents, because of the short supply of nickel. In spite of this situation in various industries, the current demand for nickel for low-alloy steels accounts for about 20 percent of the total consumption of nickel, and, in view of the greatly increased production of nickel, this represents an increased tonnage of nickel for this use, as compared to the situation earlier in the century.

### b. High-Strength Low-Alloy Structural Steels

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 automotive and mining equipment, agricultural equipment, air-conditioning equipment, materials handling equipment, military applications, and miscellaneous types of industrial equipment.

The required mechanical properties for sections up to 0.5 in. 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. Functions of the different elements have been stated [511] to be as follows:

Carbon is generally maintained at a level to insure freedom from excessive hardening after welding and to retain ductility.

Copper is commonly used to enhance resistance to atmospheric corrosion and as a strengthening element.

Manganese is used principally as a strengthening element.

Phosphorus is sometimes employed as a strengthening element and to enhance resistance to atmospheric corrosion.

Nickel, silicon, chromium, molybdenum, vanadium, aluminum, titanium, zirconium, and sometimes other elements are used, singly or in combination, for their beneficial effects on strength, toughness, corrosion resistance, and other desirable properties.

Some of these alloy combinations are nickel free, or contain only residual amounts of nickel, but the majority include nickel as an alloying element. The nickel-containing steels, from the tabulations by Hall [463] and by the editors of Materials and Methods [451], are listed in table 18. In all cases the minimum tensile and yield strengths are, respectively, 70,000 and 50,000 psi with elongations of about 20 percent, for sections up to 0.5 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 to abrasion—trend toward superiority over carbon steels.

Resistance to corrosion—Resistance to atmospheric corrosion is substantially superior to carbon steels. Results of 9 years of exposure of 71 low-alloy steels in industrial and marine atmospheres led Copson [326] 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 [571] concluded that copper, nickel, and chromium were the most useful alloying elements for resistance to atmospheric and sea-water corrosion. In inland waters the low-alloy steels are 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, for example, galvanizing, are readily applicable to these steels.

A bulletin issued by the American Iron and Steel Institute [511] gives manufacturing details and available sizes for hot-rolled or cold-rolled sheet and strip, bars, plates, beams, and other structural shapes. The high-strength low-alloy structural steels are discussed in SAE Specification 950 [732a], and the American Society for Testing Materials has several specifications [512] for these steels including A 242–55, High Strength Low Alloy Structural Steel; A 374–54T, High Strength Low Alloy Cold Rolled Steel Sheet and Strip; and A 375–54T, High Strength Low Alloy Hot Rolled Steel Sheet and Strip.

### c. Ultra-High-Strength Structural Steels

Steels can be processed to much higher strengths or to much improved strength-to-weight ratios than are usually employed for structural components, but the assumption that these higher strengths and hardnesses are always associated with dangerous brittleness formerly restricted their processing to moderate strength levels. For example, to avoid the so-called 500° F embrittlement range, the aircraft industry required that steel airframe parts must be tempered at temperatures above 800° F after quenching. Under these conditions, which automatically limited the maximum strength level to the range of 180,000 to 200,000 psi, aircraft quality type 4340 oil-quenched and tempered at about 900° F became the most commonly used material for important steel components in aircraft.

Attempts in recent years to develop steels combining tensile strengths above 200,000 psi with useful ductility and toughness have followed two courses—modification of the heat treatment and modification of the composition. A comprehensive testing program sponsored by the Lockheed Aircraft Company showed that tensile strengths of about 270,000 psi, together with useful ductility and toughness, could be obtained from type 4340 by lowering the tempering temperature to 400° or 450° F. Further lowering of the tempering temperature produced somewhat higher tensile strengths, but the unrelieved residual stresses caused unacceptable losses in yield strength, ductility, and impact strength. In modifications of the composition, the Crucible Steel Company took advantage of the fact that silicon raises the temperature of initiation of the 500° F embrittlement and simultaneously retards the softening that accompanies an increase in tempering temperature.

Table 18. *Nickel-containing high-strength low-alloy steels [541, 463]*

| Name | Producer | C (max.) | Mn | P | S (max.) | Si | Cu | Ni | Others |
|---|---|---|---|---|---|---|---|---|---|
| | | % | % | % | % | % | % | % | % |
| Cor-Ten | Republic Steel Corp., Carnegie-Illinois, and others. | 0.12 | 0.2 to 0.5 | 0.07 to 0.15 | 0.05 | 0.25 to 0.75 | 0.25 to 0.55 | 0.65 max | 0.3 to 1.25 Cr. |
| Double Strength. | Republic Steel Corp | .12 | 0.5 to 1.0 | 0.04 max | .05 | | 0.5 to 1.0 | 0.5 to 1.1 | 0.1 Mo min. |
| Dynalloy | Allan Wood Steel Co | .15 | 0.6 to 1.0 | 0.05 to 0.1 | .05 | 0.3 max | 0.3 to 0.6 | 0.4 to 0.7 | 0.05 to 0.15 Mo. |
| Hi Steel | Inland Steel Co | .12 | 0.5 to 0.9 | 0.05 to 0.12 | .05 | 0.15 max | 0.95 to 1.3 | 0.45 to 0.75 | 0.08 to 0.18 Mo;<br>0.12 to 0.27 Al. |
| Mayari R | Bethlehem Steel Co | .12 | 0.5 to 1.0 | 0.06 to 0.12 | .05 | 0.1 to 0.5 | 0.3 to 0.7 | 0.25 to 0.75 | 0.4 to 1.0 Cr. |
| Tri-Ten | Carnegie-Illinois Steel Corp. | .25 | 1.3 max | .045 max | .05 | 0.1 to 0.3 | 0.3 to 0.6 | 0.5 to 1.0 | |
| Tri-Ten E | do | .25 | 1.3 max | .045 max | .05 | 0.1 to 0.3 | 0.2 min | 0.5 to 1.0 | 0.02 V min. |
| Yoloy | Youngstown Sheet & Tube Co. | .15 | 0.6 max | 0.05 to 0.1 | .05 | | 0.75 to 1.25 | 0.5 to 2.0 | |

Thus a steel containing 1.5 to 2.0 percent of silicon can be tempered at about 600° F to provide hardness and strength equivalent to that of a similar steel of normal silicon content tempered at a much lower temperature [374]. Another fact is that at a given strength the best properties are obtained with the lowest feasible carbon content. Consequently, the Crucible Steel Company reduced the carbon content of type 4340 to 0.25 percent, raised the silicon to 1.5 percent, increased the manganese and molybdenum, and decreased the chromium to produce their Hy-Tuf steel, which develops tensile strengths of about 230,000 psi when tempered at 550° F. Another example of the desirability of low carbon contents is the modified type 4330 developed by Republic Steel Corp. in association with Bendix Aviation Corp. The lowered carbon content, plus an increase in molybdenum and the introduction of vanadium, produced a steel with better impact properties than 4340 at both the 230,000- and 250,000-psi tensile strength levels. The remaining steel that had been used commercially in 1955 is the HS–220 developed by The Timken Steel & Tube Company. It contains low-carbon and moderate silicon; is similar in properties to the modified type 4330, but is reported more easily to meet minimum impact specifications.

Information about these four steels that have been accepted by the aircraft industry, together with others that were under investigation but not yet in production status, according to Sands and Miller [727], is presented in table 19. All of the nonestablished steels, including the Tricent steel originated in the International Nickel Company Research Laboratory, are aimed for tensile strengths of 300,000 psi or better. This requires carbon contents of 0.40 percent or more, and in some instances the silicon content of 4340 is raised to about 1.5 percent, as was shown to be practical by the work of Shih, Averbach, and Cohen [730]. Rosenberg and Irish [783] reported 285,000 psi ultimate tensile strength with 10 percent elongation for a heat-treated, modified 4340 similar to Tricent. In other cases the use of a relatively high tempering temperature, for high strength without embrittlement, is attained with less silicon and an altered alloy content.

As was stated by Sands and Miller [727], it should be emphasized that the use of steel at very high strength and high hardness levels involves careful consideration of certain factors that are relatively unimportant and easily coped with at lower strength levels. These include sensitivity to hydrogen embrittlement in plating operations, to damage in grinding, to the effects of surface decarburization in heat treatment, and difficulties in welding, machining, and forming operations. Careful handling and meticulous inspection are required, and particular effort must be made to design to minimize notch effects and other stress raisers.

## 3.3. Cast Steels and Cast Irons

### a. Cast Steels

Very soon after nickel began to be used commonly as an alloying element in hot-worked steels, its effect in increasing the strength and ductility of cast steels was noted. By 1910 the properties of cast steel containing about 3.5 percent of nickel were well known, and the steel was widely used for cast sections in heavy ordnance. In early work on centrifugally cast gun tubes at Watertown Arsenal, a 2.80-percent nickel steel containing 0.35 percent of carbon was found to be satisfactory [23, 25]. Cone [18] 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

TABLE 19. *Proposed and established ultra-high-strength steels* [727]

| Steel | AMS No. [a] | Average composition | | | | | | | Tempering temperature | Mechanical properties | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | Si | Ni | Cr | Mo | Others | | Tensile strength | Yield strength | Elongation in 2 in. | Reduction of area | Charpy V-notch impact |
| Used in 1955 production airplanes | | | | | | | | | | | | | | |
| | | % | % | % | % | % | % | % | °*F* | *psi* | *psi* | % | % | *ft-lb* |
| 4340 | 6415 | 0.40 | 0.75 | 0.27 | 1.83 | 0.80 | 0.25 | ------ | 450 | 270,000 | 212,000 | 10 | 35 | 19 |
| 4330 Modified | 6427 | .30 | .90 | .27 | 1.83 | .85 | .43 | 0.08 V | 475 | 255,000 | 209,000 | 10 | 42 | 17 |
| HS–220 | 6407 | .30 | .70 | .55 | 2.05 | 1.20 | .45 | ------ | 610 | 237,000 | 195,000 | 11 | 42 | 16 |
| Hy-Tuf | 6418 | .25 | 1.35 | 1.50 | 1.83 | 0.30 | .40 | ------ | 550 | 230,000 | 190,000 | 13 | 49 | 30 |
| Under investigation | | | | | | | | | | | | | | |
| 4350 | ---- | 0.50 | 0.75 | 0.27 | 1.83 | 0.80 | 0.25 | ------ | 400 | 317,500 | 244,000 | 8 | 15 | 11 |
| HS–260 | ---- | .40 | .85 | .60 | 2.20 | 1.45 | .50 | ------ | ------ | 290,000 | ------ | ------ | ------ | ------ |
| Super Hy-Tuf | ---- | .40 | 1.30 | 2.30 | ---- | 1.40 | .35 | 0.20 V | 550 | 294,000 | 241,000 | 10 | 35 | 14 |
| Hi C Super Hy-Tuf | ---- | .47 | 1.28 | 2.42 | ---- | 1.11 | .42 | .25 V | 500 | 325,000 | ------ | ------ | 24 | 10 |
| 98B40 Modified | ---- | .40 | 0.75 | 0.27 | 0.85 | 0.80 | .20 | Boron | 480 | 287,000 | 236,000 | 7 | 28 | 13 |
| USS Strux | ---- | .43 | .90 | .55 | .75 | .90 | .55 | do | ------ | 290,000 | ------ | ------ | ------ | ------ |
| Tricent | ---- | .43 | .80 | 1.60 | 1.83 | .85 | .38 | 0.08 V | 500 | 297,000 | 242,000 | 8 | 23 | 18 |
| Super Tricent | ---- | .55 | .80 | 2.10 | 3.60 | .90 | .50 | ------ | 400 | 342,000 | ------ | ------ | ------ | 12 |

[a] Aeronautical Materials Specifications (SAE).

carbon steels of approximately the same ductility. It is now known that the beneficial effects of nickel in cast steels result primarily 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 3.5 percent, nickel is useful alone, and in smaller amounts, 0.40 to 1.5 percent, it is effective in combination with manganese and other alloying elements. The most favorable combinations of mechanical properties, in cast as well as in wrought steels, are 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 tensile properties of cast plain nickel steels were reviewed by Lorig and Williams [53], and the results of a number of investigations in the 1930's were summarized by Hall [463], as shown in table 20. The Steel Casting Handbook [247] contains tables of the mechanical properties of cast nickel steels of the 2300 series after commercial heat treatments. Armstrong [57, 83] reported typical properties of 30-ton naval castings and large railroad frames, made of steel containing 0.30 percent of carbon, 0.90 percent of manganese, and 3 percent of nickel, 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 nickel steels, as reported by Lorig [96], are given in table 21. Chromium functions as a ferrite strengthener in low-carbon steels and also has a strong tendency to form hard carbides. Chromium therefore increases the strength and hardness of cast nickel steels, but the increase in strength is accompanied by some loss of 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. The Steel Casting Handbook [247] contains tabulations of the mechanical properties of cast nickel-chromium steels of the 3100 series and of cast nickel-molybdenum steels of the 4600 series after commercial heat treatments. Vanadium is an effective grain refiner and, therefore, is frequently added to cast nickel steels, usually in amounts between 0.08 and 0.15 percent, to improve the yield to tensile

TABLE 20. *Typical properties of cast nickel steels [463]*

| Composition | | | Treatment | Tensile strength | Yield strength | Elongation in 2 in. | Reduction of area | Charpy value |
|---|---|---|---|---|---|---|---|---|
| C | Mn | Ni | | | | | | |
| | | | | *psi* | *psi* | % | % | *ft-lb* |
| 0.17 | 0.80 | 2.05 | Double normalized and tempered | 80,000 | 53,000 | 29 | 60 | [a] 58 |
| .17 | .40 | 2.50 | _____do | 80,000 | 56,000 | 31 | 59 | 30 |
| .24 | .60 | 2.40 | _____do | 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 | 0.60 | 3.25 | Annealed | 95,500 | 61,000 | 22 | 48 | ________ |
| .39 | .75 | 3.50 | _____do | 115,000 | 65,000 | 22 | 35 | ________ |
| .33 | .60 | 3.35 | Water-quenched and tempered | 134,000 | 120,000 | 17 | 40 | ________ |

[a] Izod value.

TABLE 21. *Mechanical properties of some nickel and nickel-alloy cast steels [96]*

| Composition, percent | | | | | | | Normalized from— | Tempered at— | Tensile strength | Yield strength | Elongation in 2 in. | Reduction of area |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | Si | Mn | Ni | Cr | Mo | V | | | | | | |
| | | | | | | | *°F* | *°F* | *psi* | *psi* | % | % |
| 0.30 | 0.35 | 0.90 | 2.15 | ______ | ______ | ______ | 1,650 | 1,200 | 103,000 | 62,500 | 25 | 50 |
| .32 | .35 | .90 | 1.33 | 0.79 | ______ | ______ | 1,650 | 1,250 | 100,000 | 60,000 | 22.5 | 43 |
| .30 | .35 | .90 | 1.45 | .54 | 0.21 | ______ | 1,650 | 1,200 | 104,000 | 79,000 | 22 | 46 |
| .29 | .35 | .90 | 1.82 | ______ | .35 | ______ | 1,650 | 1,200 | 92,000 | 65,000 | 22.5 | 47 |
| .32 | .39 | 1.15 | 0.67 | ______ | ______ | ______ | 1,650 | 1,275 | 94,500 | 57,000 | 24.5 | 48 |
| .31 | .35 | 1.60 | 1.37 | ______ | ______ | ______ | 1,550 | 1,200 | 101,000 | 68.000 | 24.5 | 56 |
| .24 | .29 | 0.74 | 1.29 | ______ | ______ | 0.10 | 1,725 | 1,200 | 81,500 | 64,000 | 30.5 | 61 |

strength ratio and ductility. Manganese is the cheapest of the alloying elements, and its use in combination with nickel produces high ratios of yield to tensile strengths, and good ductility. Armstrong [65] concluded that the benefits of manganese in cast low-alloy steels were most apparent when the manganese content was above 1 percent. The cast nickel-manganese steels whose properties are tabulated in the Steel Casting Handbook contain from 1.35 to 1.60 percent manganese. Complex steels are also used in the cast condition; the Steel Casting Handbook contains tabulations of the mechanical properties of cast Ni–Cr–Mo steels of the 4300 and 8600 series, cast Mn–Ni–Cr–Mo steels of the 9500 series, and cast Ni–Mn–Cr–Mo steels.

The cast nickel and nickel-alloy steels have been extensively used for heavy-section castings, subject to high dynamic and fatigue stresses, used in the railroad, automotive, and petroleum industries, and in rolling mill, excavating, road building, and agricultural machinery. Specific items include gears, pinions, sprockets, cams rollers, valves, hammer dies, brake drums, bucket teeth, conveyor chain links, and railroad freight car side frames, bolsters, yokes, center posts, striking plates, and couplers. ASTM Specification A 352–55T covers ferritic steel castings for pressure-containing parts suitable for low-temperature service, including 2 percent and 3.5 percent nickel steels, which are recommended, respectively, for use at temperatures down to −100° and −150° F. ASTM Specification A–217–55, alloy steel castings for pressure-containing parts suitable for high-temperature and corrosive service, includes two Ni–Cr–Mo steels containing about 1 percent of nickel. Cast steels with higher nickel contents, for corrosion- and heat-resistant uses, are described in other specifications issued by the American Society for Testing Materials [512], including A 296–55 for corrosion-resistant iron-chromium-nickel alloy castings for general application, and A 297–55 for heat-resistant iron-chromium-nickel alloy castings for general application. The latter includes 9 chromium-nickel-steels of Alloy Casting Institute grades HF, HH, HI, HK, HE, HT, HU, HW, and HX, with chromium contents ranging from 10 to 30 percent and nickel from 8 to 68 percent. See also [784].

### b. Cast Irons

Improvement of the properties of cast iron by means of additions of nickel dates back at least to 1799, when Hickling [3] patented the use of 2.5 to 25 percent of nickel in making hollow cast-iron vessels. Additional uses of nickel, to improve the strength, malleability, surface hardness, and resistance to oxidation of cast iron, were developed empirically during the 19th century, but it was not until early in 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 by Merica [27], and additional data were presented by Wickenden and Vanick [33]. In the 1937 Howe Memorial Lecture, Merica [80] reviewed developments in alloyed cast iron. Subsequent reviews include those of Bairiot and Berthelier [260] in 1951 and of Hall [463] in 1954.

Even today the iron-nickel-carbon system is not well understood, and very little is known of the equilibria in the iron-silicon-nickel-carbon system. It has been established [463] that nickel decreases the solubility of carbon in molten cast iron, lowers 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 silicon 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. Nickel widens the field of the intermediate acicular structures, which have desirable mechanical properties. Nickel reduces the rate of cooling required to develop a martensitic matrix; an entirely austenitic matrix is obtained in normally cooled sand castings that contain 18 percent or more of nickel, or lesser amounts of nickel in the presence of other alloying elements, including copper and chromium. It is generally considered that irons with alloy contents of this magnitude are intended for special purposes, for example, resistance to corrosion, heat, and wear, whereas the engineering cast irons usually have a total alloy-content that does not exceed 3 or 4 percent.

The size, shape, and uniformity of distribution of the 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 the 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, is widely used for this purpose [94, 239]. The graphite phase in cast iron may be altered completely, from its usual lamellar flake form to spherical nodules, by special ladle additions. Morrogh [152] described the use of ladle additions of cerium or misch metal, and the International Nickel Company [198] recommended magnesium. Subsequently, other combinations were recommended to facilitate additions of magnesium to molten iron, and it was found that the nodular form of graphite could be produced in austenitic, as well as in pearlitic iron. Spheroidal or "ductile" cast irons possess high tensile strength and ductility and at the same time retain the machinability and much of the castability of standard gray irons. Holdeman and Stearns [190] reported that the tensile strength of an iron could be raised from 20,000–40,000 psi to 70,000–120,000 psi by nodularizing, and that subsequent annealing for 1 hr at 1,650° F resulted in an elongation of 20 percent with a tensile strength of about 70,000 psi. Annealing below the critical temperature increases ductility by converting the pearlite in the matrix to ferrite and graphite.

The mechanical properties considered important in cast iron include tensile strength, hardness, compressive strength, torsional strength, shear strength, shock resistance, endurance limit, transverse strength, and deflection. When elastic moduli are reported they are generally based on the stress-strain relationship at one-fourth of the ultimate load. Except for the malleable and ductile irons, cast iron generally is brittle, has poor shock resistance, and shows little elongation or reduction of area in a tensile test. The American Society for Testing Materials Specification A 48–48 [512], for gray iron castings where strength is a consideration, subordinates chemical composition to physical properties and establishes seven classes based on minimum tensile strengths ranging from 20,000 to 60,000 psi.

The effect of nickel additions on some mechanical properties of a cast iron is illustrated in figure 27, and the relative amounts of nickel and silicon that will produce various levels of tensile strength in castings up to 4 in. thick and containing 2.75 percent of total cabron are shown in figure 28. Chromium is a powerful carbide stabilizer, thereby increasing the tensile strength, transverse strength, and hardness. Molybdenum is a mild carbide stabilizer and an effective strengthener. Examples of typical compositions of high-strength cast irons, assembled by Hall [463] from various sources, are presented in table 22. These room-temperature properties in many cases may be improved by heat treatment. The amounts of alloying elements present in these engineering cast irons are not enough to materially improve their resistance to corrosion or to high temperatures. For example, Denison and Romanoff [450] reported that up to 3 percent of nickel, with or without other elements, had little if any effect, whereas 15 percent of nickel appreciably reduced the loss in weight and depth of pits in 14-year soil-exposure tests; Greene and Sefing [560] reported that low-alloy irons could be used up to about 1,100° F, as grate bars, annealing boxes, etc., whereas higher alloyed irons could be used at higher temperatures, and Wilks, Mathews, and Kraft [620] reported that ductile high-nickel irons were useful up to 1,200° or 1,300° F. ASTM Specification A 278–53, for gray iron castings for pressure-containing parts, recommends that in this service, classes 20, 25, 30, and 35 be restricted to temperatures below 450° F, and that only the 40, 50, and 60 classes be used at temperatures between 450° and 650° F. According to Hall [463] compressive strengths of these cast irons range from 80,000 to 220,000 psi; the 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,

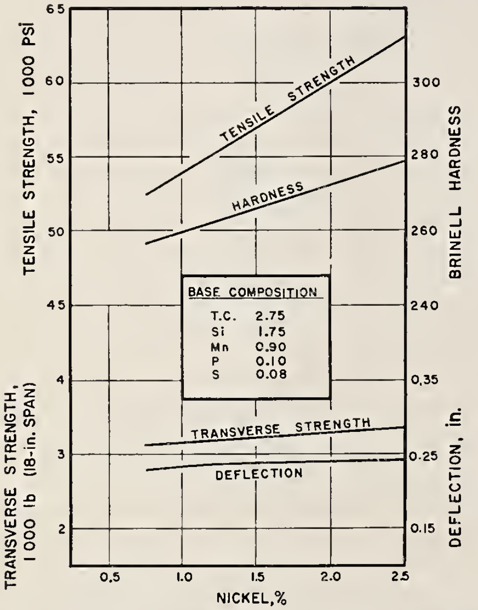

Figure 27. *Effect of nickel ladle additions on some mechanical properties of cupola iron of the composition indicated [110].*

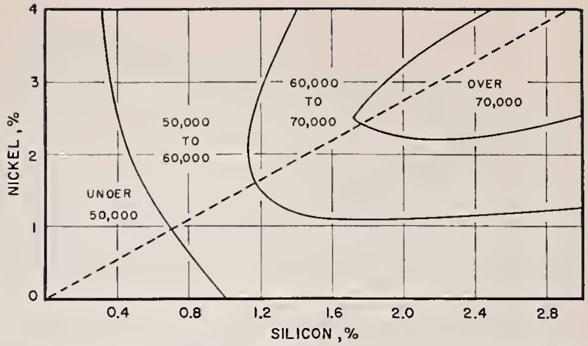

Figure 28. *Combinations of nickel and silicon with 2.75-percent total carbon to produce various ranges of tensile strength in castings ½- to 4-in. thick [110].*

The diagonal line indicates the most desirable combinations.

