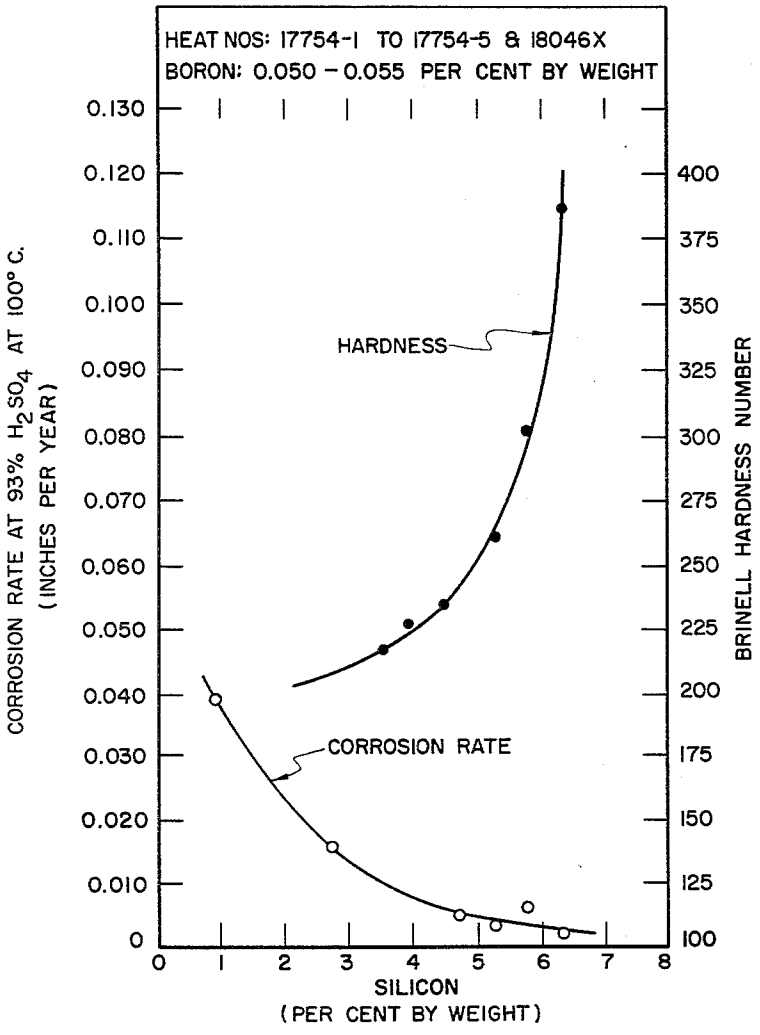
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NICKEL-BASE ALLOY CONTAINING BORON

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NICKEL-BASE ALLOY CONTAINING BORON

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This invention relates to nickel-base alloys containing certain amounts of boron. More particularly, the invention relates to alloys composed primarily of nickel, but including a substantial amount of chromium and smaller amounts of other elements including specific amounts of boron and silicon. These alloys are extremely hard without an excessive brittleness so as to be readily machinable and possess a remarkable resistance to corrosion.

In the chemical processing industry, chemicals and solutions of corrosive materials, such as acids, alkalies, and the like, are handled. In this industry, it is highly desirable that equipment and parts in contact with the corrosive environments be of a material possessing high resistance to corrosion, strength, hardness, machinability, abrasion resistance, and the like. Nickel alloys have been, and are presently, used for equipment such as pumps, impellers, shafts, cellophane hopper lips, cutter blades, valves, pipes, bearings, pipe fittings, vessels, tanks, and the like, in this industry. The present-day nickel alloys have a limited range of practical utility in this industry. Conventional nickel alloys suitable for use at either a high or low acid concentration are not satisfactory at an intermediate acid concentration. Likewise, conventional nickel alloys suitable for use at low temperatures may not be satisfactory at high temperatures. Other limitations and drawbacks of the known alloys also have handicapped their usefulness in industry. Equipment and parts made of known alloys in some applications abrade and wear rapidly with frequent replacement being necessary. For example, cutter blades in the rayon processing industry wear dull and lose their sharp edges rapidly, and bearings operated in some acidic media tend to abrade, gall, and wear rapidly. This wearing and galling at elevated temperatures in intermediate and concentrated acid environments in oxidizing and reducing media frequently proceed at rates in excess of those normally expected from erosion by the corrosive environment and from abrasion of moving, contacting metal surfaces. Frequent replacement of such equipment has been disadvantageous to this industry. Resulting economies would be possible if nickel alloys possessing superior properties were available.