TABLE 22. *Typical compositions and properties of some high-strength cast irons* [*463*]

| 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* | *in.* |
| 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.

the fatigue strength increases with increasing tensile strength, but 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, cam shafts, couplings, gears, machinery frames, dies for forming stainless steel, 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 contents. For example, the International Nickel Company's Ni-Hard contains 2.9 to 3.6 percent of C, 4 to 4.75 percent of Ni, 1.4 to 3.5 percent of Cr, and is martensitic as sand cast.

Many cast irons with higher alloy contents have been developed since about 1930, for improved heat resistance 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, etc. Hallett [341] 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. Friend and LaQue [338] provided information about the widely used Ni-Resist series, of compositions shown in table 23. 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. Friend and LaQue reported the use of these alloys for pumps and valves, and for handling hot sodium hydroxide and other caustic solutions, cold solutions containing small amounts of sulfuric, hydrochloric, phosphoric, and other nonoxidizing acids, and for pumping brines and sea water. Type 3 has a low coefficient of thermal expansion and is particularly useful as filter-press plates, drums, and grids, where cyclic changes from hot to cold solutions require material resistant to thermal cracking. Application of the ductile iron magnesium treatment to Ni-Resist irons results in marked improvement in strength, elongation, and toughness, at room temperature and at elevated temperatures. According to Wilks, Mathews, and Kraft [620], tensile, rupture, and creep tests show that the utility of the standard ferritic and pearlitic grades is limited to about 1,000° F for long-term load-

Table 23. *Ni-Resist heat-resistant and corrosion-resistant cast irons [338]*

| | Composition, percent | | | | |
|---|---|---|---|---|---|
| | Type 1 | Type 2 [a] | Type 3 | Type 4 | Type 5 (Minvar) |
| Carbon, total | 3.0 max | 3.0 max | 2.75 max | 2.6 max | 2.4 max. |
| Silicon | 1.0 to 2.5 | 1.0 to 2.5 | 1.0 to 2.0 | 5.0 to 6.0 | 1.0 to 2.0. |
| Manganese | 1.0 to 1.5 | 0.8 to 1.5 | 0.4 to 0.8 | 0.4 to 0.8 | 0.4 to 0.8. |
| Nickel | 13.5 to 17.5 | 18.0 to 22.0 | 22.0 to 32.0 | 29.0 to 32.0 | 34.0 to 36.0. |
| Copper | 5.5 to 7.5 | 0.5 max | 0.5 max | 0.5 max | 0.5 max. |
| Chromium | 1.75 to 2.5 | 1.75 to 2.5 or<br>[b] 3.0 to 6.0. | 2.5 to 3.5 | 4.5 to 5.5 | [c] 0.1 max. |

[a] For caustics, food, etc., where copper contamination cannot be tolerated.
[b] Where machining is required, chromium at the 3.0- to 4.0-percent level is recommended.
[c] Where higher hardness and strength are desired, chromium may be 2.5 to 3.0 percent at the expense of increased expansivity.

carrying applications when both scaling resistance and strength are considered, but the high-nickel austenitic irons should be useful to 1,200° or 1,300° F. Their results for the effect of temperature on the tensile strength and ductility of ductile cast irons are shown in figure 29. Greene and Sefing [560] concluded that, for grate bars, stoves, annealing boxes, and similar applications, unalloyed cast irons were useful up to about 900° F, low-alloy irons up to about 1,100° F, and high-alloy irons, like Ni-Resist, up to 1,200° F or higher. Additional information about Ni-Resist is contained in a booklet [613] issued by the International Nickel Company.

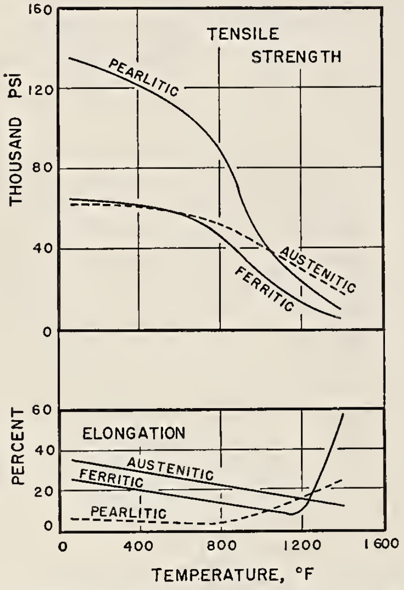

Figure 29. *Effect of temperature on the tensile strength and and elongation of ductile cast irons [620].*

## 3.4. Austenitic Chromium-Nickel Steels

### a. General

The chromium-nickel steels popularly known as stainless steels are widely used because of their resistance to corrosion, desirable mechanical properties, and ability to retain these properties at temperatures above and below room temperature. Chromium is the principal alloying element; it is always present in amounts in excess of the nickel content, and a number of stainless steels, particularly the martensitic types, are nickel free. The demand for nickel-containing stainless steels is so intense that, in spite of the low percentages of nickel involved, approximately one-fourth of the total annual consumption of nickel is required for the production of stainless steels, either wrought or cast, as listed in table 24. The ensuing discussion will be largely devoted to the wrought austenitic stainless steels; for further information on stainless steels in general, including recent modifications and developments, see the sections on heat-resistant alloys, corrosion-resistant alloys, and superalloys.

Nickel has a significant effect on corrosion-resistance in the presence of chromium, but the principal function of nickel in stainless steel is to promote the formation of austenite at high temperatures, the retention of the austenitic structure at and below room temperature, and to retard its transformation to martensite during cold-working operations. The 18-chromium 8-nickel composition was the original austenitic stainless steel, but it is now known that more than 8 percent of nickel is required to insure a stable austenitic structure under all conditions, particularly for use at subzero temperatures. The magnetic behavior supplies a rough indication of the stability of the austenite; the steels become ferromagnetic with increasing amounts of ferrite from decomposition of unstable austenite.

The austenitic stainless steels can be hot worked readily, although more power is required, for presses and rolls, than for unalloyed steels. In some of the highly alloyed stainless steels, the hot-working properties are improved by additions of small amounts of rare earth metals of the cerium group [429] or of boron [761]. The stainless steels can be cold worked subject to the limitation that they work harden readily. They are extremely resistant to shock, can be welded without difficulty, and have better strength and resistance to scaling at high temperatures than the martensitic or ferritic stainless steels. The austenitic stainless steels cannot be hardened by heat treatment; they are somewhat difficult to

TABLE 24. *Nickel-containing standard stainless steels, wrought and cast* [*539*]

Wrought stainless steels
(American Iron and Steel Institute designations, April 1955)

| Type |  | Carbon max | Chromium | Nickel | Others [b] |
|---|---|---|---|---|---|
| AISI | SAE [a] |  |  |  |  |
| AUSTENITIC STEELS |  |  |  |  |  |
|  |  | % | % | % | % |
| 301 | 30301 | 0.15 | 16 to 18 | 6 to 8 |  |
| 302 | 30302 | .15 | 17 to 19 | 8 to 10 |  |
| 302B | ------------ | .15 | 17 to 19 | 8 to 10 | Si, 2 to 3. |
| 303 | 30303F | .15 | 17 to 19 | 8 to 10 | Mo or Zr, 0.6 max; S, 0.15 min; P, 0.2 max. |
| 303 Se | ------------ | .15 | 17 to 19 | 8 to 10 | Se, 0.15 min; S, 0.06 max; P, 0.2 max. |
| 304 | 30304 | .08 | 18 to 20 | 8 to 12 |  |
| 304L | ------------ | .03 | 18 to 20 | 8 to 12 |  |
| 305 | 30305 | .12 | 17 to 19 | 10 to 13 |  |
| 308 | ------------ | .08 | 19 to 21 | 10 to 12 |  |
| 309 | 30309 | .20 | 22 to 24 | 12 to 15 |  |
| 309S | ------------ | .08 | 22 to 24 | 12 to 15 |  |
| 310 | 30310 | .25 | 24 to 26 | 19 to 22 | Si, 1.5 max. |
| 310S | ------------ | .08 | 24 to 26 | 19 to 22 | Si, 1.5 max. |
| 314 | ------------ | .25 | 23 to 26 | 19 to 22 | Si, 1.5 to 3.0. |
| 316 | 30316 | .08 | 16 to 18 | 10 to 14 | Mo, 2 to 3. |
| 316L | ------------ | .03 | 16 to 18 | 10 to 14 | Mo, 2 to 3. |
| 317 | 30317 | .08 | 18 to 20 | 11 to 15 | Mo, 3 to 4. |
| 321 | 30321 | .08 | 17 to 19 | 9 to 12 | Ti, 5×C min. |
| 322 [c] | ------------ | .12 | 16 to 18 | 6 to 8 | Ti, 1.0; Al 1.0 |
| 325 [d] | 30325 | .25 | 7 to 10 | 19 to 23 | Cu, 1.0 to 1.5. |
| 347 | 30347 | .08 | 17 to 19 | 9 to 13 | CB–Ta, 10×C min. |
| 348 | ------------ | .08 | 17 to 19 | 9 to 13 | Cb–Ta, 10×C min; Ta, 0.1 max. |
| MARTENSITIC STEELS |  |  |  |  |  |
| 414 | 51414 | 0.15 | 11.5 to 13.5 | 1.25 to 2.50 |  |
| 431 | 51431 | .20 | 15 to 17 | 1.25 to 2.50 |  |
| 443 [d] | ------------ | .20 | 18 to 23 | 0.50 max | Cu, 0.9 to 1.25; Si, 0.75 max. |

CAST STAINLESS STEELS
(Alloy Casting Institute Designations, 1954) [e]

| Type [f] | Carbon max | Silicon max | Chromium | Nickel | Others [g] |
|---|---|---|---|---|---|
|  | % | % | % | % | % |
| CA–15 | 0.15 | 1.5 | 11.5 to 14.0 | 1.0 max | (i) |
| CA–40 | 0.2 to 0.4 | 1.5 | 11.5 to 14.0 | 1.0 max | (i) |
| CB–30 | 0.30 | 1.0 | 18 to 22 | 2.0 max |  |
| CC–50 | .50 | 1.0 | 26 to 30 | 4.0 max |  |
| CE–30 | .30 | 2.0 | 26 to 30 | 8 to 11 |  |
| CF–8 | .08 | 2.0 | 18 to 21 | 8 to 11 |  |
| CF–8C | .08 | 2.0 | 18 to 21 | 9 to 12 | Cb or Cb–Ta [h]. |
| CF–8M | .08 | 1.5 | 18 to 21 | 9 to 12 | Mo, 2 to 3. |
| CF–12M | .12 | 1.5 | 18 to 21 | 9 to 12 | Mo, 2 to 3. |
| CF–16F | .16 | 2.0 | 18 to 21 | 9 to 12 | Mo, 1.5 max; Se, 0.2 to 0.35; P, 0.17 max. |
| CF–16FA [j] | .16 | 2.0 | 18 to 21 | 9 to 12 | Mo, 0.4 to 0.8; S, 0.2 to 0.4. |
| CF–20 | .20 | 2.0 | 18 to 21 | 8 to 11 |  |
| CH–20 | .20 | 2.0 | 22 to 26 | 12 to 15 |  |
| CK–20 | .20 | 2.0 | 23 to 27 | 19 to 22 |  |
| CN–7M | .07 | (k) | 18 to 22 | 21 to 31 | Mo; Cu. [k]. |
| HC | .50 | 2.0 | 26 to 30 | 4 max | (i) |
| HD | .50 | 2.0 | 26 to 30 | 4 to 7 | (i) |
| HE | 0.2 to 0.5 | 2.0 | 26 to 30 | 8 to 11 | (i) |
| HF | 0.2 to 0.4 | 2.0 | 19 to 23 | 9 to 12 | (i) |
| HH | 0.2 to 0.5 | 2.0 | 24 to 28 | 11 to 14 | N, 0.2 max.[i]. |
| HI | 0.2 to 0.5 | 2.0 | 26 to 30 | 14 to 18 | (i) |
| HK | 0.2 to 0.6 | 3.0 | 24 to 28 | 18 to 22 | (i) |
| HL | 0.2 to 0.6 | 3.0 | 28 to 32 | 18 to 22 | (i) |
| HN | 0.2 to 0.5 | 2.0 | 19 to 23 | 23 to 27 | (i) |
| HT | 0.35 to 0.75 | 2.5 | 13 to 17 | 33 to 37 | (i) |
| HU | 0.35 to 0.75 | 2.5 | 17 to 21 | 37 to 41 | (i) |
| HW | 0.35 to 0.75 | 2.5 | 10 to 14 | 58 to 62 | (i) |
| HX | 0.35 to 0.75 | 2.5 | 15 to 19 | 64 to 68 | (i) |

---

[a] SAE designations as of January 1952.

[b] *Manganese*, 1.00 max in 400 types and 2.00 max in all 300 types except SAE 30325 (0.6 to 0.9 Mn) and SAE 30347 (2.5, Mn max); *Silicon*, 1.0 max in all types except 302B (2.0 to 3.0 Si), 310 and 310S (1.5 max), 314 (1.5 to 3.0). Silicon in SAE 30321 and 30347 is 1.5 max and in 30325 is 1.0 to 2.0. *Sulfur*, 0.030 max except, as indicated, for 303 and 303 Se. *Phosphorus*, 0.045 max except, as indicated, for 303 and 303 Se.

[c] Also known as "Stainless W". Not an AISI Standard.

[d] Not an AISI Standard.

[e] Most of these are also covered by ASTM A217, A296, and A297.

[f] Initial letter C designates alloys generally used to resist corrosion at temperatures below 1,200° F. Initial H designates alloys generally used above 1,200° F.

[g] *Manganese*, 1.0 max in CA–15, CA–40, CB–30, CC–50; 1.50 max in all other C alloys; 1.0 max in HC; 1.5 max in HD; 2.0 max in all other H alloys. *Phosphorus and Sulfur*, 0.04 max each except, as indicated, for CF–16F and CF–16FA.

[h] Cb, 8×C min, 1.0% max; Cb–Ta, 10×C min, 1.35% max.

[i] Mo, 0.5 max (not intentionally added).

[j] Not an A. C. I. Standard.

[k] Proprietary alloys containing varying amounts of Si, Mo, and Cu.

machine unless they contain sulfur or selenium; at temperatures between 800° and 1,600° F they are susceptible to carbide precipitation and consequent intergranular corrosion unless they have been stabilized by additions of titanium or columbium, or the carbon content has been lowered to below 0.03 percent. Metallographic etching methods and reagents for the detection of austenite, ferrite, sigma phase, and carbides were reviewed by Braumann and Pier [528]. Commercial procedures for cleaning, grinding, pickling, descaling, polishing, buffing, plating, coloring, etc., were discussed by DuMond [273].

### b. Physical and Mechanical Properties

The physical and mechanical properties of the wrought stainless steels are of interest for their engineering applications in corrosive environments. Properties of some steels of the 300 series are listed in tables 25 and 26. Additional data for stainless-steel tubing were supplied in a data sheet [272], for high-temperature steam piping by Blumberg [785] and by Curran and Rankin [786], for low-carbon steels by Buck, Heger, Phillips, and Queneau [176], and for mechanical properties of the 300 series in torsion by Muhlenbruch, Krivobok, and Mayne [294]. Fatigue data for stainless steels were reviewed by Ludwig [234] and by Richard and his associates [787]. Thermal-expansion characteristics of stainless steels between −300° and +1,000° F were reported by Furman [222a]. The properties and behavior of austenitic stainless steels of the 300 series at low temperatures were reviewed and extended down to 20° K by Kropschot and Graham [691]. They reported that the tensile strength increased with decreasing temperature, more noticeably for annealed than for cold-worked material; the yield strength generally increased slightly with decreasing temperature; elongation and reduction of area tended to decrease with decreasing temperature, but tensile failures still exhibited appreciable ductility at 20° K; the modulus of elasticity in tension increased with decreasing temperature and was 5 to 15 per-

TABLE 25. *Physical properties of some austenitic stainless steels* [*155*]

| Type | Density | Modulus of elasticity | Specific heat at 100° C | Linear thermal expansion, millionths/°F | | | | Thermal conductivity, cal/cm sec ° C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0° to 200° F | 0° to 600° F | 0° to 1,000° F | 0° to 1,500° F | Room temp | 100° C | 500° C |
| | *g/cm³* | *Million psi* | *cal/g* | | | | | | | |
| 302 | 7.93 | 29 | 0.118 | 9.0 | 9.5 | 10.1 | 11.1 | 0.052 | 0.050 | 0.0515 |
| 303 | 7.93 | 29 | .118 | 9.0 | 9.5 | 10.1 | 11.1 | .052 | .050 | ------ |
| 309 | 7.98 | 30 | .118 | 8.0 | 8.6 | 9.5 | 10.8 | .045 | .040 | ------ |
| 310 | 7.98 | 30.5 | .118 | 8.0 | 8.5 | 9.4 | 10.0 | ------ | .039 | ------ |
| 316 | 7.98 | 28.5 | .118 | 8.4 | 9.0 | 9.7 | 11.0 | ------ | .050 | ------ |
| 321 | 8.02 | 29 | .118 | 8.8 | 9.2 | 10.2 | 11.3 | ------ | .052 | ------ |

TABLE 26. *Mechanical properties of some austenitic stainless steels* [*155*]

| Type | Condition | Hardness number | | Tensile strength | Yield strength | Elongation in 2 in. | Reduction of area | Izod impact |
|---|---|---|---|---|---|---|---|---|
| | | Brinell | Rockwell B | | | | | |
| | | | | *1,000 psi* | *1,000 psi* | % | % | *ft-lb* |
| 302 | Annealed | 135 to 185 | 75 to 90 | 80 to 90 | 35 to 45 | 60 to 55 | 65 to 55 | 110 to 70. |
| 302 | Cold-rolled | 190 to 330 | 92 to 109 | 100 to 180 | 50 to 150 | 50 to 10 | | |
| 303 | Annealed | 130 to 150 | 72 to 80 | 80 to 90 | 35 to 45 | 60 to 50 | 70 to 55 | 110 to 70. |
| 309 | do | 140 to 185 | 78 to 90 | 90 to 110 | 40 to 60 | 65 to 50 | 65 to 50 | |
| 310 | do | 145 to 210 | 80 to 95 | 90 to 110 | 40 to 60 | 55 to 45 | 60 to 50 | |
| 316 | do | 135 to 185 | 75 to 90 | 80 to 90 | 35 to 55 | 70 to 60 | 75 to 60 | 120 to 70. |
| 316 | Cold-rolled | 180 to 300 | 92 to 105 | 100 to 150 | 50 to 125 | 50 to 15 | | |
| 321 | Annealed | 135 to 185 | 75 to 90 | 80 to 90 | 35 to 45 | 60 to 55 | 65 to 55 | |
| 321 | Cold-rolled | 180 to 300 | 92 to 105 | 100 to 180 | 50 to 150 | 50 to 10 | | |

TABLE 27. *Impact values of annealed 300 series stainless steels at low temperatures*

Compiled by Kropschot and Graham [691]

| Steel | ft lb at 290° to 300° K | | | ft-lb at 190° to 200° K | | | ft-lb at 75° to 90° K | | |
|---|---|---|---|---|---|---|---|---|---|
| | Charpy V-notch | Charpy keyhole | Izod | Charpy V-notch | Charpy keyhole | Izod | Charpy V-notch | Charpy keyhole | Izod |
| 302 | 110 to 120 | 80 to 95 | | | | | 100 to 120 | 88 | |
| 303 | | | 87 | | | 90 to 115 | | | 85 to 125. |
| 304 | 110 to 160 | 80 to 140 | 90 to 120 | 110 to 125 | 95 to 100 | 115 to 135 | 90 to 110 | 70 to 80 | 120. |
| 310 | | 65 | | | | | | 49 | |
| 316 | 71 | 68 | 103 | 81 | 62 | 114 | | 60 to 70 | 110. |
| 321 | 110 to 125 | 105 to 110 | 107 | 120 to 170 | | 120 | 110 | 89 | |
| 347 | 85 to 110 | 60 to 75 | 109 | 70 to 125 | 60 to 75 | 120 | 85 to 105 | 60 to 70 | |

cent greater at 77° K than at room temperature; limited fatigue data indicated that the endurance limit increased with decreasing temperature for both notched and unnotched specimens; impact strength decreased with decreasing temperature, but the decrease was gradual, and the austenitic steels do not exhibit the abrupt and appreciable loss of notch toughness that is shown by ferritic steels. Kropschot and Graham's data for annealed 304 are reproduced in figure 30 and are indicative of results obtained from other steels of the 300 series. Their summary of low-temperature impact data is reproduced in table 27. (See also Powell, Marshall, and Backofen [788].) Supplementing these data, Armstrong and Miller [258] showed that types 310 and 316 did not become embrittled after 2 weeks of exposure in liquid nitrogen. Kropschot and Graham pointed out that welded joints can have good tensile and impact properties at low temperatures, but the welding (or soldering) must be done carefully to avoid the formation of carbides and sigma phase. The low-temperature properties, including the low thermal conductivity, of the austenitic stainless steels make them valuable materials for the construction of cryogenic equipment. Figure 31, from data compiled by Powell and Blanpied [492] for types 303, 304, 316, and 347, indicates the approximate thermal conductivity of the 300 series at low temperatures. Additional data on torsion and tension properties of steels of the 300 series at very low temperatures were supplied by Collins, Ezekiel, Sepp, and Rizika [644], who reported irregularities in tension and in torsion occurring at about 30° K.

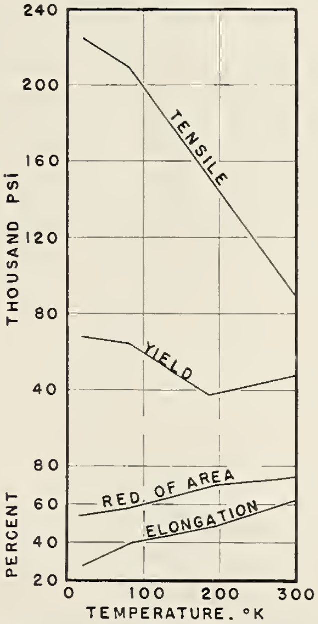

FIGURE 30. *Mechanical properties of annealed type 304 stainless steel at low temperatures* [*691*].

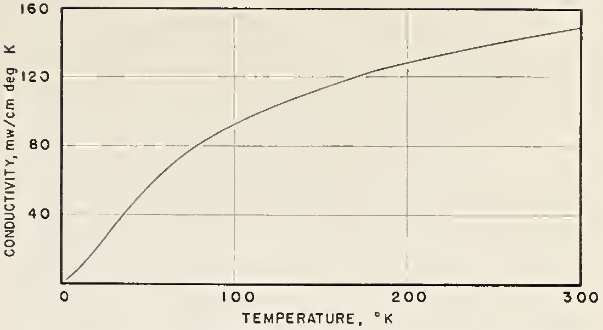

FIGURE 31. *Thermal conductivity of 300 series stainless steels at low temperatures* [*492*].

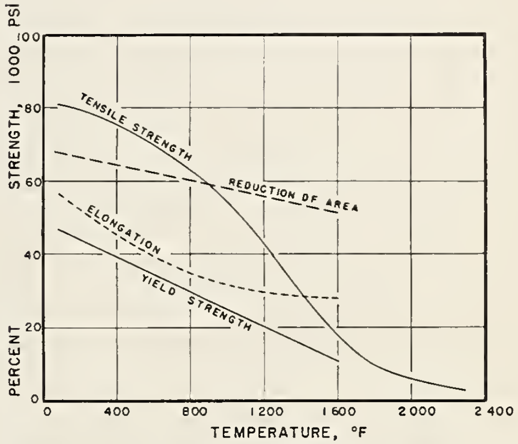

FIGURE 32. *Approximate mechanical properties of 18* Cr: *8* Ni *stainless steels at elevated temperatures.*

Figure 32 presents a rough approximation of the mechanical properties of 18-Cr 8-Ni stainless steels at elevated temperatures, based on the review of the voluminous literature by Simmons and Cross [361] for the ASTM–ASME Joint Committee on Effect of Temperature on the Properties of Metals. Simmons and Cross did not attempt any such simplified presentation of data that covered such a range; for example, their values for the room-temperature tensile strength of annealed 18:8 steels ranged from 77,000 to 92,000 psi, with corresponding values for the yield strength ranging from 28,000 to 59,000 psi. The properties of 18:8 steels were improved by cold work, for example, half-hard sheet material had a tensile strength of 154,000 psi at room temperature and 122,000 at 800° F. Steels with higher alloy contents, e. g., 18:8:Mo, 18:8:Cb, 25:20, have higher tensile strengths at room temperature but the values merge with the 18:8 curves at about 1,000° F. These indications that the economic use of austenitic stainless steels as constructional materials is limited to temperatures below about 1,200° F, as indicated by figures 32 and 33, are confirmed by Freeman and Voorhees' summary [661] of relaxation properties, i. e., of the replacement of initial elastic strain by the plastic strain of creep, with consequent reduction in stress level. Improvement in the properties by cold working that is very noticeable at room temperature 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 [695]. Increasing carbon in the range from 0.001 to 0.04 percent, and increasing nitrogen from 0.004 to 0.019 percent, have detrimental effects on the high-temperature properties [707]. These properties make stainless steels extremely useful for what are considered to be high temperatures in many industries. However, for the extreme requirements of the aircraft industry for gas turbines and jet engines, nickel-base and cobalt-base "super alloys" are superior to the stainless steels, even of the modified and precipitation-hardening types. The tendency of some austenitic stainless steels to become embrittled at high temperatures, through the formation of the intermetallic sigma phase [245, 420, 567, 712, 718] is detrimental to some of the mechanical properties. However, heating sigma-embrittled steels to 1,800° to 2,000° F eliminates sigma and restores the original toughness. Aborn [429] reported that sigma phase rarely occurs in plain 18:8 stainless steel, but almost any additional nickel or chromium increases the susceptibility to sigma formation, especially if ferrite is present; in molybdenum-bearing steels, for example, types 316 and 317, the intermetallic compound has a different structure than sigma and is called chi. Sigma formation in commercial nickel-chromium-iron alloys was summarized recently by Foley and Krivobok [758] and by Sticha [789].

The shortage of nickel in times of national emergency has presented a serious problem to the producers and consumers of stainless steel, particularly in regard to steels of the extremely popular 300 series. Since the functions of nickel in austenitic stainless steel are to form austenite at high temperatures, retain it at room temperature, and retard its transformation during cold-working operations, 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, it appeared that a combination of manganese and nitrogen could replace some of the nickel in these steels. During World War II there was developed a composition nominally 17 Cr, 4 Ni, 4 Mn, 0.10 to 0.15 N, and 0.08 to 0.12 C, that was austenitic in the solution-annealed condition, but the austenite was unstable during cold work. This instability resulted in an exceptionally high rate of work hardening during forming operations, but substantial quantities of this composition were used during the early war years. When the manganese was increased to approximately 6 percent, mechanical properties similar to those of type 301 and approaching those of type 302 were obtained. Later, because of the imposition of a 1-percent maximum on the nickel in stainless steel for civilian consumption, a composition nominally 15 Cr, 1 Ni, 17 Mn, 0.10 to 0.20 N, 0.08 to 0.15 C was produced as a substitute for type 301. The 17:4:6 and 18:5:8 compositions have been assigned AISI type numbers 201 and 202, respectively, with room-temperature mechanical properties as listed in table 28. (See also [790].) The other high-manganese, low-nickel, or nickel-free compositions that have been proposed have not yet been assigned AISI numbers to indicate their general acceptance by industry [480, 510, 552, 557, 583, 714, 726]. For a recent review of experience with steels of the 200 series, see Spencer [791].

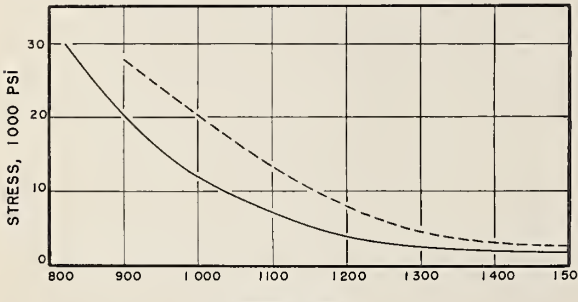

FIGURE 33. *Creep rates of 18:8 stainless steels.*

Dashed line represents 1-percent creep in 10,000 hr, solid line represents 1-percent in 100,000 hr [361].

TABLE 28. *Composition and some mechanical properties of high-manganese stainless steels [714]*

| Type | Composition, percent | | | | |
|---|---|---|---|---|---|
| | Cr | Ni | Mn | C | N [a] |
| 201 | 16 to 18 | 3.5 to 5.5 | 5.5 to 7.5 | 0.15 max | 0.25 max |
| 202 | 17 to 19 | 4 to 6 | 7.5 to 10.0 | 0.15 max | 0.25 max |

Typical mechanical properties of sheet material

| Type | Tensile strength | Yield strength [b] | Elongation in 2 in. | Rockwell hardness |
|---|---|---|---|---|
| | *psi* | *psi* | % | |
| 201 | 115,000 | 55,000 | 55 | B–90 |
| 301 | 110,000 | 40,000 | 60 | B–85 |
| 202 | 105,000 | 55,000 | 55 | B–90 |
| 302 | 90,000 | 40,000 | 50 | B–85 |

[a] Nitrogen usually 0.10 to 0.20 percent. [b] 0.2-percent offset.

### c. Resistance to Corrosion

(1) *Oxidation and atmospheric corrosion.* The resistance of stainless steel, with chromium contents in excess of 11 percent, to atmospheric corrosion is due to the presence of a passive oxide film that is richer in chromium than the underlying metal [429]. Protection afforded by this film is complete at room temperature and at moderately elevated temperatures, but the film increases in thickness as the temperature increases

and at very high temperatures becomes a scale. Eiselstein and Skinner [452] reported that scaling of stainless steels did not become pronounced until temperatures of 1,800° F or higher were reached. Stainless steels are being considered for use as the skin of airplanes, where, at supersonic speeds, the temperature of the skin may become as high as 800° F, but for this use precipitation-hardenable types, for example, 17–7 PH, are preferred because of their improved mechanical properties [758]. Paret [714] reported that the scaling resistance of the high-manganese types 201 and 202 up to about 1,550° F was equivalent to that of 301 and 302, but above 1,550° F the high-manganese steels scaled faster. Keith, Siebert, and Sinnott [574] reported that intergranular oxides formed by 100 hours exposure at 1,900° F had the same composition as the external scale, both being high in chromium and manganese, and low in nickel as compared to the underlying metal. In some of the early uses of austenitic stainless steel at high temperatures, it was observed that some of the stainless steels became embrittled and subject to intergranular oxidation and corrosion. The trouble was traced to the precipitation of chromium carbides at the grain boundaries, thereby reducing the chromium content and the oxidation- or corrosion-resistance of the adjacent matrix. The problem was attacked in two ways, first, 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 of table 24 and; second, by the addition to 0.08-carbon steels of elements such as columbium or titanium (types 321 and 347 of table 24) that formed their own stable carbides and thereby prevented the formation of chromium carbides. Both lines of attack were successful in greatly reducing the tendency to carbide precipitation at the grain boundaries [636, 726]. However, the carbide precipitation problem still exists for unstabilized, normal carbon stainless steels that are subject to prolonged heating in the temperature range 800° to 1,550° F, in the steam power and chemical industries as well as in aircraft uses [792, 793]. Testing procedure to determine the susceptibility of austenitic stainless steel to intergranular attack, using acidified copper sulfate solution, is described in ASTM Specification A 393–55T [512].

Stainless steels of 18:8 and higher alloy contents have good resistance to $H_2S$ corrosion over a range of pressures and at temperatures up to 1,000° F, in the catalytic reforming and desulfurizing units in petroleum refineries [628, 734]. Van Ness and Dodge [615] reported that hydrogen under pressure at 450° to 500° C did not have any embrittling effect on austenitic stainless steels.

(2) *General.* The resistance of austenitic stainless steels to corrosion in a great many media has resulted in extensive uses in the chemical, heavy chemical, transportation, and petroleum industries; in food processing and dairy equipment; in hospital, surgical, medical, 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. The literature on the subject is so tremendous that, in the present paper, only generalities can be presented, together with a few specific citations.

The low-carbon stainless steels generally show improved resistance to corrosion. The addition of molybdenum improves the resistance of 18:8 steel to many media, including sulfurous, sulfuric, phosphoric, formic and various hot organic acids, and substantially increases resistance to pitting in media containing halogen ions [726]. Steels stabilized with columbium or titanium are resistant to corrosive conditions that produce intergranular corrosion in unstabilized steels. Free-machining stainless steels generally are not as corrosion resistant as the low-sulfur types, and the austenitic steels are more resistant to corrosion than are the ferritic and martensitic types. The new chromium-nickel-manganese steels, types 201 and 202, are in general comparable in corrosion resistance to 301 and 302, and in some media to 304, but are not as good as the low-carbon stainless steels in resistance to carbide precipitation and consequent susceptibility to intergranular corrosion [714, 726]. Type 329, containing only 4 percent of nickel with 28 of Cr, 1.5 of Mo, and 0.8 of N, is reported [587] equal to or better than the austenitic type 304 and almost as good as 316 in resistance to a number of corrosive reagents. However, type 329 is largely ferritic and, consequently, is less easy to fabricate and is more subject to embrittlement and the formation of sigma phase than are the austenitic stainless steels.

Of the three principal industrially important acids—nitric, hydrochloric, and sulfuric acids—the austenitic stainless steels are satisfactorily resistant to nitric acid but are attacked by the other two. Type 304 is particularly effective in resisting all concentrations of nitric acid, including fuming acid, as shown in figure 34. Fontana

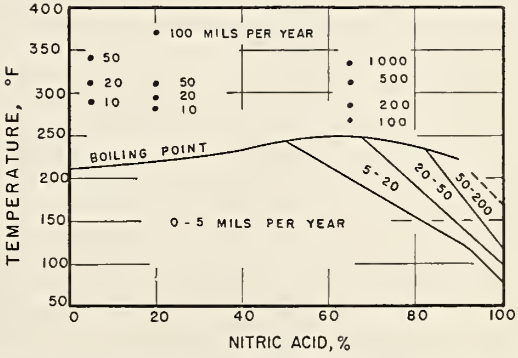

FIGURE 34. *Corrosion of quench-annealed type 304 by nitric acid as a function of temperature* [335].

and coworkers [621] reported that stainless steels were resistant to fuming nitric acid, that the resistance decreased with increasing temperature up to 160° F, and the rate of erosive-corrosive attack decreased with increased rate of flow, as shown in table 29, probably because of removal of decomposition products from the metal surface. In sulfuric acid, Kiefer and Renshaw [231] reported that molybdenum-bearing types 316 and 317 were the most resistant at low temperatures, but at about 150° F all of the stainless steels corrode in practically all concentrations of acid from ½ to 95 percent. However, Roach and Hall [726] reported that molybdenum-bearing stainless steels were useful, at room temperature, in concentrations of sulfuric acid below 15 percent and above 85 percent. The resistance to sulfuric acid is improved in some cases by additions of copper or cerium [231, 629]. In 2 $N$ mixed acids, ranging from 2 $N$ $HNO_3$ to 2 $N$ $H_2SO_4$, the behavior of type 304 reflects its immunity to nitric acid and susceptibility to sulfuric acid [692]. Hydrochloric acid and some solutions containing halide ions attack the passive film on stainless steel and produce corrosion of the pitting type. Additions of molybdenum reduce the susceptibility to pitting corrosion.

TABLE 29. *Erosion-corrosion rate of attack of fuming nitric acid on austenitic stainless steels [621]*

| Steel type | Erosion-corrosion rate, mils per year | | |
|---|---|---|---|
| | Static test | Turbulence test | Orifice test |
| 304 | 130 | 110 | 85 |
| 304 ELC | 120 | 120 | 85 |
| 347 | 110 | 130 | 65 |

In connection with atomic power-plant operation, steels of the 300 series are highly resistant to liquid sodium at temperatures up to 1,000° F, and may be useful up to 1,500° F [532]. They are less resistant to molten lead than to molten sodium at high temperatures [641]. The applications of stainless steel in the operation of petroleum refineries were reviewed recently by Mason [699]. The susceptibility of stainless steels and other heat-resistant alloys to corrosive attack by vanadium pentoxide, for example, in the operation of oil-fired gas turbines in steam power plants and marine installations, has been actively investigated in recent years [564, 657]. Cast stainless steels are generally somewhat less resistant to corrosion and to pitting than are the wrought steels, but the cast steels are used in thicker sections, so that the useful life is not affected.

The wrought and cast stainless steels may be readily fabricated by welding, but, according to Pease [715], incomplete removal of residual welding flux can initiate rapid corrosion on exposure to high temperatures.

(3) *Stress corrosion.* The presence of internal or external stresses intensifies any tendency to corrode, and the combination of stress and exposure to a corrosive medium frequently develops stress-corrosion cracking in material that is immune to either factor alone. Some stress-corrosion failures of austenitic steels have been reported in applications ranging from domestic coffee pots to industrial heat exchangers, chemical equipment, and pressure vessels. Failures were usually associated with the presence of chloride ions, even in extremely low concentrations, for example, boiling distilled water developed cracks in stainless steel above the water line because of concentration of the chlorides near the liquid level as a result of evaporation of some of the distilled water. Consequently, some investigators believe that traces of chlorides may be responsible for the damage caused by supposedly chloride-free reagents. Stress-corrosion cracks in austenitic stainless steels may follow intergranular, transgranular, or mixed paths. Intergranular cracking frequently is associated with carbide precipitation. The severity of the stress-corrosion damage varies with the composition of the steel, the nature and concentration of the corrosive medium, the temperature, the nature and extent of the tensile stresses, and probably other factors. For example, a boiling solution of magnesium chloride produced cracks in a few hours, whereas 14 yr were required to produce cracks in a stainless steel exposed to a glucose solution. The chromium-nickel-manganese steels are comparable to steels of the 300 series in susceptibility to stress corrosion [471, 474, 566, 648, 678, 724].

The mechanism of stress-corrosion cracking and the development of a reproducible test of susceptibility to stress corrosion cracking have been actively investigated in recent years. In the initial phases of an investigation of the mechanism of stress-corrosion cracking of type 304 steel, sponsored by the Pressure Vessels Research Committee of the Welding Research Council, Logan and Sherman [694] adopted a solution containing 3.5 percent of sodium chloride and 1 percent of sodium or ammonium nitrite, with a $p$H of 7.0 and operated at the boiling point, as the test solution to produce reproducible failures in a reasonable time.

## 3.5. Ferrous Super Alloys, Wrought and Cast

In the 1930's, according to Krivobok and Skinner [581] the demands of various industries, for materials of construction to withstand increasingly severe operating requirements, began to require the development of new and basic concepts of alloying and heat treatment. These demands for materials with combinations of high-temperature strength and resistance to oxidation, corrosion, fatigue, creep, and impact built up to the demand for materials for aeronautic jet engines and gas turbines. Aeronautic uses continue to supply the greatest challenge to metallurgical research for the development of these new alloys that have been called "super alloys" and various other names. According to Levy [584], temperatures up to 1,900° or 2,000° F are encountered in jet engines, and, according to Townsend [761], when materials to withstand 4,000° to 5,000° F become available the speed of ramjet powered aircraft can increase to Mach 7 and the range of rockets will increase fourfold. Figure 35, from data of Cremer [647], shows the effect of temperature on the strength-weight ratio of some modern aircraft alloys including high-strength aluminum and magnesium alloys, standard and precipitation-hardened stainless steels, a nickel-base alloy, a titanium alloy, and molybdenum. Aeronautic uses of metallic alloys at temperatures above 1,200° F are limited by thermal expansion, heat conduction, surface emissivity, and scaling resistance, as well as by strength-weight ratio. To date it appears that certain nonferrous alloys, including nickel-base alloys, cobalt-base alloys, and if protective coatings are developed, high-tungsten, high-titanium, and high-molybdenum alloys may be used at higher temperatures than the best of the iron-base alloys can withstand, but the desires of the aeronautic designers exceed the capacity of metallic alloys in such applications as turbojet afterburners, and in ramjet and rocket engine design [518]. Consequently, intensive studies of cermets and ceramics, as well as metallic alloys, are in progress. Nickel appears in cermets primarily as a binder for the refractory carbides or oxides, but the binding material may constitute half of the total weight of the cermet [664].

Much of the development of super alloys involved modifications of the austenitic stainless steels, to extend their excellent properties and performance to still higher temperatures. Among the modifications were precipitation-hardening steels, an increase in the amounts of nickel and chromium, and the addition of appreciable amounts of tungsten, molybdenum, columbium, and other elements. Precipitation hardening may result from the precipitation of carbides, for example, of molybdenum, tungsten, or columbium, or of intermetallic compounds such as $Ni_3Al$ or $Ni_3Ti$ [671, 674]. The functions of the various elements were summarized [518] as follows:

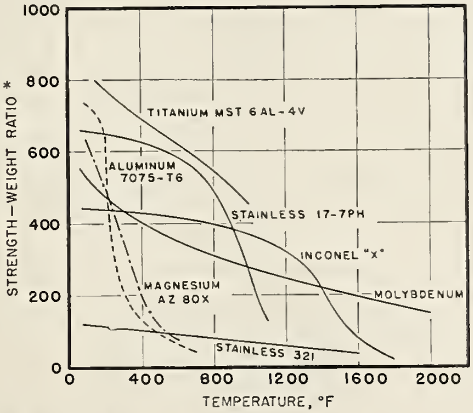

Figure 35. *Effect of temperature on the strength-weight ratio of some aircraft materials* [647].

*Strength-weight ratio is obtained by dividing the 0.2-percent-offset yield strength in 1,000 psi by the density in pounds per cubic inch.

Aluminum—primarily a precipitation hardener.

Chromium—primary source of oxidation resistance.

Cobalt—improves the high-temperature strength of mixed alloys.

Columbium—stabilizer and adds high-temperature strength.

Iron—foundation element for structural steels.

Molybdenum—improves the high-temperature strength and corrosion resistance; imparts precipitation-hardening potential in some alloys.

Nickel—acts as austenitizer and improves the high-temperature strength and resistance to corrosion and oxidation.

Silicon—improves resistance to oxidation.

Titanium—stabilizer, improves high-temperature strength and in some cases imparts precipitation hardening.

Tungsten—improves high-temperature strength.

Vanadium—believed to improve creep resistance.

The literature of the super alloys in the last 10 yr has been voluminous, including the classification of the various alloys (most of which are patented) and the development of test procedures for over-all evaluation of the high-temperature performance. Early evaluations were made on the basis of short-time stress-rupture tests, but it was soon evident that creep occurred at these high temperatures. At the present time, evaluation usually is based on rupture strengths for 100 and 1,000 hr at temperatures of 1,200° F or higher. (See also Steurer [794].) High-temperature testing procedure has not yet been adequately standardized, and for any particular material, results of individual tests may deviate very considerably from the "characteristic" value unless details of processing, annealing temperatures, and stress-relieving or aging are carefully controlled.

The subject was reviewed in 1955 by Krivobok and Skinner [581] and by Simmons, Krivobok,[6] Mochel, and Franks [605]. Results for ferrous materials from the two reviews have been combined with a few data from other sources in table 30, to show the marked improvement in high-temperature properties of the super alloys as compared to the stainless steels. Incompleteness of the rupture data is due in part to the facts that information for some of the alloys was not available for specified temperatures and that some of the alloys were in the development stage when the compilation was made. According to Krivobok and Skinner, 19–9–DL, GT–45, Timken 16–25–6, HS–88, CSA, EME, Incoloy, and N–155 were accepted in 1955 in the sense that they had been produced in commercial quantities and employed

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[6] See also Simmons and Krivobok [770].