It is an object of this invention to provide new nickel-base alloys of great utility in the chemical processing industry, which alloys are superior over a wide range of applications and overcome the foregoing disadvantages of conventional nickel alloys. It is another object to provide new nickel-base alloys containing certain related amounts of silicon and boron, which alloys possess a superior corrosion resistance, an increased hardness without excessive brittleness, and a superior durability and abrasion resistance when compared to prior art nickel alloys. It is a further object to provide alloys, composed primarily of nickel, but including a substantial amount of chromium and smaller amounts of other elements including silicon and boron, which alloys possess new, desirable, useful, and superior properties not found in conventional nickel alloys.

A further object of this invention is to provide a series of nickel-base alloys containing silicon and boron in such related amounts that the resultant hardness of any alloy within such series may be predetermined; thus a wide range of alloys of varied hardness all possessing good corrosion resistance in both oxidizing and reducing media can be made, consequently increasing the utility of the alloys for varied industrial applications. These, and other objects, will be readily apparent from the description that follows:

Generally, silicon, usually present in conventional nickel alloys, is present only as an incidental concomitant element in an amount of a fraction of one percent. Silicon, when included in amounts larger than about one percent, generally was present for imparting an extreme hardness and a high corrosion resistance. Silicon, when present in substantial amounts, resulted in nickel alloys that, while of increased hardness, also were extremely brittle, susceptible to fracture and cracking, difficult to machine, and capable of little or no hot or cold working.

Boron, if used in conventional nickel alloys, generally was used in extremely small amounts for purposes of a flux or degasifier with little or no boron content remaining in the final alloy composition upon its being analyzed. Generally, boron, if included in substantial amounts, provided a deleterious effect on corrosion resistance, although increased hardness also resulted. Boron contents of substantial amounts, like substantial silicon contents, also resulted in hard, extremely brittle alloys susceptible to little or no machining and of little utility.

Generally, the addition of boron to a nickel alloy increases the alloy's hardness and decreases the alloy's corrosion resistance, and an addition of silicon increases both the alloy's hardness and corrosion resistance. In the alloys of the invention, the boron and silicon contents complement each other to the extent that a deleterious effect of boron on the corrosion resistance is offset by a beneficial effect on the corrosion resistance by the silicon content. The relationship of the amounts of boron and silicon in the alloys of the invention is such as to provide corrosion resistance superior to conventional nickel-base alloys. The boron and silicon contents supplement each other to provide a significantly increased hardness and durability without an accompanying excessive brittleness. The resulting alloys possess a corrosion resistance substantially equivalent to, and generally superior to, alloys of the same base composition lacking these silicon and boron contents and also possess an increased hardness along with the machinability and other desirable properties and characteristics, such as the requisite mechanical strength for use in the chemical process industry. This corrosion resistance and increased hardness, without excessive brittleness, provide superior

alloys having superior wear, abrasion resistance, and antigalling properties. For example, these alloys receive a sharpened edge without chipping and retain this sharpened edge in corrosive environments for longer periods than presently used nickel alloys. The boron content of these silicon-containing alloys offsets a brittling effect of the silicon, thus making a noticeable contribution to the machinability properties. The over-all superiority of the alloys of the invention results in important economies for numerous applications in the chemical processing industry.

In the drawing, there is shown a plot of a corrosion rate and a plot of the hardness at varied silicon contents for a number of preferred alloys of relatively constant boron content.