TABLE 30. *Stainless steels and ferrous super alloys [581, 605, 714]*

| Alloy | Nominal composition, percent | | | | | | | | | | Characteristic rupture strengths,[a] 1,000 psi | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | Si | Cr | Ni | Mo | W | Cb [b] | Ti | Other | 1,200° F | | 1,350° F | | 1,500° F | | 1,600° F | | 1,800° F | |
| | | | | | | | | | | | 100 hr | 1,000 hr | 100 hr | 1,000 hr | 100 hr | 1,000 hr | 100 hr | 1,000 hr | 100 hr | 1,000 hr |
| AUSTENITIC STAINLESS STEELS | | | | | | | | | | | | | | | | | | | | |
| AISI 201 | 0.15 max | 5.5 to 7.5 | 1.0 max | 16 to 18 | 3.5 to 5.5 | ---- | ---- | ---- | ---- | N, 0.25 max | ---- | 21.0 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| AISI 202 | .15 max | 7.5 to 10 | 1.0 max | 17 to 19 | 4 to 6 | ---- | ---- | ---- | ---- | N, 0.25 max | ---- | 23.5 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| AISI 304 | .08 max | 2.0 max | 1.0 max | 18 to 20 | 8 to 12 | ---- | ---- | 10xC | ---- | ---- | 22.5 | 16.0 | ---- | ---- | 6.5 | 4.0 | ---- | ---- | ---- | ---- |
| AISI 309 | .20 max | 2.0 max | 1.0 max | 22 to 24 | 12 to 15 | ---- | ---- | ---- | ---- | ---- | 27.0 | 18.0 | ---- | ---- | 7.8 | 4.3 | ---- | ---- | ---- | ---- |
| AISI 310 | .25 max | 2.0 max | 1.0 max | 24 to 26 | 19 to 22 | ---- | ---- | ---- | ---- | ---- | 26.0 | 18.0 | ---- | ---- | 11.0 | 5.0 | ---- | ---- | ---- | ---- |
| AISI 316 [c] | .08 max | 2.0 max | 1.0 max | 16 to 18 | 10 to 14 | 2 to 3 | ---- | ---- | ---- | ---- | 32.5 | 23.8 | ---- | ---- | 8.3 | 5.8 | ---- | ---- | ---- | ---- |
| AISI 321 | .08 max | 2.0 max | 1.0 max | 17 to 19 | 9 to 12 | ---- | ---- | ---- | ---- | ---- | 28.0 | 18.0 | ---- | ---- | 7.0 | 4.0 | ---- | ---- | ---- | ---- |
| AISI 330 | .25 max | ---- | ---- | 14 to 16 | 33 to 36 | ---- | ---- | ---- | ---- | ---- | 21.0 | 12.0 | ---- | ---- | 7.5 | 4.0 | ---- | ---- | ---- | ---- |
| AISI 347 | .08 max | 2.0 max | 1.0 max | 17 to 19 | 9 to 13 | ---- | ---- | ---- | 5xC | ---- | 27.5 | 22.0 | ---- | ---- | 8.0 | 4.0 | ---- | ---- | ---- | ---- |
| CHROMIUM-NICKEL-IRON ALLOYS [d] | | | | | | | | | | | | | | | | | | | | |
| 19-9 W Mo | 0.10 | 0.5 | 0.6 | 19 | 9 | 0.4 | 1.3 | 0.44 | ---- | ---- | 41 | 34 | 28.5 | ---- | 11 | ---- | ---- | ---- | ---- | ---- |
| 19-9 DL | .30 | 1.1 | .6 | 19 | 9 | 1.25 | 1.2 | .4 | 0.3 | ---- | 52 | 38 | 28 | 19 | 17 | 10 | ---- | ---- | ---- | ---- |
| 19-9 DX | .30 | 1.0 | .55 | 19.2 | 9 | 1.5 | 1.2 | ---- | .55 | ---- | 52.5 | 42 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| 19-9 WX | .11 | ---- | ---- | 20.5 | 8.5 | 0.5 | 1.5 | 1.3 | .2 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Inco 425 | .05 | 1.2 | 0.7 | 5.3 | 25 | ---- | ---- | ---- | 2.3 | Al, 0.7 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Inco 901 | .05 | 0.48 | .22 | 12.8 | 43 | 5.68 | ---- | ---- | 2.43 | ---- | 80 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Croloy 15-15N | .15 max | 2.0 max | .75 max | 16 | 15 | 1.55 | 1.4 | 1.05 | ---- | N, 0.15 max | ---- | ---- | ---- | 18 | ---- | 10 | ---- | ---- | ---- | ---- |
| 17-14 Cu Mo, GT-45 | .12 | 0.75 | .5 | 15.9 | 14.1 | 2.5 | ---- | 0.45 | 0.25 | Cu, 3 to 0 | 43 | 37 | 26 | 20.5 | 16.5 | 12 | ---- | ---- | ---- | ---- |
| Timken 16-25-6 | .10 | 1.35 | 0.7 | 16 | 25 | 6.0 | ---- | ---- | ---- | N, 0.15 | 45 | 34 | 25 | 17 | 13.5 | 9 | ---- | ---- | ---- | ---- |
| Discaloy 24 | .03 | 0.64 | .92 | 13.1 | 25.5 | 2.83 | ---- | ---- | 1.83 | Al, 0.16 | 55 | 41 | 32 | 20 | 15 | ---- | ---- | ---- | ---- | ---- |
| HS-88 | .07 | 1.5 | .5 | 12.5 | 15 | 2.0 | 0.6 | ---- | 0.6 | B, 0.15 | 59 | 49 | 42 | 31 | 25.5 | 16 | 13.5 | ---- | ---- | ---- |
| A-286 | .05 | 1.35 | .95 | 15 | 26 | 1.75 | ---- | ---- | 2.0 | Al, 0.20; V, 0.3 | 61 | 46 | 35 | 21 | 13.8 | 7.7 | ---- | ---- | ---- | ---- |
| Cinidur | .25 | ---- | ---- | 19 | 24 | 2.0 | 1.0 | ---- | 2.25 | Al, 1.0 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| S-495 | .40 | 1.0 | 1.0 | 14 | 20 | 4.0 | 4.0 | 4.0 | ---- | ---- | 43 | 36 | 26 | 21 | 18 | 14 | 13.3 | 9.2 | ---- | ---- |
| S-588 | .42 | 1.5 | 0.8 | 18.4 | 20 | 4.0 | 4.0 | 4.0 | ---- | ---- | 41 | 30 | 25 | 18 | 15 | 10 | ---- | ---- | ---- | ---- |
| CSA | .25 | 4.0 | .4 | 18 | 5 | 1.3 | 1.3 | 1.0 | ---- | ---- | 50 | 39 | 22.5 | 12.5 | ---- | ---- | ---- | ---- | ---- | ---- |
| EME | .10 | 0.5 | .7 | 19 | 12 | ---- | 3.2 | 1.2 | ---- | N, 0.15 | 44 | 35 | 22 | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| Incoloy | .10 | 1.0 | .6 | 20.5 | 32 | ---- | ---- | ---- | ---- | ---- | 30 | 23 | 18 | 15 | ---- | 5.7 | ---- | 3.6 | ---- | 1.6 |
| Incoloy T | .10 | 1.0 | .4 | 20.5 | 32 | ---- | ---- | ---- | 1.0 | ---- | 33 | 26.1 | 20.1 | 14.7 | 10.8 | 7 | ---- | ---- | ---- | ---- |
| ATV-3 | .35 | 1.36 | 1.17 | 14.9 | 27.4 | ---- | 4.0 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 10.5 | ---- | ---- | ---- | ---- | ---- |
| Gamma Columhium | .40 | 0.54 | 0.62 | 15.2 | 24.6 | 4.1 | ---- | 2.2 | ---- | ---- | 44 | 36 | ---- | ---- | 16.7 | 11 | 10.8 | 8.0 | ---- | ---- |
| RL-35-100 [e] | .85 | 1.5 | .5 | 28 | 35 | 8.0 | ---- | ---- | ---- | B, 0.15 | ---- | ---- | 41 | 32 | 24 | 15 | 16 | 10.5 | 7 | 4.5 |
| Turhaloy 13 | .13 | 1.68 | .75 | 17.8 | 23.6 | 2.5 | 1.0 | ---- | 1.4 | Al, 1.4 | 65 | 54 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| M-813 | .08 | ---- | ---- | 18 | 35 | 4.0 | ---- | ---- | 2.25 | Al, 1.4 | ---- | 52 | 41 | 30 | 22 | 13 | ---- | ---- | ---- | ---- |
| CHROMIUM-NICKEL-COBALT-IRON ALLOYS | | | | | | | | | | | | | | | | | | | | |
| N-153 | 0.32 | 1.5 | 0.5 | 17 | 15 | 3.0 | 2.0 | 1.0 | ---- | Co, 12 | ---- | 38 | ---- | 23 | 19.5 | 12 | ---- | ---- | ---- | ---- |
| N-154 | .32 | 1.5 | .5 | 17 | 24 | 3.0 | 2.0 | 1.0 | ---- | Co, 21 | ---- | ---- | ---- | ---- | 20 | 15 | ---- | ---- | ---- | ---- |
| N-155, HS-95 | .15 | 1.5 | .5 | 21 | 20 | 3.0 | 2.5 | 1.0 | ---- | Co, 20; N, 0.15 | 50 | 40 | 31 | 24 | 18 | 13 | 12 | 8 | 5 | 2.5 |
| HS-96 | .10 | 1.5 | .5 | 20 | 20 | 3.0 | 2.0 | ---- | ---- | Co, 20 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- |
| S-497 | .42 | 0.47 | .61 | 14 | 19.5 | 4.0 | 4.0 | 4.0 | ---- | Co, 19 | 45 | 33.5 | 28.5 | 23 | 18 | 14.5 | 12 | 9.6 | ---- | ---- |
| Haynes No. 99 | .10 | 1.5 | .7 | 21 | 18 | 4.0 | 2.5 | ---- | ---- | Co, 12; B, 0.05 | 50 | ---- | ---- | ---- | 15 | ---- | ---- | ---- | ---- | ---- |
| Timken X | .13 | 1.44 | .75 | 16.8 | 28.6 | 10.5 | ---- | ---- | ---- | Co, 30.7; N, 0.10 | ---- | ---- | ---- | ---- | 17 | ---- | ---- | ---- | ---- | ---- |
| Ticonium | .01 | 0.8 | .27 | 23 | 35 | 6.0 | ---- | ---- | ---- | Co, 31 | 52.5 | 33 | 22 | 16 | ---- | ---- | ---- | ---- | ---- | ---- |

[a] Not for design purposes. [b] Usually columhium plus tantalum. [c] Improved stress rupture values of type 316 at 1,350° and 1,500° F are obtained by modifying the composition, i. e., by additions of C, Ti, and B. [d] Containing more than 30 percent of iron. [e] Cast.

for specific services in which their satisfactory performance has been established. Ferrous super alloys have been described [581] as a useful class of engineering materials for highly stressed applications within a temperature range of 1,200° to 1,500° F, with strengths considerably above those of conventional stainless steels. The N–155 alloy has been called [518] somewhat of a workhorse in the range above 1,200° F. For additional information on N–155, see Freeman et al. [183] and Binder [263].

Apblett and Pellini [318] reported values for the thermal-expansion characteristics of some ferrous super alloys shown in table 31.

Table 31. *Thermal expansion of some ferrous super alloys [318]*

| Alloy [a] | Average coefficient, millionths per ° F | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 70° to 1,000° F | 70° to 1,200° F | 70° to 1,400° F | 70° to 1,600° F | 70° to 1,800° F | 70° to 2,000° F | 70° to 2,200° F | 70° to 2,400° F |
| 19–9–DL | 9.8 | 10.2 | 10.4 | 10.7 | 11.1 | 11.3 | 11.6 | 12.0 |
| 16–25–6 | 9.6 | 10.2 | 10.8 | 11.7 | 12.0 | 12.4 | 13.0 | 13.3 |
| EME | 10.8 | 11.4 | 11.9 | 12.4 | 12.9 | 13.2 | 14.0 | 14.5 |
| N–155 | 9.7 | 9.8 | 10.2 | 10.5 | 10.9 | 11.4 | 11.7 | ([b]) |

[a] See table 30 for compositions. [b] Incipient melting occurred.

For a given composition and comparable heat treatment, castings usually exhibit higher hot strengths and creep resistance than forgings. Grant [668] discussed two of the super alloys shown in table 30 as follows; N–155 at 1,500° F and under stress of 20,000 psi developed 115 hr rupture life with 18 percent elongation for forged pieces, and 155 hr and 8 percent for castings; S–497 at 1,500° F and 20,000 psi showed 43.5-hr rupture life with 24-percent elongation for forged pieces, and 174.5 hr and 8.9 percent for castings. The Alloy Casting Institute's standard grades of heat-resisting alloys, as discussed by Mathews [235], include austenitic alloys HH, HK, HT, HU, HW, and HX, with nickel contents ranging from 12 to 65 percent, which might be classed as super alloys because they exhibit 100-hr stress-rupture values of 4,500 to 6,500 psi at 1,700° F, 3,300 to 4,900 psi at 1,800° F and 2,500 to 3,700 psi at 1,900° F, but these cast alloys are classed by Rose [358] as general-purpose high-temperature alloys rather than super alloys.

The American Society for Testing Materials [512] has issued a number of specifications for corrosion-resisting and heat-resisting steels, some of which might be classed as super alloys. For example, ASTM B 190–50 covers chromium-nickel-iron alloy castings of the 25:12 class for use in electric furnaces, petroleum still tube supports, and similar applications at temperatures up to 2,000° F. ASTM Special Technical Publication No. 170 [605] was prepared by Committee A–10, as a basis for the preparation of specifications for high-temperature super-strength alloys. The Society of Automotive Engineers has issued Aeronautic Materials Specifications including:

AMS 5355 for corrosion- and heat-resistant precision investment castings.

AMS 5370 for low-carbon corrosion- and heat-resistant investment castings.

AMS 5556 for corrosion- and heat-resistant tubing.

AMS 5736 for corrosion- and heat-resistant bars, forgings, and forging stock.

### 3.6. Thermal-Expansion Alloys

The fact that iron-nickel alloys containing about 36 percent of nickel have extremely low coefficients of thermal expansion was observed by Guillaume [12] in 1897, in a search for less expensive materials than the platinum-iridium alloy that was the standard for metrology. Because the 36-percent-nickel alloy had coefficients of expansion so low that the length was almost invariable for 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, as discussed in the section on magnetostriction of nickel. Today; low-expansion alloys find extended use as length standards, rods and tapes for geodetic work, compensating pendulums and balance wheels in clocks and watches, struts in automobile pistons, tuning forks, glass to metal seals, and, in combination with a high-expansion alloy, as bimetallic or thermostatic strip [795]. Alloys of the Elinvar type find particular applications as spring materials.

Subsequent investigations here and abroad confirmed and extended Guillaume's original observations. Owen, Yates, and Sully [81] showed that increasing the temperature above room temperature increased the minimum coefficient of expansion and shifted it toward higher nickel contents. Figure 36 shows their data for alpha

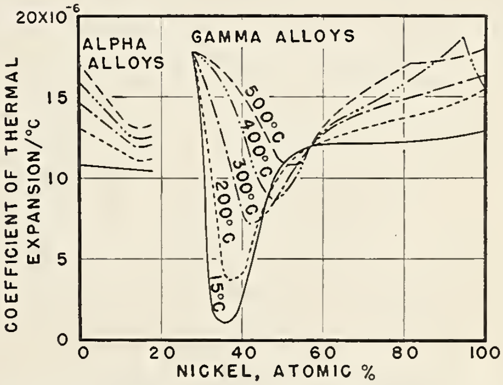

Figure 36. *Coefficient of thermal expansion of iron-nickel alloys at temperatures up to 500° C [81].*

and for gamma alloys. Compositions between 18.6 and 28 percent of nickel are mixtures of alpha and gamma. Atomic percentages of nickel in iron-nickel alloys are approximately the same as weight percentages, i. e., 36 atomic percent is 35 weight percent.

Scott [40] 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 37, from data supplied by Hunter [147] 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. Harvey [565] commented that the coefficient of Invar is approximately one-thirtieth that of steel and is effective to about 500° F. According to the International Nickel Company, Inc., [425], the alloys that have become most widely used are 36 Ni (Invar) up to about 400° F, 42 Ni up to 650° F, and 47 to 50 Ni for temperatures up to 1,000° F.

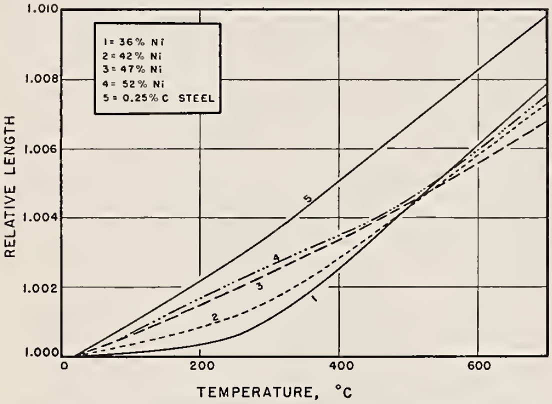

Figure 37. *Thermal expansion of iron-nickel alloys [147].*

The linear expansion of Invar, and particularly the minimum expansion values, are affected by cold work and heat treatment, 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 [288] reproduced in table 32. 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 [237]. 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 [40, 49], and titanium raises the minimum value of the coefficient and shifts it toward higher nickel contents [121].

Table 32. *Effect of heat treatment and impurities on the thermal expansion of Invar [288]*

| Composition, 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 | .0 | 1.0 |

[a] Furnace cooled after 30 min. at 830° C.

[b] Water quenched after 30 min. at 830° C.

[c] Stabilized, after treatment (b), by reheating at 95° C for 48 hr, followed by air cooling.

A series of age-hardening alloys, each containing about 2.5 percent of titanium was reported by Mudge and Talbot [121]. 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–Hi, 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 use of constant modulus alloys as spring materials was reviewed recently by Carlson [639] as follows, with compositions reported by Woldman [509]:

Elinvar—first of the constant modulus materials, for watch hairsprings, etc. 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—42 Ni, 5.5 Cr, 2.4 Ti, 0.6 Al, iron alloy developed by the International Nickel Company. Most popular of the constant modulus alloys. Usually formed in the 50-percent cold-worked condition and precipitation hardened at 900° F for 8 hr, or at 1,250° F for 3 hr, to produce hardness of Rockwell C 40 to 44, 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 Fe. Developed by John Chatillon & Sons. Easier to fabricate than Ni–Span–C and popular for scales, dynamometers, and instruments. Used at Rockwell C hardnesses of 30 to 36 to withstand torsional stresses of 40,000 to 60,000 psi.

Elgiloy—40 Co, 20 Cr, 15 Ni, 7 Mo, 2 Mn, 0.05 Be, 15 Fe alloy also called 8J Alloy, Durapower, and Cobenium. Developed at Battelle Memorial Institute [464] 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 48 to 50 Rockwell C hardness. It is used in Elgin watches and in 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.

Several of the iron-nickel and modified alloys, including Fernico (28 Ni, 18 Co, 54 Fe) and Kovar (29 Ni, 17 Co, 0.3 Mn, balance Fe), are used in making glass-to-metal seals for electrical connections into vacuum tubes, laboratory apparatus, etc. For stress-free and vacuum-tight joints the expansion-temperature curves of the metal and glass must be close together, and a 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. Grosvenor [458] 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 38. For borosilicate glasses, an alloy containing 30 percent of Ni, 17 Co, and 53 Fe has been recommended [188, 244].

Minovar is an austenitic iron that contains 36 Ni, 1.5 Si, 0.5 Cr, and 2.40 maximum total carbon [531]. 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 of Ni, 5 Mo, 67 Fe or 42 Ni, 5 Mo, 53 Fe have been used for the high-expansion side of thermostatic bimetals [105].

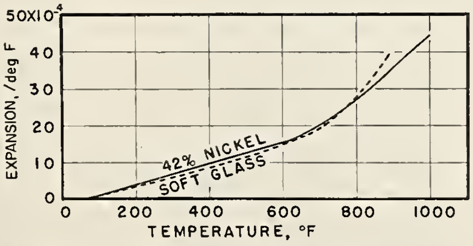

FIGURE 38. *Thermal-expansion curves of 42-percent nickel-iron alloy and soft glass [458].*

### 3.7. 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 [125]. 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. The present discussion will be confined to the magnetically soft and permanent magnet ferrous materials in which nickel is a major constituent. For applications of magnetic nickel-iron alloys, see Smith [795].

#### a. Magnetically Soft Materials

It became generally recognized about 1920, as a result of the work of G. W. Elmen [26] 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-percent 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 [86]. Even more remarkable properties were exhibited by Permalloys when the material was exposed to a magnetic field of several 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 39. During World War II a great

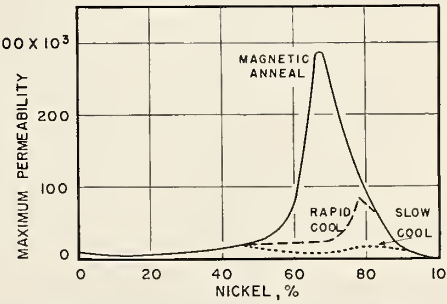

FIGURE 39. *Effect of annealing treatments on the maximum permeability of iron-nickel alloys [125].*

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 the weak signals of communication apparatus, whereas Hypernik, which contains 50 percent of nickel and was developed by T. D. Yensen, has been used in the transmission of power [125].

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 the electrical resistivity, which is desirable for alternating-current applications. Of the alloys summarized in table 33, 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 as high as 125,000 and maximum permeabilities of more than 1,000,000 obtainable commercially even in thin sheets [125, 266].

Elmen [41] 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 of nickel, 30 iron, and 25 cobalt is a good example; a permeability of 300 is obtainable for a field of about 3 oersteds, corresponding to a flux density of 1,000 gausses. The resistivity of the Perminvars is low but can be increased by additions of molybdenum or chromium [205]. Useful alloys in the Perminvar class include nickel-iron alloys Conpernik (50 Ni) and Isoperm (40 Ni).

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 [205].

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).

Magnetically soft materials generally are used as solid metals. For some uses, for example, inductances in telephonic and radiofrequency 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 0.004 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 radiofrequencies. The ferromagnetic oxides or ferrites also are used in powdered form for high-frequency applications because of their high electrical resistance and consequent low eddy-current losses. Typical examples are NiO·$Fe_2O_3$, MgO·$Fe_2O_3$, and NiO·ZnO·$Fe_2O_3$, but many oxides with low loss and high permeability have been identified, for example, by Snoek [122]. 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 [205]. The barium ferrites, with the type formula BaO·$6Fe_2O_3$, currently are receiving attention as nonstrategic materials that, in some applications, can replace the strategic metal magnets.

The magnetically soft nickel-irons have been established for some time. Consequently, recent articles have been concerned more with the theory of magnetic behavior than with the development of new alloys. For example, Bozorth [380] studied the effect of cooling rate on the magnetic anisotropy, magnetostriction, and permeabilities 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 [535], in connection with the strong magnetic anisotropy developed by cold rolling iron-nickel alloys. Schindler and Salkovitz [604] reviewed published data on the Hall coefficients of binary nickel alloys and offered explanations for anomalous behavior. The galvanomagnetic properties and Goldhammer effect in iron-nickel alloys were discussed by Grum-Grzhimailo [669].

TABLE 33. *Magnetic properties of some iron-nickel alloys [205]*

| Alloy | Composition, percent | | | Hydrogen heat treatment | Permeability | | Coercive force | Saturation | Resistivity | Curie temperature |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ni | Fe | Other | | Initial | Maximum | | | | |
| | | | | ° C | | | | $4\pi I_s$ | $\mu\omega$-cm | ° C |
| 45 Permalloy | 45 | 54 | | 1,050 | 2,500 | 25,000 | 0.3 | 16,000 | 50 | 440 |
| Hipernik | 50 | 50 | | 1,200 | 4,000 | 80,000 | .05 | 16,000 | 35 | 500 |
| 78 Permalloy | 78 | 21 | | 1,050 | 8,000 | 100,000 | .05 | 10,000 | 16 | 580 |
| 4–79 Permalloy | 79 | 16 | Mo 4 | 1,100 | 20,000 | 80,000 | .05 | 8,700 | 57 | 420 |
| Mumetal | 75 | 18 | Cr 2; Cu 5 | 1,100 | 20,000 | 110,000 | .03 | 7,200 | 60 | 430 |
| Supermalloy | 79 | 15 | Mo 5 | 1,300 | 100,000 | 800,000 | .004 | 8,000 | 60 | 400 |

### b. Permanent Magnets

Magnetically hard or permanent magnet materials have large coercive force sometimes because of internal stress involving lattice distortion. 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 accompanied precipitation-hardening and aging processes. The quality of a permanent magnet is characterized not only by the residual induction, $B_r$, and coercive force, $H_c$, 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 [205, 125].

Uses of permanent magnets fall into four classifications: (a) Converting mechanical to electrical energy, e. g., dynamic microphones, phonograph pickups, (b) converting electrical to mechanical or acoustical energy, e. g., electric motors, electrical instruments, radio loudspeakers, (c) attraction of ferromagnetic materials, e. g., magnetic chucks, magnetic separators, (d) focusing of electrons and ions in some types of scientific apparatus. The largest use is in radio loudspeakers and the next largest in electrical measuring instruments.

The first permanent magnets were martensitic plain carbon steels. Before World War I, it was found that additions of tungsten improved the permanent magnets. During World War I, iron-chromium-carbon alloys were developed, and Honda and Saito introduced the K. S. or cobalt magnet steel, which contained 35 to 41 percent of cobalt, 2.0 to 3.75 percent of chromium, 3.75 to 7.0 percent of tungsten, and 0.9 percent of carbon. 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 [54] in Japan and developed by Ruder [63] in this country. Subsequent modifications, by additions of cobalt, copper, and titanium brought the number of Alnicos up to 12, with Alnico 5 remaining the workhorse of the family. Permanent magnets can be obtained from a large number of binary, ternary, and quaternary alloys, but the iron-nickel-aluminum system is the basis for the most important of these to date.

Table 34 presents data on the composition and magnetic properties of important members of the Alnico series and some other well-known nickel-bearing ferrous permanent magnets. All of these alloys are age hardening, because of the precipitation of Ni–Al or Ni–Ti compounds or complexes like (Fe, Ni, Co)$_3$Ti [277, 278, 342]. 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 [277] reported that overaging appreciably reduced all of the magnetic properties, for example, the energy product for Alnico 5 was reduced from 5.00 to $0.09 \times 10^6$ and for Alnico 4 from 1.30 to $0.02 \times 10^6$. The principal function of cobalt is to decrease the cooling rate necessary to obtain optimum properties, thus permitting the casting of larger magnets. All of the Alnicos and some of the other compositions are brittle, unmachinable, and must be finished by grinding, as indicated by the Vickers hardness numbers cited in table 34. Alnico magnets prepared by powder-metallurgy processes have magnetic properties equivalent to those of cast alloys, and the powder-metallurgy products are more homogeneous magnetically. The cast alloys 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. According to Stanley [205], the Alnicos are probably the most popular of permanent magnet materials, especially where cost considerations allow use of such high-grade materials. Hadfield [462] suggested that magnetically

Table 34. *Composition and properties of some permanent magnet alloys [125, 205, 277]*

| Alloy | Nominal composition, percent | | | | | | Optimum properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ni | Al | Co | Cu | Fe | Other | Coercive force | Residual induction | Energy product | Vickers hardness No. |
| | | | | | | | $H_c$ | $B_r$ | $BH$ max | |
| Alnico 1 | 20 | 12 | 5 | ---- | 63 | | 440 | 7,280 | $1.40 \times 10^6$ | -------- |
| Alnico 2 | 17 | 10 | 12.5 | 6 | 54.5 | | 560 | 7,280 | 1.65 | -------- |
| Alnico 3 [a] | 25 | 12 | ---- | ---- | 63 | | 450 | 6,700 | 1.38 | 530 |
| Alnico 4 | 28 | 12 | 5 | ---- | 55 | | 700 | 5,200 | 1.30 | 534 |
| Alnico 5 | 14 | 8 | 24 | 3 | 51 | | 575 | 12,000 | 5.00 | 579 |
| Alnico 6 | 15 | 8 | 24 | 3 | 48.75 | Ti 1.25 | 750 | 10,000 | 3.50 | -------- |
| Alnico 12 | 18 | 6 | 35 | ---- | 33 | Ti 8 | 950 | 5,800 | 1.75 | 780 |
| 349 | 14 | 8 | ---- | ---- | 78 | | 90 | 9,900 | 0.34 | 508 |
| 348 | 38 | 16 | ---- | ---- | 46 | | 750 | 3,700 | .86 | 511 |
| New K. S | 16 | ---- | 30 | ---- | 42 | Ti 12 | 920 | 6,350 | 2.0 | -------- |
| Cunife | 20 | ---- | ---- | 60 | 20 | | 550 | 5,400 | 1.55 | -------- |

[a] Composition corresponds to that of the Mishima alloys.

anisotropic Alnicos may be about the maximum obtainable in solid magnets, but that further improvement may result from powder metallurgy techniques.

Discussion of the ferrous binary and complex systems that do not contain nickel, and of nonferrous permanent magnet alloys, is beyond the scope of the present article. It may be mentioned, however that Cunico magnets (Ni 21, Co 29, Cu 50) are useful, and that Vectolite ($Fe_2O_3$ 30, $Fe_3O_4$ 44, $Co_2O_3$ 26) is a permanent-magnet material, although, as noted earlier in this section, the $Fe_2O_3$ ferrites are usually magnetically soft. Precipitation hardening gold-nickel magnets, with compositions in the vicinity of 70 Au and 30 Ni, are of interest on theoretical grounds [223]. A platinum-cobalt alloy (Pt 77, Co 23) when properly heat treated has an energy product about 50 percent higher than that of Alnico 5, according to E. M. Wise [769].

## 4. Nonferrous Alloys

### 4.1. General

Alloys discussed in this section include nickel-copper and copper-nickel alloys noted particularly for their resistance to corrosion in structural applications, nickel-chromium electrical resistance and thermocouple alloys, and nickel-base heat-resistant and super alloys. This classification includes the "nonferrous" and some of the "high temperature and electrical resistance" and "all other" groups shown in figure 4. Alloys covered in this section account for about one-third of the current annual consumption of nickel.

### 4.2. Nickel-Copper Alloys (more than 50 percent nickel)

The phase diagram for the nickel-copper system was established by Guertler and Tammann [15] in 1907, and has been confirmed by subsequent investigators; Pilling and Kihlgren [157] presented the diagram shown in figure 40. The solid-solution alloys have a face-centered cubic structure, and the lattice constant varies linearly with atomic concentration, from 3.60 A for copper to 3.54 A 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 100-percent nickel to 25° C for the 70 Ni–30 Cu alloy, and to about −170° C for the 50 Ni–50 Cu alloy.

Impurities affect the physical and mechanical properties of the high-nickel alloys in much the same manner as 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.

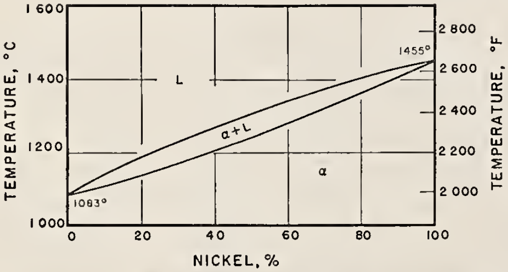

FIGURE 40. *The nickel-copper phase diagram* [*157*].

On the International Temperature Scale of 1948, the freezing point of nickel is 1,453° C.

The most important of the high-nickel alloys is Monel and its modifications. Technically the lightly alloyed nickels, Duranickel, Permanickel, and the electronic nickels, are nickel alloys, but they have been discussed as alloyed nickels, in an early portion of this publication.

#### a. Monel

(1) *Development.* According to Mudge [593], 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 the matte, which contained roughly twice as much nickel as copper, reducing the oxidized matte with charcoal, and adding magnesium to produce a wrought alloy that was silvery white and brighter than nickel, stronger than mild steel and notably resistant to sulfuric acid and to sea water. The new alloy was named Monel in honor of Ambrose Monel, then president of the International Nickel Company.

The first large order for Monel was for sheet which was installed in 1909 as roofing for the Pennsylvania Railroad station in New York City. Intensive research developed ever widening use of this engineering material, and by 1955, according to Mudge, there were 800 recorded uses of Monel, with corrosion resistance responsible for the majority of them. Throughout the development of Monel, additions of chromium, manganese, aluminum, iron, molybdenum, tungsten, titanium, and other metals were tried for increased strength and for other reasons. In the 1920's it was found that additions of about 4 percent of aluminum made Monel age hardenable [69]. It is now known that 16 different elements confer age-hardening characteristics on nickel and high-nickel alloys, the most important being aluminum, titanium, and silicon, with magnesium, molybdenum, tungsten, and beryllium used to a lesser extent. The age-hardened Monels are readily fabricated in the soft condition, and can be hardened to strength levels comparable to those of quenched and tempered alloy steels and still retain their resistance to corrosion. Nominal compositions of the grades and modifications of Monel that are currently available from the International Nickel Company, Inc., are shown in table 35.

Regular Monel is available in all commercial forms and a variety of tempers. It is a general purpose alloy and is used by aircraft, building, marine, chemical, houseware, oil refinery, paper and pulp, and many other industries in the manufacture of articles requiring bending, forming, upsetting, and similar operations [654].

Table 35. *Nominal compositions of wrought and cast Monel [763]*

| | Nominal composition, percent | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ni | C | Mn | Fe | S | Si | Cu | Other |
| Wrought alloys: | | | | | | | | |
| Monel | 66 | 0.12 | 0.90 | 1.35 | 0.005 | 0.15 | 31.5 | |
| "R" Monel | 66 | .18 | .90 | 1.35 | .050 | .15 | 31.5 | |
| Monel 402 | 58 | .12 | .90 | 1.20 | .005 | .10 | 39.8 | |
| Monel 403 | 57.5 | .12 | 1.80 | 0.50 | .005 | .25 | 39.8 | |
| LC Monel | 84 | .10 | 0.90 | 1.35 | .005 | .15 | 13.5 | |
| "K" Monel | 65.3 | .15 | .60 | 1.00 | .005 | .15 | 29.5 | Al, 2.8; Ti, 0.5. |
| "KR" Monel | 65.2 | .23 | .60 | 1.00 | .005 | .15 | 29.5 | Al, 2.8; Ti, 0.5. |
| Casting alloys: | | | | | | | | |
| Monel | 64 | 0.20 | 0.8 | 1.0 | 0.008 | 1.5 | 31.5 | |
| "H" Monel | 63 | .10 | .8 | 1.5 | .008 | 3.2 | 30.5 | |
| "S" Monel | 63 | .08 | .8 | 2.0 | .008 | 4.0 | 29.5 | |
| Weldable Grade Monel. | 62 | .20 | .8 | 2.0 | .008 | 1.5 | 31.5 | Cb+Ta, 1.4 |

"R" Monel is free machining and is available as hot-rolled or cold-drawn bars and rods, and as cold-drawn wire. It is intended primarily for use in automatic screw machine work and is not generally recommended for forging [654].

Monel 402, formerly called "326" Monel, is intended primarily for handling hot sulfuric acid and has a low susceptibility to hydrogen embrittlement [763].

Monel 403 has higher manganese and silicon and lower iron than "402", for low permeability and electronic applications [763].

LC Monel, the LC denoting low copper, is useful for specific applications involving resistance to corrosion, for example, in transporting potable water [769].

"K" Monel is age hardenable because of the aluminum and titanium contents. It is available as forgings, bars, rods, sheet, strip, and wire, hot finished, cold drawn, annealed, and with various heat treatments. According to Mudge [593], 37,500,000 lb of "K" Monel had been used industrially prior to 1955.

"KR" Monel is free machining because of small amounts of precipitated graphite and is available in the form of rounds, hexagons, squares, and flats, cold drawn or hot finished, with or without aging treatment [655].

Monel Casting alloy is intended for use in parts requiring moderate strength, high ductility, and high resistance to corrosion. It is not heat-treatable to any considerable extent and, while weldable to a degree, is usually not recommended where extensive welding is expected [656].

"H" Monel is intended for applications involving nongalling and antiseizing characteristics coupled with moderately high hardness and relative ease of machinability. Welding is limited to minor repairs [656].

"S" Monel is intended for use where nongalling and antiseizing characteristics combined with high hardness are desired. It may be solution treated for optimum machinability, and subsequently be age hardened [656].

Weldable grade Monel is similar in application to Monel Casting Alloy, and extensive welding can be accomplished with this material [656].

(2) *Physical and Mechanical Properties.* Data on the physical constants of the Monel alloys have been reported irregularly and in different units, so that a tabulation will not be attempted. The density of wrought Monel and "R" Monel is 8.84 g/cm$^3$; of "K" and "KR" 8.47; Cast Monel 8.63; "H" Monel 8.48; and "S" Monel 8.36. The melting range is approximately 1,300° to 1,350° C except for "H" and "S" alloys, which melt at slightly lower temperatures. The specific heat of wrought Monel varies in linear fashion with increasing temperature, from 0.1009 cal/g °C at 0° C to 0.1142 at 300° C [544]. Other values reported for the specific heats of different Monels range from 0.127 to 0.130 cal/g °C. The coefficient of linear thermal expansion per °C for the range 25° to 100° C is $14.0 \times 10^{-6}$ for the wrought Monels and 12.2 to $12.9 \times 10^{-6}$ for the casting alloys. Data for the thermal expansion of Monel and K Monel at elevated temperatures are shown in figure 41. Data for the thermal conductivity of Monel at low temperatures were assembled by Powell and Blanpied [492] from various sources and are shown in figure 42, expressed in milliwatts per cm °K. The mean specific heat from 20° to 400° C is 0.127 cal/g °C.

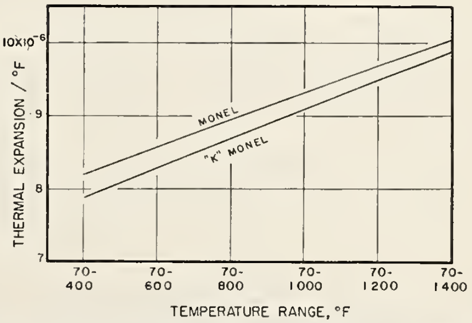

Figure 41. *Thermal expansion of Monel and "K" Monel for temperature ranges from 70°–400° F to 70°–1,400° F [591].*

The electrical resistivity at 20° C of wrought Monel is 46.8 microhm-cm, of cast Monel 53.3, of "K" and "KR" slightly more than 58, of "H" Monel 61.6, and of "S" Monel 63.3. The Curie temperature of casting Monel is −8° C, of wrought Monel 27° to 95° C depending upon composition, working and heat treatment, and of "K" Monel below −100° C. Reflectivity values for rolled Monel, as determined by Coblentz [24], vary from 54 percent for a wavelength of 4358 A to 91 percent for 40000 A. The reflectivity, absorption coefficient, and refractive index of Monel approximate those of nickel.

Mechanical properties of the Monels vary with the shape and size of the product, method of fabrication, and with heat treatment. Typical ranges of room-temperature properties for some of the wrought and cast Monels are presented in table 36. Results obtained at the National Bureau of Standards on the effect of temperature on the tensile and yield strengths of high-purity and commercial-purity Monel are shown in figure 43. The strengthening effect of the iron, manganese, carbon, and cobalt in the commercial alloy is evident. The properties of commercial Monel begin to fall off rapidly with increasing temperature above about 300° C whereas the break for the high-purity alloy comes at about 400° C. The elastic constants of Monel and "K" Monel, re, ported by Michel [591] and shown in figure 44- also show the decrease in mechanical properties at temperatures above 300° C. Likewise, the creep strength of Monel falls off rapidly above 400° C (750° F) [304]. Grant and Bucklin [390] presented data for the creep-rupture behavior of annealed Monel at temperatures from 700° to 1,300° F, as shown in figure 45. The break in each curve, for

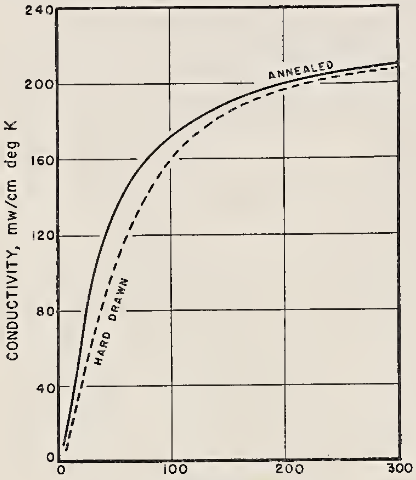

Figure 42. *Thermal conductivity of annealed and hard-drawn Monel at low temperatures [492].*

Table 36. *Typical mechanical properties at room temperature of some Monels [654, 655, 763]*

| | Tensile strength | Yield strength, 0.2-percent offset | Elongation in 2 in. | Brinnell hardness number at 3,000 kg[a] |
|---|---|---|---|---|
| Wrought alloys: [b] | *1,000 psi* | *1,000 psi* | % | |
| Monel | 70 to 110 | 25 to 85 | 35 to 8 | |
| "R" Monel | 70 to 85 | 25 to 50 | 35 to 8 | |
| "K" Monel | 130 to 145 | 90 to 110 | 20 to 15 | 250 to 290 |
| "KR" Monel | 130 to 140 | 85 to 100 | 20 to 15 | 250 to 265 |
| Casting alloys (as-cast): [c] | | | | |
| Monel | 65 to 85 | 30 to 40 | 50 to 25 | 120 to 170 |
| "H" Monel | 95 to 135 | 50 to 95 | 15 to 5 | 240 to 290 |
| "S" Monel | 120 to 145 | 80 to 130 | 4 to 1 | 275 to 350 |
| "S" Monel, annealed | 100 to 125 | 55 to 90 | 15 to 5 | 175 to 270 |

[a] For information only.

[b] In the indicated ranges of properties of the wrought alloys, the first values are minima for annealed (or for annealed and aged) material, and the second values are minima for work-hardened (or work-hardened and aged) material. For details of the effect of hot and cold work, heat treatment, and size and shape of material, see Federal Specifications QQ-N-281a and QQ-N-286a.

[c] Indicated ranges of properties are typical ranges (not minima) for the casting alloys.

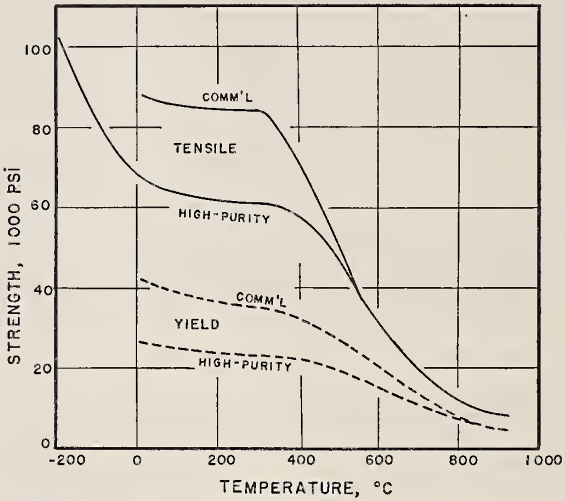

Figure 43. *Effect of temperature on the tensile and yield strengths of high-purity and commercial-purity Monel [339, 573].*

| | Ni | Cu | Mn | Fe | C | Co | Si | S |
|---|---|---|---|---|---|---|---|---|
| High-purity Monel | 70.08 | 29.71 | 0.01 | 0.01 | 0.017 | ---- | 0.12 | 0.002 |
| Commercial-purity Monel | 66.97 | 29.79 | 0.89 | 1.56 | 0.15 | 0.38 | 0.17 | 0.006 |

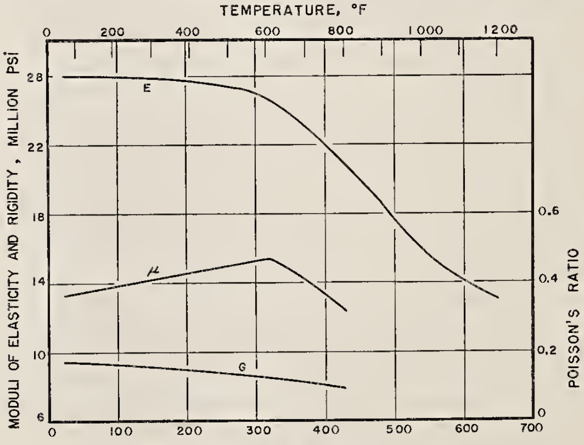

Figure 44. *Effect of temperature on the modulus of elasticity (E), modulus of rigidity (G), and Poisson's ratio (μ) of Monel and "K" Monel [591].*

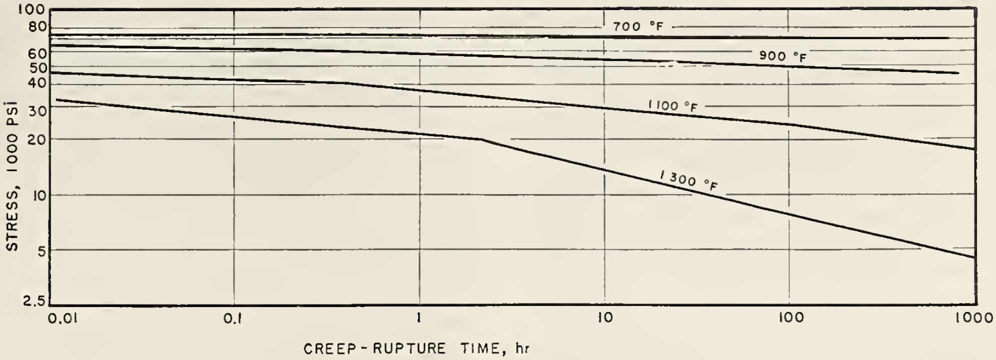

Figure 45. *Stress versus creep-rupture life for annealed Monel at 700° to 1,300° F* [390].

example, where the 1,300° curve crosses the 20,000-psi stress, indicates the zone where the fracture changes from the (low-temperature) transcrystalline type to the (high-temperature) intercrystalline type. Grant and Bucklin also reported that 30-percent cold working effectively improved the creep-rupture strength of Monel up to 900° F, but at temperatures above 1,100° F there is no benefit from cold working.

According to Van Ness and Dodge [615] hydrogen under pressure at 450° to 500° C has adverse effects on the mechanical properties of Monel and "K" Monel, and for Monel the embrittling effect is evident at room temperature.

In general, both Monel and "K" Monel have good mechanical properties at subzero temperatures. The strength increases with decreasing temperature, as shown in figure 43, without appreciable loss in ductility or impact values. There is no evidence of low-temperature embrittlement in Monel [311].

The wear- and friction-resistance of the Monels and other nickel alloys, for use in roller-bearing cages at temperatures to and above 600° F, was discussed by Johnson, Swikert, and Bisson [347].

American Society for Testing Materials specifications for nickel-copper alloys of Monel composition include B 164–49T for rods and bars, and B 165–49T for seamless pipe and tubing.

(3) *Corrosion Resistance.* Broadly speaking, Monel is more resistant than commercial nickel to acids, less resistant to alkalies, and equally resistant to salts. Monel is a single-phase alloy and, therefore, does not suffer from the galvanic effects that appear in multiphase alloys. In general, "K" Monel combines improved mechanical properties with corrosion resistance very similar to that of Monel.

*Atmospheres.* The results of the ASTM 20-year atmospheric exposure tests of Monel, as reported by Copson [645], are shown in figure 46. Comparison with results reported for nickel in figure 5 shows that Monel 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 exposed at Altoona decreased 16 percent from the pre-exposure 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. Mudge [593] in 1955 reported that the Monel roof installed in 1909 on the Pennsylvania Railroad station in New York City was still free from trouble. Monel cable racks were free from corrosion [179], and Monel spools are used to support test specimens in many of the ASTM exposure racks. According to Grant and Bucklin [390], Monel has very good resistance to oxidation at temperatures up to about 900° F. From 900° to 1,300° F the surface scale is still thin and very adherent, but grain boundary penetration of oxide is evident. Above 1,500° F the bulk oxide grows rapidly, remains adherent and apparently quite dense, but is poorly protective.

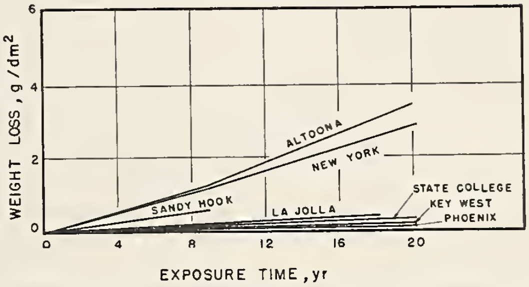

Figure 46. *ASTM 20-year atmospheric exposure tests of Monel* [645].