In accordance with the present invention, there have been found new nickel-base alloys consisting essentially of certain amounts of chromium, molybdenum, copper, silicon, boron, and the balance essentially nickel except for very small amounts of other elements and concomitant impurities, which may be included and generally are present. The nickel-base alloys of the invention consist essentially of 26 to 30 percent chromium, 7.5 to 9.0 percent molybdenum, 4 to 6.5 percent copper, 1.5 to 6.5 percent silicon, 0.025 to 0.55 percent boron, and the balance essentially nickel. Generally, up to 1.6 percent manganese, up to 3.5 percent iron, and up to 0.12 percent carbon, also are included in the alloys. Titanium may be included in these alloys and may be present in residual amounts up to a maximum of 0.25 percent. Small or residual amounts of other elements and/or concomitant impurities (i.e., sulfur, phosphorus, etc.) generally found in nickel alloys up to 0.15 percent also may be tolerated. In the application and claims, unless expressly stated otherwise, all parts and percents are expressed as parts and percents by weight.

The nickel-base alloys of the invention have compositions of constituents upon analysis (percent by weight) falling within the broad and preferred ranges as set forth in the following Table I:

Table I

Composition	Amount, percent by Weight	
	Broad Range	Preferred Range
Chromium	26–30	27–29
Molybdenum	7.5–9	8.5–9
Copper	4–6.5	5–6
Silicon	1.5–6.5	4.5–6.0
Boron	0.025–0.55	0.025–0.20
Manganese	up to 1.6	1–1.5
Iron	up to 3.5	up to 2.0
Carbon	up to 0.12	up to 0.06
Titanium	up to 0.25	up to 0.15
Total of Other Elements	up to 0.25	up to 0.15
Nickel	balance	balance

The broad range of compositions in Table I sets forth the alloys providing an increased hardness without excessive brittleness and providing improved corrosion resistance over broad ranges of temperature and corrosive material concentration for many corrosive materials. The preferred range of compositions in Table I sets forth the preferred alloys providing an increased hardness without excessive brittleness and providing a corrosion resistance superior to known alloys in intermediate and concentrated acid environments in oxidizing and reducing media at elevated temperatures.

The alloys of the invention may be prepared by present-day melt procedures for nickel alloys with only minor modifications thereof. One method of preparation is as follows: An induction furnace is charged with a suitable grade of commercially pure nickel. Grades of nickel, such as nickel scrap, electrolytic nickel, powdered nickel briquettes, nickel powder, or nickel shot may be used. After the nickel is charged and the nickel brought to a molten state, the molten nickel preferably is protected by a slag of any known type suitable for nickel alloys. Depending greatly on the particular grade of nickel being used and its carbon content, a carbon boil may be used to adjust the carbon content of the alloy. Chromium and molybdenum in the required amounts are then added. When the mass is again molten, the requisite amount of copper is added. Desirably, in practice the various constituents employed are in a commercially pure state to avoid introduction of unwanted constituents and to control carefully the final alloy composition. Preferably, to minimize chromium losses, a suitable conventional reducing agent is added to the slag. When the molten mass reaches a desired pouring temperature, generally a temperature between 2750° to 2950° F., a suitable scavenger of the desired type is added. The scavenger may contain manganese, silicon, and titanium, and is capable of eliminating oxides and gases, and reducing the sulfur level, while bringing the manganese and titanium to within the ranges of the alloys of the invention. Addition of boron and silicon constituents to assure the desired composition is necessary. Preferably the boron and silicon additions are made, after the addition of the scavenger, with the molten composition at or near the pouring temperature and just prior to quickly pouring and casting into a suitable form or mold. The boron and silicon constituents both should be introduced through the scavenger slag to avoid losses. Preferably the boron is added in the form of a compound or master alloy, such as ferroboron, nickelboron, chromeboron, or the like. Preferably, the silicon is added in the form of silicon metal, although a silicon master alloy may be used if the desired alloy composition may be realized. Generally, amounts of boron and silicon slightly in excess of the amounts desired in the alloy are used to allow for oxidation losses with the excess amounts being determined by the losses during mixing and time elapsing before pouring.

For their greatest utility, the nickel-base alloys of the invention are cast into various shapes which are useful in cast form as impellers, blades, pump casings, spools, valves, and the like. This cast form is capable of being readily machined (i.e., lathe turning, drilling, and milling) and welded.

Table II, which follows, sets forth compostions by analysis of: a presently used commercial alloy (G); an experimental alloy (17340) containing no boron and less than one percent silicon; an experimental alloy (17873) containing no boron and more than five percent silicon; and specific examples (the other illustrated alloys) of the invention which have been prepared and have been shown to provide the advantages of the invention. Table II also sets forth hardness and corrosion resistance data for a number of these alloys.