*Waters.* Monel is highly resistant to the corrosive action of both fresh and salt water; according to Mudge [593], some of the first uses of Monel were based on its resistance to corrosion by fresh water (and steam) and by salt water. For extreme conditions in handling fresh water, for example, potable waters containing appreciable amounts of carbon dioxide, the low-copper (LC) Monel listed in table 35 was developed recently. The resistance of Monel to corrosion and erosion in sea water has resulted in a variety of marine-engineering applications, including pump shafts and valves, turbine nozzles, marine propellors, porthole frames, and sheathing for the protection of steel drilling rigs in offshore operations [233]. "K" Monel has equivalent resistance to corrosion, improved mechanical properties, and was reported to be outstandingly successful for high-speed marine propellors where impingement and cavitation factors are involved [116], and for the construction of pressure vessels [747]. If marine organisms and other solids are allowed to accumulate on Monel or "K" Monel, particularly in stagnant sea water, pitting corrosion may occur under the accumulations.

*Salt Solutions.* Neutral and alkaline salts, including chlorides, carbonates, sulfates, nitrates, acetates, and others, rarely attack Monel at a rate greater than 0.005 in./yr, making it a useful material for handling refrigerating brines, laundry solutions, and the brines and wet salts of salt-producing plants.

Solutions of salts of nonoxidizing acids, such as zinc chloride, ammonium sulfate, and aluminum sulfate, usually attack Monel at rates less than 0.02 in./yr. Salts of oxidizing acids, such as ferric chloride, ferric sulfate, and cupric chloride, are severely corrosive, as are oxidizing alkaline hypochlorites when the available chlorine content exceeds 3 g/liter.

*Mineral Acids.* The resistance of Monel to corrosion by mineral acids is affected by the temperature, acid concentration, and extent of aeration. Sulfuric acid, air-free and in concentrations up to 80 percent, does not attack Monel at room temperature, and Monel is widely used for acid-pickling tanks in the steel and other industries. In air-saturated solutions a maximum in the rate of corrosion occurs at a concentration of 5 percent. Boiling sulfuric acid of concentrations less than 20 percent may be handled in Monel. In hydrochloric acid the rate of attack at room temperature varies from 0.005 in./yr for 1-percent, air-free acid to 0.25 in./yr for 30-percent, air-saturated acid. Monel has been used as pickling baskets and fruit-washing machines in 2-percent aerated hydrochloric acid at 50° C and in 1-percent acid at 80° C. Monel has a long record of excellent service in handling hydrofluoric acid. Copson and Cheng [646] reported that no trouble has been encountered in totally immersed portions of distillation apparatus but that some stress-corrosion cracks had been observed recently in still parts exposed to moist, aerated vapor; stress-corrosion cracking in hydrofluosilicic acid had been previously observed but cracking in hydrofluoric acid was new. In phosphoric acid, Bunger [534] reported that Monel was practically unaffected by any concentration of acid, over a range of temperatures. Miller, Treseder, and Wachter [477] reported that 85-percent phosphoric acid under pressure at 250° C appreciably attacked Monel. Nitric and other oxidizing acids corrode Monel severely, except in circumstances involving very low concentrations and temperatures at or below room temperature.

*Organic Acids and Compounds.* In general, Monel is resistant but not immune to attack by these reagents, the resistance to attack varying with the nature and concentration of the corroding medium, with the temperature, and with the degree of aeration. The resistance to aldehydes and to phthallic anhydrides is excellent, and to alcohols and phenol very good. The resistance to formic acid is generally good but is decreased if the solution is saturated with air or if the temperature is raised, for example, to 170° C. Monel is resistant to attack by acetic acid, ketones, and butyric acid. Monel is extensively used in canning and soap-making machinery [237, 366, 477].

*Gases.* Dry gases have little effect on Monel at ordinary temperatures. Hydrogen under pressure and at moderately elevated temperatures, has an embrittling action. Monel is resistant to anhydrous chlorine up to 850° F and to hydrogen chloride up to 500° F. It is resistant to anhydrous hydrogen fluoride to about 1,200° F and to fluorine to about 1,000° F [252].

*In Petroleum Refineries.* Monel is used in petroleum refineries in such applications as gasoline condenser tubes and coolers, regenerators of caustic soda solutions, pumps and valves in the acid treatment of lubricating oils, in hydrofluoric acid alkylation, and furfural recovery [699].

## 4.3. Copper-Nickel Alloys (less than 50 percent nickel)

The cupro-nickels find a variety of uses because of their combinations of physical and mechanical properties and their resistance to corrosion. The oldest use was for coinage, the largest use today is in heat-exchange equipment, other uses depend upon the electrical resistance of the alloys or their thermal electromotive force in relation to other metals or alloys.

### a. Coinage Alloys

The alloy that accounts for the great bulk of the nickel consumed in the free-world production of nickel-containing coinage is the traditional coinage alloy of 75 copper and 25 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 copper-5 nickel in some of the coins of Columbia; silver-copper-5 nickel-zinc alloys used in Sweden and Australia; copper-aluminum-2 nickel in Finland and Denmark; and a copper-zinc-1 nickel alloy was used in Pakistan, Paraguay, and the United Kingdom. France used 303 short tons of nickel, the United States 268, United Kingdom 260, India 257, and the requirements of the other 34 nickel-coinage nations brought the total to 1,891 short tons of nickel, for the 1954 Free-World production of coinage [739].

### b. Corrosion-Resistant Engineering Alloys

All of the cupro-nickels 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 cupro-nickels sometimes improperly referred to as "reverse Monels", the 80:20 and 90:10 groups.

Cupro-nickels 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. Shortly before 1950, it was observed [182] that additions of iron improved the resistance of the cupro-nickels to corrosion and erosion by salt water. According to LaQue [470], the optimum effect is obtained by adding 0.4 to 0.7 percent of iron to the 70:30 alloy, and, depending upon the observer, 0.8 or 1.5 percent of iron to the 90:10 alloy. Additions of about 1 percent of manganese also are beneficial. Improvement in the resistance of the cupro-nickels 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 power plant applications, such as steam condensation from turbines, and to extended use in heat exchangers in the chemical and petroleum industries. As LaQue [470] 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 cupro-nickels 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; they are superior to other copper-base alloys in resisting ammonia and its compounds but the presence of hydrogen sulfide in ammoniacal atmospheres is detrimental, particularly to the 70:30 alloy; data were presented on their resistance to halogens and halogen compounds other than brines. Ordinarily the cupro-nickels have good resistance to chlorinated solvents, and the 90:10 alloy is better than the 70:30 in resistance to miscellaneous organic compositions; the 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.

The compositions and some mechanical properties of the cupro-nickels, as indicated in ASTM Specification B 111–55 for copper and copper-alloy seamless condenser tubes [513], are listed in table 37. Similar composition and property requirements for the 70:30 and 90:10 alloys are included in ASTM Specification B 171–55 for copper-alloy condenser tube plates. Mechanical properties of the cupro-nickels, as was the case for the Monels, improve at low temperatures, for example, Geil and Carwile [339] reported that the tensile strength of annealed, high-purity, 70:30 cupro-nickel increased in almost linear fashion from 54,000 psi at room temperature to 83,000 psi at —196° C. In Powell and Blanpied's [492] review of thermal conductivities at low temperatures, values cited for the cupro-nickels are: for the 90:10 alloy, 470 mw/cm deg K at room temperature, 380 at 80° K, and 12 at 4.2° K; for the 80:20 alloy, 4.5 mw/cm deg K at 9° K and 2.9 at 1.9° K; for the 70:30 alloy, 290 mw/cm deg K at room temperature. The mechanical properties of the cupro-nickels fall off at moderately elevated temperatures. Port and Blank [491] 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. According to Hawthorne and Burth [676], the 70:30 cupro-nickel has long been considered readily weldable, and the recently introduced 70:30 filler metal facilitates gas welding of the 90:10 alloy, which formerly was difficult in part because of the high thermal conductivity of the alloy.

The 70:30, 80:20, and 90:10 alloys are used as castings, as well as in wrought form. Vanick [369] discussed the production, processing, and use of castings. The alloys that are called cupro-

TABLE 37. *Composition and some mechanical properties of 70:30, 80:20, and 90:10 cupro-nickels as listed in ASTM specification B 111–55* [513]

| Copper-nickel alloy | Composition, percent | | | | | | Properties, annealed temper | |
|---|---|---|---|---|---|---|---|---|
| | Copper min | Nickel | Lead max | Iron max | Zinc max | Manganese max | Tensile strength min | Yield strength min |
| | | | | | | | *psi* | *psi* |
| 70:30 | 65 | 29 to 33 | 0.05 | 0.4 to 0.7 | 1.0 | 1.0 | 52,000 | 18,000 |
| 80:20 type A | 74 | 19 to 23 | .05 | 0.6 | 1.0 | 1.0 | 45,000 | 16,000 |
| 80:20 type B | 70 | 19 to 23 | .05 | .6 | 3 to 6 | 1.0 | | |
| 90:10 | 86.5 | 9 to 11 | .05 | 0.5 to 2.0 | 1.0 | 1.0 | 40,000 | 15,000 |

nickels in the United States are called Kunifers in England, with numbers to indicate the nickel content, for example, Kunifer 30, Kunifer 10, Kunifer 5 [315]. Mechanical properties of the low-nickel cupro-nickels are responsible 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. Additional data on the physical and mechanical properties of copper-nickel alloys were presented in the Nickel Bulletin [316].

### c. Thermocouple and Electrical Resistance Alloys

The cupro-nickel that contains 45 percent of nickel, and is generally known as constantan but has been 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 [163]. It is used with copper and especially with iron [164]. According to Roeser and Dahl [87] the emf of the platinum-constantan thermocouple increases regularly with increasing temperature, to about 43 mv at 1,800° F; the iron-constantan thermocouple produces higher emf values at any particular temperature, for example, 57 mv at 1,800° F; the copper-constantan thermocouple up to 750° F produces emfs only slightly lower than those of iron constantan.

The electrical resistivity versus composition curve for the cupro-nickels reaches a maximum at 50 to 55 percent of nickel, according to Shibuya [498]. Constantan has about the maximum resistivity of the cupro-nickels and has been used as a heating element and as a resistance unit in rheostats and electrical instruments. According to Stauffer and Graham [163] the resistivity of constantan is 49 microhm-cm; the temperature coefficient of resistivity from 30° to 500° C is ±0.000025, depending on variations in composition and in amount of cold work; and the maximum temperature for use as a resistor is 500° C (930° F). Cupro-nickels with lower nickel contents and correspondingly lower resistivities have been used occasionally as electrical-resistance units, but the 45-percent-nickel alloy is the outstanding cupro-nickel for this use. The standardization of constantan wire for use as resistance standards and precision resistors for electrical apparatus is described in ASTM Specification B 84–52 [513].

### d. Copper-Nickel-Zinc Alloys

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 do not contain any silver, although they are silvery in appearance. Consequently, they are technically known as copper-nickel-zinc alloys, but the Nickel Silver term is so well established in the trade that the ASTM specification titles usually refer to copper-nickel-zinc (nickel silver) alloys.

According to Grosvenor [458] the alloys contain the three major elements in the approximate ranges—copper 45 to 75 percent, nickel 5 to 30 percent, and zinc 5 to 45 percent. 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 satisfactorily. Lead is often added to improve the machinability.

The mechanical properties, corrosion resistance, and attractive appearance of these alloys have led to a variety of engineering and decorative uses, in spring applications, in food-handling equipment, gift and tableware usually silver-plated, ornamental metal work and architectural uses, 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. Data for the thermal conductivity of copper-nickel-zinc alloys at low temperatures were reviewed by Powell and Blanpied [492]. According to Dume [219] 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.

Table 38 indicates some of the popular compositions of wrought and cast alloys included in ASTM specifications. The tensile strengths of the alloys listed in specification B 122 range from 54,000 psi minimum for quarter-hard alloy number 7 to 122,000 psi maximum for spring-temper alloy number 8. Tensile strengths of the rod and bar forms listed in specification B 151 cover a similar range from 60,000 psi minimum to 110,000 psi maximum, depending upon the composition, temper, and rod or bar diameter and shape. The 18-percent nickel alloys in strip and wire form have been particularly popular for use as springs because of their high elastic strength and good fatigue resistance. Gohn, Guerard, and Herbert [456] reported that the World War II restrictions on the use of nickel in strip led to the development of alloy number 8 (12% nickel), and the Korean restrictions led to further investigation of possible substitutes for the 18-percent alloy. They concluded that either alloy number 8 or a 60 Cu–12

TABLE 38. *Copper-nickel-zinc (nickel-silver) alloys as listed in several ASTM specifications [513]*

| ASTM specification | ASTM alloy | Composition, percent | | | | | |
|---|---|---|---|---|---|---|---|
| | | Cu | Ni | Pb max | Fe max | Mn max | Zn |
| B 122-55T, plate, strip, and rolled bar | 1 | 70.5 to 73.5 | 16.5 to 19.5 | 0.10 | 0.25 | 0.50 | rem. |
| | 2 | 63.0 to 66.5 | 16.5 to 19.5 | .10 | .25 | .50 | rem. |
| | 3 | 63.5 to 68.5 | 9.0 to 11.0 | .10 | .25 | .50 | rem. |
| | 4 | 53.5 to 56.5 | 16.5 to 19.5 | .10 | .25 | .50 | rem. |
| | 5 | 65 min | 29.0 to 33.0 | .05 | .7 | 1.0 | 1.0 max |
| | 6 | 74 min | 19.0 to 23.0 | .05 | .6 | 1.0 | 1.0 max |
| | 7 | 70 min | 19.0 to 23.0 | .05 | .6 | 1.0 | 3.0 to 6.0 |
| | 8 | 55.0 to 58.0 | 11.0 to 13.5 | .10 | .25 | 0.50 | rem. |
| | 9 | 69.0 to 73.5 | 9.0 to 11.0 | .10 | .25 | .50 | rem. |
| B 151-55, rod and bar | A | 63.0 to 66.5 | 16.5 to 19.5 | .05 | .25 | .50 | rem. |
| | B | 53.5 to 56.5 | 16.5 to 19.5 | .05 | .25 | .50 | rem. |
| | B-1 | 58.5 to 61.5 | 16.5 to 19.5 | .05 | .25 | .50 | rem. |
| | C | 59.0 to 66.5 | 16.5 to 19.5 | 0.8 to 1.2 | .25 | .50 | rem. |
| | D | 63.5 to 66.5 | 11.0 to 13.0 | 0.05 | .25 | .50 | rem. |
| | E | 63.5 to 66.5 | 9.0 to 11.0 | .05 | .25 | .50 | rem. |
| B 206-54, wire | (a) | (a) | (a) | (a) | (a) | (a) | (a) |
| B 283-53 T, die forging (hot pressed), nickel silver | 45-10 | 45.0 | 10.0 | ---------- | ---- | ---- | 45.0 |
| | | | | | | Sn | |
| B 149-52, sand casting | 10 A | 57.0 | 12.0 | 9.0 | ---- | 2.0 | 20.0 |
| | 11 A | 64.0 | 20.0 | 4.0 | ---- | 4.0 | 8.0 |
| | 11 B | 66.5 | 25.0 | 1.5 | ---- | 5.0 | 2.0 |

[a] Same compositions and designations as A, B, B-1, C, and D rod and bar.

Ni-28 Zn alloy was a suitable substitute for alloy number 4 in spring applications, but that alloys with only 10 percent of nickel, for example, 60 Cu-10 Ni-30 Zn were not satisfactory for springs. Vanick [308] reviewed the composition, properties, and uses of the leaded casting alloys listed in ASTM B 149. He reported that tin strengthens and hardens the alloys, lead promotes machinability, zinc is a useful deoxidizer, and nickel is progressively beneficial to the corrosion resistance, color, and mechanical properties. The cast alloys have many uses, including ornamental plaques, fittings, internal structural parts in buildings, plumbing fixtures, railroad and dining car fixtures, marine fittings, household ware, and food-handling equipment. According to Bagger [170], leaded nickel-silver forgings containing 45 Cu-42.5 Zn-10 Ni-2.5 Pb have tensile strengths of 65,000 to 75,000 psi, yield strengths of 40,000 to 50,000 psi, good corrosion resistance with high strength and hardness, and are used extensively for valve parts and fittings in the food, chemical, and other industries.

### e. Miscellaneous Copper-Base Alloys

(1) *Brass.* Nickel contents up to 1 percent are listed in ASTM B 62-52 for ounce metal (85-5-5-5) castings and in ASTM B 145-52 for leaded red brass sand castings. Pelzell [411] reported that the tensile strength of 50-Cu brass was increased 20 to 25 percent by additions of 0.5 percent of nickel in the presence of 0.1 percent of silicon.

(2) *Tin-nickel bronze.* Vanick [305] discussed the "Ni-Vee" bronzes based on the 5 nickel plus 5 tin composition and covering a range of 1 to 5 Ni, 2.5 to 10 Sn, 0 to 20 Pb, and 0 to 5 Zn. These alloys have good castability, low shrinkage, pressure tightness, fine grain, and are versatile and economic. The effect of nickel in replacing tin in bronze is ascribed to the formation of a nickel-tin constituent that has limited solubility in the solid metal. Vanick's data for the mechanical properties of the 5 Ni-5 Sn bronze, as cast and after several heat treatments, are shown in figure 47. Fetz [549] reported that age-hardenable copper-nickel-tin bronzes, for example, 15 Ni-7 Sn-bal Cu, could be prepared by powder metallurgy techniques. Approximately 1 percent of nickel is present in the tin-bronze and leaded-tin bronze sand castings described in ASTM B 143-52, in the high-leaded tin bronze for cast bearings and bushings in ASTM B 144-52, in two of the bronze castings for bridges and turntables in ASTM B 22-52, and in the steam or valve bronze castings described in ASTM B 61-52.

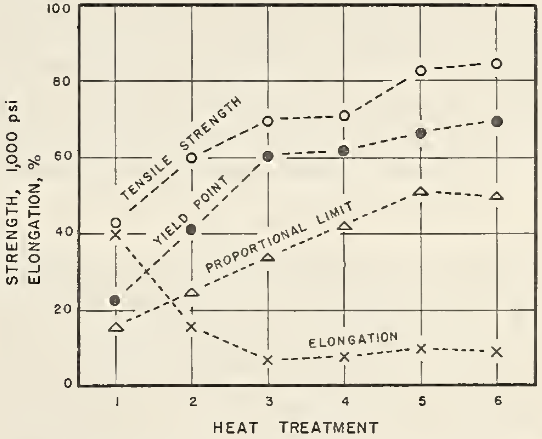

FIGURE 47. *Effect of heat treatment on the mechanical properties of 5 Ni-5 Sn bronze [305].*

1, as cast; 2, held 5 hr at 550° F; 3, held 10 hr at 550° F; 4, held 10 hr at 1,400° F, cooled slowly, then 5 hr at 600° F; 5, held 10 hr at 1,400° F, air cooled, then 5 hr at 550° F; 6, held 10 hr at 1,400° F, oil quenched, then 5 hr at 550° F.

(3) *Aluminum-nickel bronze.* ASTM Specification B 148–52, for aluminum-bronze sand castings, includes grade D containing 4 Ni–4 Fe–11 Al, and B 150–54, for aluminum-bronze rod, bar, and shapes, includes one alloy containing 4 to 5.5 percent of nickel and another containing 1 percent maximum of nickel. Vanick [307] reported that the nickel-aluminum bronzes had good resistance to oxidation and corrosion, and retained a high proportion of their strength up to about 750° F (400° C). They are used in steam power plants, chemical-engineering applications, glass manufacture, and in wear-resisting applications. Cahill [638] reported that the 5 Ni–9 to 10 Al– about 5 Fe alloy is being used successfully for propellors on tankers, etc., particularly in cold weather as in Arctic areas, and that this alloy may eventually supplant the long-established manganese bronze because of its improved resistance to erosion, cavitation, and dezincification. For inert-gas-shielded welding of this alloy an aluminum-bronze filler wire is preferable to nickel-aluminum bronze.

(4) *Manganese-nickel bronze.* Vanick [306] defined manganese bronze as essentially a 60 Cu–40 Zn brass to which had been added about 1 percent each of Al, Fe, and Mn. He reported that additions of up to 3 percent nickel assist diffusion of the iron, retard pitting and dezincification, and have favorable effects on the mechanical properties and resistance to corrosion. He compared the properties of three alloys used for large and small impellers in marine service, a nickel-free manganese bronze, "Turbadium" containing 2 percent of nickel, and "Turbine Metal" containing 3 percent of nickel. One of the high-strength manganese bronzes discussed in ASTM B 147–52 contains 0.5 percent of nickel.

## 4.4. Nickel-Chromium Alloys

Nickel-chromium and nickel-chromium-iron alloys have many applications, ranging from thermocouples to structural units, depending upon their electrical properties, mechanical properties, and resistance to heat, oxidation, and corrosion. The present discussion is limited to some of the prominent alloys of the group and their applications other than those in the super alloy category.

### a. Chromel P

This 90 Ni- 10 Cr alloy is widely used, with the Ni- Mn- Al- Si alloy known as Alumel, as a base-metal thermocouple [164]. Roeser, Dahl, and Gowens [70] reported the values shown in table 39 for the thermal emf of this thermocouple at temperatures up to 1,400° C. In oxidizing atmospheres above about 1,100° C, the life of the thermocouple is short, and in an alternately oxidizing and reducing atmosphere the emf is subject to change.

Table 39. *Thermal electromotive force of chromel-alumel, with cold junction at 0° C [70]*[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.

### b. 80 Ni-20 Cr Alloy

This alloy was developed in 1906, by A. L. Marsh, for use as an electrical resistance alloy [742]. According to Gatward [141] the electrical resistivity at 68° F (20°C) is 107.9 microhm-cm and the effect of increasing temperature on the resistivity is as shown in figure 48. The use of the drawn or rolled alloy for electrical-heating elements is discussed in ASTM Specification B 82–52 [513]. Resistance to oxidation is important in heating units. Zima [752] reported that the rate of oxidation at 1,096° C, 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 nickel are appreciably less in air than in oxygen, for example, Zima cited results of others to show that the rate of oxidation of nickel in oxygen at 1,000° C was more than 10 times as great as the rate in air at 900° C. Gulbransen and Andrew [459] reported that pure chromium 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, Gulbransen and Andrew [562] reported that the rates of oxidation at about 900° C were lower for continuous exposure than for hot-cold cycling. Values for the specific heat

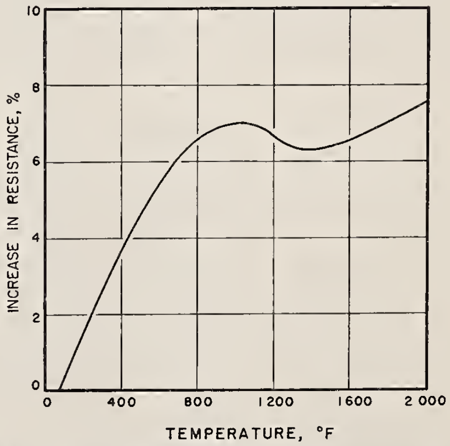

Figure 48. *Effect of temperature on the electrical resistance of 80* Ni–*20* Cr [*141*].

of 80 Ni–20 Cr from 0° to 900° C, as reported by Douglas and Dever [544], and shown in figure 49, show a discontinuity in the vicinity of 600° C that has not as yet been fully explained. Mechanical properties of 80 Ni–20 Cr at room temperature include tensile strengths ranging from 95,000 psi in the annealed condition to 200,000 psi in the extra-spring condition, with accompanying elongations of 25 to 35 percent (annealed) and 0 percent (extra spring), and a modulus of elasticity of 31,000,000 psi [141].

These properties plus the resistance to various corrosive media make wrought 80 Ni–20 Cr available for engineering construction, particularly for use at higher temperatures than the less expensive nickel-chromium-iron alloys can withstand. However, as stated in ASTM B 76–39 [513], 80 Ni–20 Cr is subject to plastic flow under relatively light loads at high temperatures and, therefore, does not appear in the lists of super alloys. Carburization and oxidation in industrial gases at 900° to 1,000° C is avoided if 2 percent of silicon is added to 80 Ni–20 Cr [216]. Because of its heat-resistant and corrosion-resistant properties, 80 Ni–20 Cr was proposed recently for use in poppet valve heads and seats [688].

According to Bagger [170] 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.

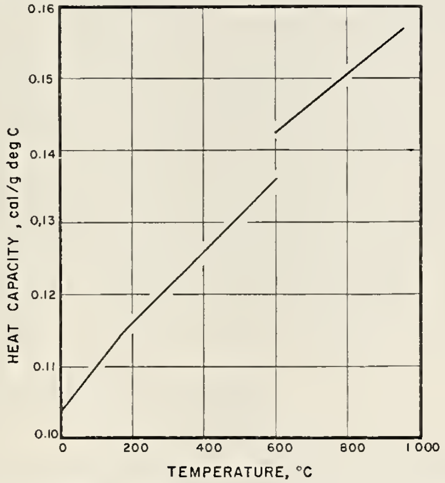

Figure 49. *Specific heat of 80* Ni–*20* Cr [*544*].

### c. Nickel-Chromium-Iron Alloys

(1) *Inconel.* The 80 Ni–14 Cr–6 Fe alloy, made by adding ferrochromium to nickel, was offered in 1932 to the dairy industry for its resistance to corrosion by milk [581]. The present composition is 77 Ni–15 Cr–7 Fe. It is resistant to oxidation at elevated temperatures. It is used for the alkaline digesters in paper making [424], it shows excellent resistance to sulfur dioxide but is corroded by hydrogen sulfide [332]. It's uses in petroleum refineries were discussed by Mason [699] and in the soap and fatty acids industry by Friend and Mason [184]. Moore and Mason [292] reported that Inconel was more resistant than stainless steel to lead bromide vapor at 1,350° to 1,650° F, and Farber and coworkers [548] reported that Inconel was the most resistant, of all the metals tested, to nitric oxide at temperatures up to 1,700° F. According to Johnson, Swikert, and Bisson [346], the wear and sliding friction properties of cast Inconel, against hardened SAE 52100 steels, compared favorably with the performance of nodular iron. Weldments made in inert gas with an Inconel 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 [729]. Some of the room-temperature mechanical properties of Inconel, according to Mudge [153] are tensile strengths ranging from 80,000–100,000 psi for annealed rod and bar to 165,000–185,000 psi for spring-temper wire. Corresponding yield strengths are 25,000–50,000 psi and 150,000–175,000 psi, with elongations in 2 in. of 50 to 35 percent and 10 to 2 percent respectively. Rose [358] reported that the tensile strength of Inconel was above 80,000 psi at 1,000° F, but fell off rapidly at higher temperatures.

Additions of aluminum and, to a lesser extent, titanium improve the mechanical strength of precipitation-hardenable, high-nickel alloys like Inconel [482, 631, 796, 797], and additions of columbium further stiffen the matrix and stabilize the carbides as they did in stainless steels. Some of these modified Inconels are in the super alloy class [798] but, according to Patton [763] others such as Inconel "M", Inconel "600", and Inconel "702" find uses other than in aircraft engines. Inconel "M", 71 Ni–16.5 Cr–7 Fe–2.24 Mn–3.1 Ti–0.05 Al, has low susceptibility to corrosion from leaded fuels and is used in reciprocating engine valve stems. Inconel "600", 73.3 Ni–15.9 Cr–7.65 Fe–2.45 Cb, is a matrix-stiffened Inconel for industrial gas turbines and some nuclear applications. Inconel "702", 78 Ni–15.85 Cr–3 Al–0.6 Ti, has high resistance to oxidation at 1,900° to 2,300° F.

Some physical constants of Inconel and Inconel "X", according to Patton [763], are:

| | Inconel | Inconel "X" |
|---|---|---|
| Density ---------- $g/cm^3$ | 8. 43 | 8. 25 |
| Melting range ---------- °F | 2,540 to 2,600 | 2,540 to 2,600 |
| Specific heat ---------- cal/g° C | [a] 0. 109 | [b] 0. 13 |
| Electrical resistivity ohms/cir mil ft | [c] 590 | [d] 750 |
| Thermal conductivity at 392° F Btu in./$ft^2$ hr ° F | 119 | 106 |
| Mean coefficient of thermal expansion ---------- per ° F | [e] $8.96 \times 10^{-6}$ | [f] $9 \times 10^{-6}$ |
| Modulus of elasticity ---------- psi | $31 \times 10^6$ | $31 \times 10^6$ |

[a] 25° to 100° C. [b] 20° to 900° C. [c] 20° C. [d] 50° C. [e] 100° to 1,400° F. [f] 100° to 1,500° F.

Inconel forges readily at 1,850° to 2,100° F with only light hammering permissible at lower temperatures down to about 1,600° F. Inconel

"X" is forged at 1,850° to 2,200° F but is much stiffer than Inconel.

The preferred temperature range for annealing Inconel is 1,800° to 1,950° F. The preferred range for Inconel "X" is 1,900° to 2,100° F, with subsequent rapid cooling required for optimum softness.

(a) Spring materials for elevated temperatures. Commonly used spring materials (other than the constant-modulus watch mainsprings previously discussed) include high-carbon, alloy, and stainless steels, copper-base alloys, and nickel-base alloys. For service at ordinary temperatures, beryllium copper is used principally in electrical equipment and instruments, music wire is the most widely used material for small springs, and type 302 is the most widely used stainless steel. Most of the nickel-base spring materials have properties resembling those of stainless steel, and Inconel "X" has properties approaching those of music wire and tool steels. However, the allowable design stresses, ultimate tensile strengths, and fatigue properties of the nickel-base alloys are, in general, enough lower so that size-for-size substitution for steel springs is not practical. Shot peening may improve the fatigue properties of steel by as much as 100 percent, but is much less effective in improving the properties of the nickel alloys and introduces a strong possibility of embedded steel particles that decrease the resistance to corrosion [639, 682].

The load-carrying capacity of helical springs decreases with increasing temperature above room temperature, principally because of relaxation under constant deflection or creep under constant load. Relaxation data for some of the spring materials on the basis of a 6-percent load loss, which is generally considered the maximum acceptable value for all except some very special applications, are presented in figure 50. It is evident that music wire and beryllium copper lose strength rapidly at temperatures only slightly above room temperature, and chromium-vanadium steel (SAE 6150) should not be used above 425° F. The selection of spring materials for service at temperatures above about 400° F generally is limited to stainless steels and high-nickel alloys. Assuming 50,000 psi for the allowable torsional stress, K Monel may be used up to about 525° F; type 302 stainless to about 550° F; Inconel, Permanickel, and Duranickel to approximately 700° F. According to Carlson [639], Inconel "X" aged 4 hr at 1,200° F can be used up to 850 F at stresses up to 55,000 psi, and, according to the International Nickel Company [682], Inconel "X" aged 16 hr at 1,350° F can withstand 1,000° F continuously or 1,100° F for short periods of time.

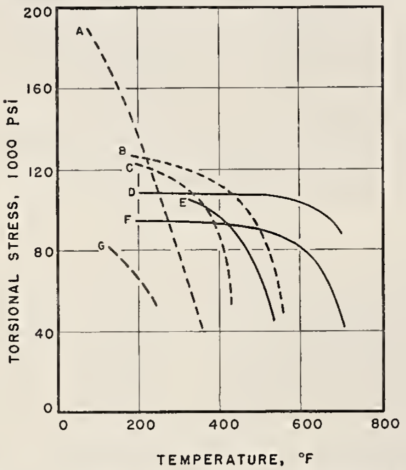

Figure 50. *Torsional stress of spring materials at elevated temperatures, for 6-percent-relaxation load loss in 7 days [639, 682].*

Curve A, music wire, SAE 1085, 1090; B, stainless-steel type 302; C, Chromium-vanadium steel, SAE 6150; D, Inconel "X"; E, K Monel; F, Inconel, Permanickel, Duranickel; and G, beryllium-copper.

(2) *Nimonic Alloys.* The Nimonic alloys were developed in England during World War II, primarily for use in aircraft engines, as described in 1950 in Ministry of Supply D. T. D. Specifications 703 (Nimonic 75), 714 (Nimonic 75 F), 725 (Nimonic 80), 736 (Nimonic 80A), and 747 (Nimonic 90). Although they are primarily super alloys, and as such as considered in another section of this report, the Nimonics find other uses, including furnace components, springs, combustion chambers, marine and power station turbines [212, 314, 317].

All of the Nimonic alloys are modifications of the basic composition 80 nickel-20 chromium. According to the D. T. D. Specifications, Nimonic 75 contains 18 to 21 Cr–5 max Fe–0.2 to 0.6 Ti; Nimonic 75 F is the same as 75 except for higher Fe (5 to 11); Nimonic 80, 18 to 21 Cr–5 max Fe–2 max Co–1.8 to 2.7 Ti–0.5 to 1.8 Al; Nimonic 90, same composition as alloy 80 except that cobalt is raised to 20 percent and nickel is reduced accordingly. Recent values reported by Patton [763] differ in minor respects from the compositions reported in the 1950 Specifications. Some physical properties, as reported in the Nickel Bulletin in 1950 are shown in table 40. Tensile

Table 40. *Physical properties of Nimonic alloys [212]*

| | Nimonic 75 | Nimonic 80 | Nimonic 90 |
|---|---|---|---|
| Specific gravity ........g/cm³.. | 8. 35 | 8. 25 | 8. 27 |
| Specific heat— | | | |
| 20° to 100° C...cal/g ° C.. | 0. 11 | 0. 103 | ---- |
| 20° to 900° C...cal/g ° C.. | ---- | . 128 | ---- |
| Thermal conductivity— | | | |
| 100° C.....cal/cm ° C sec.. | . 03 | . 029 | ---- |
| 900° C.....cal/cm ° C sec.. | ---- | . 066 | ---- |
| Mean coefficient of thermal expansion— | | | |
| 20° to 100° C millionths/° C.. | 12. 2 | 11. 9 | 11. 6 |
| 20° to 300° C millionths/° C.. | 13. 4 | 13. 0 | 12. 7 |
| 20° to 500° C millionths/° C.. | 14. 1 | 13. 7 | 13. 7 |
| 20° to 700° C millionths/° C.. | 15. 4 | 14. 5 | 15. 0 |
| 20° to 900° C millionths/° C.. | 16. 0 | 15. 8 | 17. 0 |
| Electrical resistivity— | | | |
| 20° C.........microhm cm.. | 109 | 126 | about 115 |

strengths reported in the same article include Nimonic 75, 103,000 psi at room temperature and 40,000 at 800° C; Nimonic 80, 150,000 psi at room temperature and 70,000 at 800° C; Nimonic 90, 165,000 psi at room temperature and 85,000 at 800° C. The endurance limits under reversed loading for $40\times10^6$ cycles were reported as; for Nimonic 80, 49,000 psi at 20° C, 42,500 psi at 600° C, 37,500 at 700° C, 28,000 at 750° C, and 20,000 at 800° C; for Nimonic 90, 42,000 psi at 700° C, 36,000 at 750° C, and 26,500 psi at 815° C.

The chemical polishing and etching of the Nimonic alloys was discussed by Meace [703].

(3) *Other Ni–Cr–Fe alloys.* (a) ACI CASTING ALLOYS. Alloy Casting Institute alloys in general are considered as cast steels but the HT, HU, HW, and HX alloys contain 50 percent or more alloying elements (and less than 50% iron), as follows:

| ACI Designation | Nickel | Chromium |
|---|---|---|
| | % | % |
| HT | 35 | 15 |
| HU | 39 | 19 |
| HW | 60 | 12 |
| HX | 67 | 17 |

These are general-purpose, heat-resistant castings for use at temperatures up to or above 2,000° F [784], but they do not have the high-temperature strength and rigidity to qualify as super alloys for aeronautic use. According to Clauser [214] and to Rose [358], alloy HT can be used to 2,100° F in oxidizing atmospheres and to 2,000° F in reducing atmospheres, and is widely used in furnace construction, retorts, carburizing equipment, radiant tubes, cyanide, lead, and salt pots, and hearth plates. Alloy HU has somewhat higher hot strength and resistance to oxidation because of its increased chromium content. Alloy HW is not as strong but is more resistant to oxidation, carburization, and thermal shock, making it especially useful for retorts, furnace parts, and quenching fixtures. Alloy HX is more corrosion-resistant at high-temperatures and in contact with sulfurous gases. It is used in carburizing and quenching fixtures, and for some types of salt baths. HW and HX can be used in oxidizing atmospheres to 2,050° F and in reducing atmospheres to 1,900° F.

(b) 72 NI–16 CR–8 FE. This alloy is widely used for general corrosion- and heat-resisting purposes, as indicated by its appearance in three ASTM specifications, B 166–49T for rods and bars, B 167–49T for seamless pipe and tubing, B 168–49T for plate, sheet, and strip [513].

(c) 60 NI–16 CR–24 FE. This alloy is described in ASTM Specification B 83–52 [513] for drawn or rolled material, for electrical heating elements.

(d) MISCELLANEOUS NI–CR–FE ALLOYS. Ilium G. This alloy contains 58 Ni–22 Cr–6 Cu–6 Mo–6 Fe and is used to resist the attack of sulfuric, nitric, phosphoric acids, mixed acids, salt and acid mixtures, and is especially resistant to sea water and saline atmospheres. It is useful as a heat-resistant alloy where severe corrosion is encountered [148].

Nivco. According to Unterweiser [741], this Ni–Cr–Fe–Co alloy has a creep-rupture life of 100 hr at 1,200° F and 50,000 psi, an endurance limit at 1,200° F of about 45,000 psi, excellent damping capacity, and is useful as a blading alloy in steam turbines.

The 50 Ni–28 Cr–6 W–16 Fe alloy has been recommended for its strength and resistance to corrosion in air at 1,800° to 2,300° F [275].

The 60 Ni–12 Cr–3 Mo–Sn–Bi–Mn–Si–Fe alloy has been recommended for food handling machinery [737].

The 68 Ni–15 Cr–11 Fe–3 Cb and 66 Ni–15 Cr–11 Fe–Cb–Ti–Al alloys are among the high-nickel alloys covered by ASTM Specification B 295–54T [513], for covered welding electrodes.

Brazing alloys may contain 60 to 85 Ni, up to 20 CR, up to 30 Mn, and Si, B, Mo, and Fe [520].

The 60 Ni–25 Cr–4 Fe–4 Cu–Co–Mo–W alloy has been proposed for hardfacing exhaust valves [633].

The 40 Ni–20 Cr–12 Co–6 W alloy was proposed for cast valve-seat inserts [717].

Nickel-chromium-iron alloys will withstand short exposures up to 3,500° F when they are coated with a flame-sprayed mixture of nickel oxide and magnesium oxide [486].

## 4.5. Hastelloy Alloys

The first of the high-nickel corrosion-resistant alloys known as Hastelloys were nickel-molybdenum-iron alloys, but in subsequent alloys the composition was considerably changed. This discussion will be confined to the corrosion-resistant alloys A, B, C, D, and F. Hastelloy R and Hastelloy X were designed for high-temperature mechanical properties, i. e., for super alloy service.

Hastelloy A contains 56 Ni–22 Mo–22 Fe. It is usefully resistant to all concentrations of hydrochloric acid at room temperature and to unaerated solutions at temperatures below about 160° F. It is usefully resistant to sulfuric acid of all concentrations at temperatures up to about 160° F, and up to the boiling point for concentrations below 50 percent. It is resistant to acid chlorides, acid phosphates, organic acids and compounds, to atmospheric oxidation, and to oxidizing and reducing flue gases at temperatures up to about 1,450° F. It is not recommended for service with nitric or strongly oxidizing acids, and the presence of oxidizing salts such as ferric and cupric salts makes other acids corrosive. Forgings of Hastelloy A have tensile strengths of 110,000 to 120,000 psi with yield strengths of 47,000 to 50,000 psi [138, 140, 170].

Hastelloy B contains 62 Ni–32 Mo–6 Fe. It is notable for its unusually high resistance to all concentrations of hydrochloric acid at temperatures up to the boiling point. Hastelloy B is more resistant than A to sulfuric acid and is at least as resistant as A to acid chlorides, phosphates, organic acids and compounds, oxidation and flue gases. It is not recommended for use with strongly oxidizing acids or salts. Hastelloy B forgings have tensile strengths of 130,000 to 140,000 psi with yield strengths of 60,000 to 65,000 psi [138, 140, 170, 370].

Hastelloy C contains 53 Ni–17 Mo–17 Cr–5 W–6 Fe. It possesses an unusual degree of resistance to oxidizing solutions, especially to those containing chlorides, and to hypochlorite solutions and moist chlorine. It has excellent resistance to acetic acid, sea water, and many corrosive organic acids and salts. Hastelloy C forgings have tensile strengths of 115,000 to 128,000 psi with yield strengths of 55,000 to 65,000 psi [138, 140, 170, 370, 747].

Hastelloy D contains 85 Ni–10 Si–3 Cu. Its most important property is its resistance to concentrated solutions of sulfuric acid at elevated temperatures. It is also resistant to hydrochloric acid under mild conditions and to other non-oxidizing acids and salts [138, 140].

Hastelloy F contains 45 Ni–22 Cr–6 Mo–2 Cb. According to Scheil [416], it has mechanical and physical properties similar to those of austenitic stainless steel and is especially suitable for lining digesters of the sulfite- and kraft-pulp industry.

Ebling and Scheil [274] reported that the A, B, C, and D alloys were satisfactorily used in the manufacture of phosphoric acid, but were not so satisfactory in the catalytic process for the production of 65-percent acid, operating at 1,000 to 1,350 psi and 500° to 600° F. The composition of the oxide films (spinels, etc.) formed on Hastelloy A, B, C, and D at 300° to 900° C was determined by Hickman and Gulbransen [145]. According to Bagger [170], the A and B alloys are light forged at 1,600° F, heavy forged at 1,900° to 2,250° F, and annealed at 2,150° F; alloy C is light forged at 1,700° to 2,000° F, heavy forged at 2,000° to 2,250° F, and annealed at 2,225° F.

## 4.6. Nonferrous Super Alloys

The development of nonferrous super alloys, with strength and load-carrying capacity at very high temperatures, paralleled the development of ferrous super alloys, which were discussed in a prior section of this Circular. Many of the nonferrous super alloys are modifications of heat-resistant, corrosion-resistant alloys. Grant [668] pointed out that single phase alloys such as Nichrome and Inconel are weak above about 1,250° 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. The compounds $Ni_3Al$ and $Ni_3Ti$ are the principal hardening agents for nickel-base alloys with $Ni_3Al$ the more efficient and more effective. Guard and Prater [671] reported that a cobalt-base alloy developed good high-temperature properties when hardened by titanium without any aluminum present, and that precipitated alloy carbides in cobalt-base and other alloys served as strengtheners up to about 1,350° F but have little effect at or above 1,500° F. Another method of improving the high-temperature strength properties is to increase the content of alloying elements such as cobalt, tungsten, and molybdenum. Both procedures have been employed, with the result that nickel-base and cobalt-base alloys are the best available super alloys and may be used at higher temperatures than the best of the ferrous alloys can withstand [518, 668, 799]. Figure 51 illustrates the improvement obtained in the stress-rupture properties of nickel-base alloys modified by precipitation hardening and alloying additions, according to VerSnyder [742], and figure 52

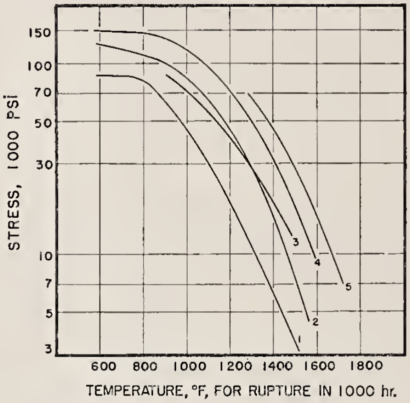

FIGURE 51. *Effect of modified compositions on the stress-rupture properties of nickel-base alloys* [*742*].

| *Curve* | *Additional elements* | *Typical alloys* |
|---|---|---|
| 1 | None | Inconel; 80 Ni–20 Cr. |
| 2 | 2.5 Ti–0.6 Al | Inconel "W"; Nimonic 80. |
| 3 | 19 Mo–5 W | Hastelloy 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 700; Udimet 500. |

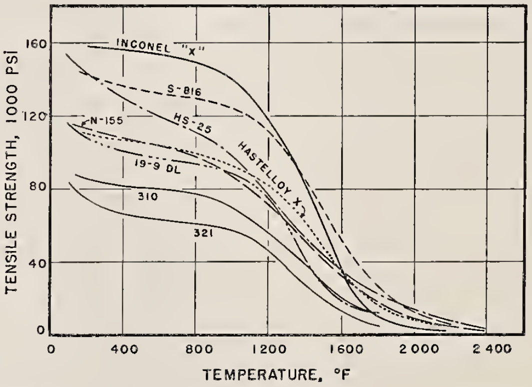

FIGURE 52. *Typical tensile strengths of high-temperature alloys* [*518*].

illustrates the superior short-time tensile strengths of nonferrous over ferrous super alloys, as reported in the SAE symposium [518]. The high-temperature strengths of the super alloys increase the difficulty of hot working or, as Foley [658] expressed it, alloys with extra-special properties require extra-special care in forging. The selection of tools, cutting fluids, and machinability data for machining super alloys were discussed by Halverstadt [675]. Because of forming difficulties, some of the nonferrous super alloys, especially those high in cobalt, tungsten, and molybdenum, are used in cast or precision-cast forms [444].

Mechanical properties at high temperatures are the principal basis for evaluating super alloys but physical properties such as the 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 applied load and have been responsible for many cases of failure [518]. In general a low coefficient is desired; in the case of dissimilar metal joints, the two coefficients may be either high or low as long as they are equal. Data for several of the nonferrous super alloys, as reported in the Nickel Bulletin [212] and by Apblett and Pellini [318] and Hidnert [760], are shown in figure 53. Clauser [444] reported that the nickel-base super alloys as a class had coefficients of thermal expansion between 6.95 and $9.0\times10^{-6}$ per ° F, and cast cobalt-base alloys between 8.40 and 9.25, both for the range from room temperature to 1,500° F.

Thermal conductivity becomes critical in applitions 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 [518].

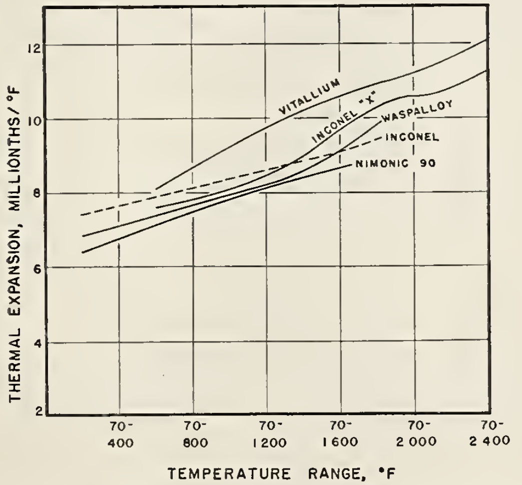

FIGURE 53. *Thermal expansion of some nonferrous super alloys [212, 318, 760].*

Examples of reported thermal conductivities are for Nimonic 80 [212], 0.029 cal/cm °C sec at 100° C and 0.066 at 900° C; for Inconel [763], 104 Btu in./$ft^2$ hr ° F at 212° F; for Hastelloy R–234 [627] 72 Btu in./$ft^2$ hr ° F at 212° F and 180 at 1,700° F. (1 cal/cm sec equals 2903 Btu in./$ft^2$ hr ° F).

A property only recently considered important by power plant designers is the emissivity that affects the amount of incident radiant heat that is absorbed by or leaves the surface. In combustion chambers it is important to have an inside surface with as low an emissivity factor as possible, to reflect a maximum amount of radiated heat from the combustion gases. On the other hand, the outer surface of a ramjet engine combustion chamber is open to the sky and should have high emissivity to radiate heat from the wall [518]. Emissivity data for the super alloys at high temperatures are not as yet readily available.

Evaluation of the nonferrous super alloys is made primarily on the basis of stress-rupture data, for example, for 100 and 1,000-hr life at and above 1,200° F.[7] Simmons, Krivobok,[8] Mochel, and Franks [605] in 1955 reported results of a comprehensive survey of ferrous and nonferrous super alloys. The nonferrous alloys for which they reported stress-rupture data, and a few subsequently reported data, are presented in table 41. The group classification of a few alloys has been changed from the classification assigned by Simmons et al. Comments on some of the alloys are as follows:

*S–816* is high on the critical alloy list but has excellent strength at the higher temperatures and has been used extensively for forged turbine blades [518]. According to VerSnyder [742], when S–816 became available it replaced alloys of the Hastelloy type that were used as bucket alloys in early jet engines.

*J–1570*, according to Guard and Prater [671], was developed from statistically designed experiments to determine the optimum composition and treatment of alloys containing molybdenum, tungsten, and titanium.

*Inconel "X"* is an age-hardening modification of Inconel that is superior to other high-temperature alloys in short-time tensile strength at elevated temperatures up to about 1,400° F, and in many cases up to 1,600° F, as shown in figure 52. It has found widespread use as a combustion chamber material for afterburners and many other applications [518], and is used in highly stressed applications up to 1,600° and even 1,700° F [581]. Operating details for spot and seam welding of Inconel "X" were discussed by Nippes, Savage, and Moazed [710].

*Nimonic alloys* were developed in England and are similar to Inconel "X" in composition and function. Pfeil [240] reported that they were uni-

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[7] A new criterion is the Schapiro index [764], yield strength at 1,200° F divided by density, that has been proposed for evaluating aircraft alloys for thermal flight. This criterion, like the stress-rupture data, shows that the high-temperature properties of nickel-base and cobalt-base alloys are superior to those of iron-base alloys, as indicated by the data for selected alloys supplied by Badger [754]. See also Steurer [794].

[8] See also, Simmons and Krivobok [770].

TABLE 41. *Nonferrous super alloys [605, 627, 671, 685, 763]*

| Alloy | Nominal composition, percent | | | | | | | | | | | | Characteristic rupture strengths,[a] 1,000 psi— | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | Si | Ni | Cr | Co | Mo | W | Ti | Al | Fe | Other | 1,200° F | | 1,350° F | | 1,500° F | | 1,600° F | | 1,800° F | |
| | | | | | | | | | | | | | 100 hr | 1,000hr | 100 hr | 1,000hr | 100 hr | 1,000hr | 100 hr | 1,000hr | 100 hr | 1,000hr |
| NICKEL-CHROMIUM BASE, COMPLEX ALLOYS | | | | | | | | | | | | | | | | | | | | | | |
| NA-22H (cast) | 0.50 | 1.3 | 1.0 | 48 | 27 | --- | -- | 6 | -- | --- | 17 | | --- | --- | --- | --- | --- | --- | --- | --- | 5.0 | 3.5 |
| S-590 | .40 | 1.5 | 0.7 | 20 | 20 | 20 | 4 | 4 | -- | --- | 24 | Cb, 4 | 48 | 38 | 30 | 22 | 20 | 16 | 12.5 | 9 | 5.6 | 3.5 |
| S-816 | .38 | 1.5 | .7 | 20 | 20 | 43 | 4 | 4 | -- | --- | 3 | Cb, 4 | 66 | 50 | 40 | 30 | 26 | 18 | 15.5 | 10 | 5.5 | 3 |
| V-36 | .31 | 0.9 | .5 | 20 | 25 | 42 | 4 | 2 | -- | --- | 3 | Cb, 2.2 | --- | --- | 35 | 26.5 | 23 | 18 | 15 | 11 | 8.5 | 5 |
| K-42-B | .05 | .7 | .7 | 43 | 18 | 22 | -- | -- | 2.5 | 0.2 | 13 | | 66 | 40 | 37 | 27 | 17.5 | 11 | -- | --- | --- | --- |
| Refractaloy 26 | .05 | .7 | .7 | 37 | 18 | 20 | 3 | -- | 2.8 | .2 | 18 | | 80 | 63 | 51 | 38 | 27 | 18 | --- | --- | --- | --- |
| Refractaloy 70 | .05 | 2.0 | .2 | 20 | 20 | 30 | 8 | 4 | -- | --- | 15 | | 56 | 42 | 33 | 24 | 19 | 15 | 12 | 10 | --- | --- |
| M-203 | .07 | --- | --- | 24.5 | 19.5 | 36.5 | -- | 12 | 2.15 | .75 | 1.6 | Cb, 1.5 | 84 | 69 | 54.5 | 40 | 29.5 | 18.8 | --- | --- | --- | --- |
| M-204 | .07 | --- | --- | 24.5 | 18.5 | 40.5 | -- | 12 | -- | --- | 1.6 | Cb, 1.2; B, 0.22 | 83 | 67.5 | 53 | 38.7 | 28.5 | 17.5 | --- | --- | --- | --- |
| M-205 | .07 | --- | --- | 24.5 | 18.5 | 37.5 | -- | 12 | -- | 2.75 | 1.6 | Cb, 1.2 | 79 | 64 | 50.5 | 36.8 | 27 | 16.8 | --- | --- | --- | --- |
| 25 Ni | .17 | --- | --- | 24.5 | 19 | 42.5 | -- | 10 | -- | --- | 1.0 | Cb, 1.5 | 52 | 42.5 | 34.5 | 26 | 19 | 11.2 | --- | --- | --- | --- |
| J 1570 | .20 | --- | --- | 30 | 20 | 39 | -- | 6.5 | 4.1 | --- | | | 98 | 84 | --- | 47 | 34 | 24 | 22.5 | 15.5 | --- | --- |
| NICKEL-BASE ALLOYS | | | | | | | | | | | | | | | | | | | | | | |
| Inconel | .04 | 0.35 | .2 | 76 | 15.5 | --- | -- | -- | -- | --- | 7 | | 22 | 14.5 | 16.5 | 6.8 | 5.7 | 3.7 | 4.2 | 2.7 | 2.5 | 1.6 |
| Inconel "W" | .04 | .6 | .25 | 75 | 15 | --- | -- | -- | 2.5 | 0.6 | 7 | | 74 | 54 | 45 | 30 | 19 | 11.5 | 7.5 | 4.8 | 3.2 | --- |
| Inconel "X" | .04 | .7 | .3 | 73 | 15 | --- | -- | -- | 2.5 | .9 | 7 | Cb, 0.9 | 80 | 68 | 50 | 40 | 28 | 18 | 18 | 9 | 3.3 | 2.3 |
| Inconel "X" Type 550 | .04 | .7 | .4 | 73 | 15 | --- | -- | -- | 2.4 | .9 | 7 | Cb, 0.9 | --- | --- | --- | --- | 34 | 21 | 18 | 10.2 | 3.3 | --- |
| Inconel 700 | .1 | [b]2.0 | [b]1.0 | 46 | 15 | 29 | 3 | -- | 2.25 | 3.0 | [b]4 | | --- | 70 | 75 | 64 | 42 | 25 | 28 | 16 | 6 | --- |
| Inconel 739 | .07 | 0.5 | 0.15 | 77 | 15.5 | --- | -- | -- | 1.7 | 2.7 | 0.5 | | --- | --- | --- | --- | 34 | 20 | 19 | 11 | 5.3 | --- |
| Nimonic 80, 80 A | .05 | .7 | .5 | 76 | 20. | --- | -- | -- | 2.3 | 1.0 | .5 | | 67.3 | 56 | 46.4 | 31 | 21.5 | 9.8 | --- | --- | --- | --- |
| Nimonic 90 | .05 | .5 | .2 | 57 | 20.6 | 17 | -- | -- | 2.3 | 1.4 | .5 | | 76.1 | 63 | 50.6 | 38 | 28 | 17.9 | --- | --- | --- | --- |
| Nimonic 95 | .08 | .5 | .4 | 58 | 20 | 16 | -- | -- | 2.5 | 1.6 | .5 | | --- | --- | 55.5 | --- | 33 | --- | 21.1 | --- | --- | --- |
| Hastelloy A | .10 | 2.0 | .7 | 59 | | --- | 20 | -- | -- | --- | 20 | | --- | --- | --- | --- | 11.6 | 8.8 | --- | --- | --- | --- |
| Hastelloy B (cast) | .10 | 0.8 | .7 | 65 | 1 | --- | 28 | -- | -- | --- | 5 | | 51 | 40.5 | 35 | 25.5 | 18.5 | 12.7 | --- | --- | --- | --- |
| Hestelloy C (cast) | .10 | .8 | .7 | 57 | 16 | --- | 17 | 4 | -- | --- | 5 | | 49.5 | 42.5 | 32 | 25 | 19 | 14.5 | 13.2 | 9.2 | --- | --- |
| Hastelloy R-235 | .15 | --- | --- | 62 | 15.5 | [b]2.5 | 5.5 | -- | 2.5 | 2.0 | 10 | | --- | --- | 65 | 50 | 35 | 30 | 25 | 18 | --- | --- |
| Hastelloy X | .15 | --- | --- | 45 | 22 | --- | 9 | -- | -- | --- | 24 | | 44.5 | 30.5 | 26 | 18.5 | 15.5 | 10 | --- | --- | --- | --- |
| Waspalloy | .05 | .7 | .4 | 58 | 19 | 14 | 3 | -- | 2.5 | 1.2 | 2 | | --- | --- | 57.5 | --- | 31.5 | 20 | 19.5 | --- | --- | - |
| Udimet 500 | .12 | [b]1.0 | [b].25 | 59 | 20 | 10 | 4 | -- | 3.0 | 2.75 | [b]2 | | --- | --- | --- | --- | 41 | 30 | --- | --- | --- | --- |
| GMR-235 (cast) | .15 | [b]0.25 | [b].6 | 63 | 15.5 | --- | 5.3 | -- | 2.0 | 3.0 | 10 | B, 0.05 | --- | --- | 62 | 47 | 37 | 29 | 25 | 18 | 11 | --- |
| M-252 | .10 | 1.0 | .7 | 54 | 19 | 10 | 10 | -- | 2.5 | 0.75 | 2 | | --- | --- | 52 | 35 | 29 | 18 | 16 | 10 | --- | --- |
| GE-B-129 (cast) | .06 | 0.4 | .4 | 65 | 5 | --- | 15 | -- | -- | 6.0 | 4 | Cb, 2; B, 0.5 | --- | --- | --- | --- | 47 | 29 | --- | --- | --- | --- |
| M-600 | .08 | --- | --- | 55.5 | 19 | --- | 7 | -- | 2.3 | 1.1 | 13 | | --- | --- | 55 | 39 | 28 | 17 | --- | --- | --- | --- |
| I-1360 (cast) | .10 | --- | --- | 70.5 | 10 | --- | 5 | -- | -- | 6.0 | 4.5 | Cb, 2; B, 0.3 | --- | --- | 70 | 52.5 | 40.5 | 27.3 | 26 | 16.5 | 9.4 | 4.8 |
| | .15 | 1.0 | .6 | 53 | 19 | 10 | 9 | -- | 2.5 | 0.75 | [b]5 | | --- | --- | --- | --- | 26 | --- | --- | --- | --- | --- |
| COBALT-BASE ALLOYS | | | | | | | | | | | | | | | | | | | | | | |
| HS-21, Vitallium (cast) | .25 | 0.6 | .6 | 3 | 27 | 62 | 5 | -- | -- | --- | 1 | | 51 | 44.2 | 32 | 22 | 22 | 14.2 | 16.7 | 13.2 | 9.4 | 7 |
| HS-23, 61 (cast) | .4 | .3 | .6 | 2 | 24 | 66 | -- | 6 | -- | --- | 1 | | 58 | 47 | 36 | 27 | 27.2 | 21.8 | 16 | 12 | 8.6 | 5.4 |
| HS-25, L 605 | .12 | 1.5 | 1.0 | 10 | 20 | 51 | -- | 15 | -- | --- | 1 | | 70 | 58 | 43 | 33 | 23 | 17 | 15.5 | 10.5 | 7 | 3.8 |
| HS-27, 6059 (cast) | .4 | 0.3 | 0.6 | 32 | 25 | 34 | 6 | -- | -- | --- | 1 | | 55 | 46 | 36.5 | 30.5 | 23.4 | 18.4 | 16 | 12 | 9.3 | 6.8 |
| HS-30, 422-19 (cast) | .4 | .6 | .6 | 16 | 24 | 51 | 6 | -- | -- | --- | 1 | | --- | --- | 47 | 36 | 28.6 | 21.7 | 15.8 | 14.8 | 10 | 7.1 |
| HS-31, X-40 (cast) | .4 | .6 | .6 | 10 | 25 | 55 | -- | 8 | -- | --- | 1 | | 56 | 45 | 44 | 33 | 28.4 | 23.4 | 21 | 17 | 9.4 | 7.0 |
| HS-36, L 251 (cast) | .4 | 1.2 | .5 | 10 | 19 | 54 | -- | 14.5 | -- | --- | 1 | B, 0.03 | --- | --- | 48 | 41.5 | 29 | 25.5 | 23 | 18.5 | 10.5 | 7.2 |
| X-50 (cast) | .76 | 0.6 | .5 | 20 | 22.5 | 40 | -- | 12 | -- | --- | 2.5 | | --- | --- | --- | --- | 29.5 | 22 | --- | --- | 10 | 7.7 |
| X-63 (cast) | .4 | --- | --- | 10 | 23 | 58 | 6 | -- | -- | --- | 1 | | 54 | 45.5 | 38 | 30.1 | 24.3 | 17.7 | --- | --- | 8 | --- |
| WF-31 | .15 | 1.42 | .4 | 9.9 | 20.3 | 49 | 2.6 | 10.7 | 1.0 | --- | 4 | | --- | --- | --- | --- | 25 | 18 | --- | --- | --- | --- |
| I-336 | .19 | --- | --- | 15.5 | 19.2 | 50 | -- | 12 | -- | --- | 1.3 | Cb, 0.9 | 80 | 62.5 | 48 | 34.6 | 25.8 | 17 | --- | --- | --- | --- |
| HE-1049 (cast) | .4 | 0.8 | .8 | 10 | 26 | 44 | -- | 15 | -- | --- | [b]3 | B, 0.4 | --- | --- | --- | --- | 45 | 35 | --- | --- | --- | --- |

[a] Not for design purposes. [b] Maximum.

versally adopted for moving turbine blades in all British aircraft gas turbines in production in 1950. The increased hardening elements in Nimonic 95 provide equal strengths at approximately 50° F higher temperatures as compared with Nimonic 90 [487].

*Hastelloy B* has good strength up to at least 1,600° F, but the absence of chromium and the high molybdenum content lower its scaling temperature. Hastelloy C contains chromium for resistance to scaling, and has been used for high-strength applications at 1,800° F or higher, but its high critical alloy content and fabricating characteristics limit its use. Hastelloy X combines good strength and excellent resistance to scaling in spite of the reduction in critical alloy content and is widely used in combustion chamber and component applications of power plants [518]. Hastelloy R–235 has excellent properties through 1,750° F [627]. Fox [556] discussed the susceptibility of some molybdenum-base alloys to oxidation at high temperatures.

*HS–21, 23, 25, 30, and 31* are cobalt-base casting alloys commonly used for cast turbine blades and other applications requiring strength at high temperatures [518]. The effect of different heat treatments and microstructure, of specimens of HS–21 from two sources, on the service life of turbine blades and small turbo superchargers was discussed by Clauss, Garrett, and Weeton [537]. HS–25, also known as L 605, has a high critical alloy content and is used where high stresses exist at temperatures above 1,700° F [518]. The cobalt-base alloys as a group exhibit somewhat better strength at 1,500° F, and pronouncedly better at 1,600° F, than the complex chromium-nickel-iron alloys [581].

High-temperature testing procedure has not yet been standardized and results of individual tests may deviate very considerably from the "characteristic" values, as indicated by the footnote warning that the values of table 41 are not intended for design purposes. Krivobok and Skinner [581] called attention to the need for careful control and standardization of processing (hot-cold working), annealing temperatures (grain size), and stress relieving or aging (dispersion of phases), for better interpretation of stress-rupture data. Dance and Clauss [756] added another variable, thickness of specimen, as they obtained consistently lower and sometimes appreciably lower stress-rupture values for 0.04- to 0.05-in. sheet than are reported for bar specimens in table 41, for several alloys, including Inconel "X", GMR–235, and Refractaloy 26. Weissman [744] found a relation between substructural characteristics and room-temperature tensile properties of nickel alloys, which may extend to elevated temperatures. The possibilities of vacuum melting to reduce the scatter of high-temperature test data are being discussed currently [618, 649, 742, 759]. To supplement the compilations of stress-rupture data, Freeman and Voorhees [661] compiled data on the relaxation properties of super alloys, i. e., the residual elastic stresses remaining after the replacement of an initial elastic stress by the plastic stress of creep during relaxation for time periods up to 10,000 hr. For a preliminary, rapid approximation of the strength of metals and alloys at temperatures up to 3,000° F, Semchyshen and Torgerson [765] developed a hot-hardness tester using synthetic sapphire for the penetrator.

The problem of the susceptibility of most of the super alloys to vanadium-pentoxide corrosion [487, 800] is an active problem in fuel-oil-fired marine and stationary power plant engines but does not apply to the use of these alloys in aviation turbines and jet engines, which operate on refined fuels with $V_2O_5$ contents greatly reduced by the refining processes. Moore, Richmond, and Harrison [151] pointed out that high temperature coatings containing alkalies, lead compounds, or some rare earths react at 1,500° F with super alloys such as Hastelloy B, S–816, and HS–21.

Because it appears that the desires of aircraft engine designers exceed the capacities of metallic alloys that are now available or may be developed in the near future, attention has been devoted to cermets that have high strength at high temperatures but in general are poorly resistant to thermal shock. An example of the increased strength of cermets, reported by Grant [668], is that a nickel—$Al_2O_3$ cermet had more than 500 times as long a stress-rupture life at 1,500° F as did nickel itself. The nickel—$Al_2O_3$ cermet was made by adding 10 percent of fine $Al_2O_3$ to nickel powder and hot working the compact. For further information on the high-temperature properties of cermets, see Long [586].

## 4.7. Miscellaneous Nonferrous Alloys

Some alloys that have been mentioned in the recent technical literature, but do not fall in any of the categories so far discussed in this report, are:

Foerster and Kopituk [553] 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.

Nickel-tungsten alloys, containing 60 to 95 percent of Ni, produced by powder-metallurgy techniques, exhibit several of the desirable qualities of cathode core metal for radio tube construction [651]. Tungsten-nickel and ternary alloys were suggested as heavy alloys for use as high-inertia masses or for X-ray protection [524]. A 57.5 tungsten-40 silver-2.5 nickel alloy prepared by powder metallurgy, was proposed as a contact point alloy [473].

Nickel-chromium-gold-cobalt alloys were suggested as platinum-colored alloys for dentures [250].

Uranium-nickel alloys approximating the formula $U_6Ni$ have better resistance than uranium metal to corrosion in reactors [443].

Nickel - chromium - molybdenum - cobalt alloys were recommended for pen nibs [435].

Manganin, 84 copper-12 manganese-4 nickel, is an electrical resistance alloy described in ASTM Specification B 84–52 [513].

The presence of 1 percent of nickel produces hard particles of $Ni_3Ti$ which are responsible for the superior wear resistance of zinc-alloy forming dies [680].

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 [667].

## 5. Binary and Ternary Alloy Systems

In the review of recent technical literature, references pertaining to the phase diagrams of binary and ternary systems, of which nickel is a component, were noted as follows:

Binary systems, nickel and:

Aluminum [224, 334, 413, 577].
Beryllium [193].
Boron [211].
Chromium [265, 577].
Cobalt [289].
Columbium [194, 713].
Gallium [485].
Gold [276].
Indium [226].
Iron [202, 210, 230, 289, 367].
Lead [594].
Manganese [259, 269, 331].
Molybdenum [529, 610].
Osmium [285].
Palladium [728, 750].
Platinum[195].
Rhenium [489].
Silicon [286].
Sulfur [733].
Tantalum [399].
Tin [585].
Titanium [196, 363, 401, 405, 476, 577, 596, 716].
Uranium [392].
Tungsten [180, 576, 577, 651].
Vanadium [356, 495].
Zinc [351, 413].
Zirconium [393, 488, 801].

Ternary systems, nickel with:

Chromium and aluminum [422].
Chromium and carbon [578].
Chromium and cobalt [298].
Chromium and molybdenum [298].
Chromium and titanium [363, 689, 736].
Cobalt and manganese [468].
Cobalt and zinc [690].
Copper and aluminum [343, 614].
Copper and chromium [704].
Copper and tin [402].
Iron and aluminum [282, 302, 319].
Iron and chromium [241].
Iron and molybdenum [385].
Iron and nitrogen [186, 359].
Iron and phosphorus [309].
Magnesium and carbon [415].
Magnesium and copper [350].
Magnesium and zinc [350].
Molybdenum and cobalt [328].
Molybdenum and iron [328].
Titanium and aluminum [364].

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# THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its headquarters in Washington, D. C., and its major field laboratories in Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside front cover.

## WASHINGTON, D. C.

**Electricity and Electronics.** Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

**Optics and Metrology.** Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

**Heat.** Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Engine Fuels. Free Radicals Research.

**Atomic and Radiation Physics.** Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Physics. Nuclear Physics. Radioactivity. X-rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. AEC Radiation Instruments.

**Chemistry.** Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

**Mechanics.** Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

**Organic and Fibrous Materials.** Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

**Metallurgy.** Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

**Mineral Products.** Engineering Ceramics. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure.

**Building Technology.** Structural Engineering. Fire Protection. Air Conditioning, Heating, and Refrigeration. Floor, Roof, and Wall Coverings. Codes and Specifications. Heat Transfer.

**Applied Mathematics.** Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

**Data Processing Systems.** SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Application Engineering.

- Office of Basic Instrumentation
- Office of Weights and Measures

## BOULDER, COLORADO

**Cryogenic Engineering.** Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

**Radio Propagation Physics.** Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships.

**Radio Propagation Engineering.** Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering.

**Radio Standards.** High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.

DEPARTMENT OF COMMERCE ★ UNITED STATES OF AMERICA ★