The corrosion resistances reported in Table II were determined on cast-machined specimens of the alloys by immersion in aqueous solutions of various acid concentrations at approximately 100° C. The alloy samples were supported on glass supports in the acid solutions. After each 48-hour period of immersion, each sample was removed, rinsed with distilled water, rinsed with acetone, and then oven-dried. Loss of weight of a sample was converted to the calculated reduction in thickness which a large casting would undergo under similar conditions in a one-year period. Data obtained are reported in inches of penetration per year (i.p.y.) on the basis of the average of replicate samples for three 48-hour periods of immersion.

Table II

Alloy No.	Composition (percent by weight) [1]								
	Cr	Mo	Cu	Fe	Mn	C	Si	B	Ni
G	22.5	6.4	6.5	6.5	1.25	.20	.65	-------	56.5
17340	27.22	8.45	5.20	1.32	.72	.05	.56	-------	56.35
17754-2	26.36	8.50	5.56	2.00	1.52	.04	3.88	.055	Bal.
17754-4	26.36	8.50	5.56	2.00	1.52	.04	5.28	.055	Bal.
18046-X	26.30	8.75	5.54	3.30	1.40	.05	5.78	.05	53.70
17576-2	27.52	8.75	4.33	0.88	0.98	.06	2.24	.20	Bal.
17754-7	26.36	8.50	5.56	2.00	1.52	.04	3.84	.23	Bal.
17754-9	26.36	8.50	5.56	2.00	1.52	.04	5.78	.23	Bal.
17754-11	26.36	8.50	5.56	2.00	1.52	.04	2.79	.40	Bal.
17754-13	26.36	8.50	5.56	2.00	1.52	.04	5.08	.40	Bal.
17873	28.04	8.60	5.48	1.86	1.09	.08	5.90	-------	53.40

[1] Less than 0.1% titanium, less than 0.005% sulfur, less than 0.005% phosphorus, with a total of these and other residual elements of less than 0.25%.

Alloy No.	Corrosion Rates at 100° C. (inches per year, i.p.y.)						BHN [2]
	25% HNO_3	78% H_2SO_4	85% H_2SO_4	93% H_2SO_4	Conc. H_2SO_4	Conc. H_2SO_4 +3% Conc. HNO_3	
G	.197	>.2	>.2	.067	.060	-------	162
17340	.020	.008	.026	.020	.018	-------	154
17754-2	-------	-------	-------	-------	.004	.010	228
17754-4	.105	.015	.009	.002	.001	.005	262
18046-X	-------	-------	-------	-------	-------	-------	302
17576-2	-------	-------	-------	-------	-------	-------	201
17754-7	-------	-------	-------	-------	.006	.009	241
17754-9	.122	.018	.009	.006	.0008	.005	321
17754-11	-------	.029	.026	.014	-------	-------	235
17754-13	-------	.028	.021	.006	.004	.008	302
17873	-------	-------	-------	-------	-------	-------	[3] 384

[2] Brinell hardness number.
[3] Excessively brittle as illustrated by cracking and fracturing upon a Brinell hardness test and by chipping upon attempted lathe turning.

From the preparation and testing of experimental alloys, it has been found that, if the chromium content in the alloys of the invention is decreased to less than 26 percent, generally inferior corrosion resistances are obtained whether the molybdenum and copper levels are above, below, or within their amounts in the alloys of the invention. If the chromium content is increased to more than 30 percent, the alloys are more difficult to machine and weld. Any slight benefit in corrosion rates that may be realized from chromium contents in excess of 30 percent does not offset a resulting increased cost and other disadvantages. The chromium may range from 26 to 30 percent and within this range a preferred range of 27 to 29 percent provides a corrosion resistance superior to known nickel alloys at one or more acid concentrations. It also has been found that increasing the molybdenum content in nickel-base alloys of a standard chromium content generally improves the corrosion resistance. In the alloys of the invention, these corrosion-resisting benefits are at a maximum over a molybdenum level of 7.5 to 9.0 percent with lower or higher molybdenum levels generally providing no appreciable improvement in corrosion resistance. Preferred molybdenum levels are from 8.5–9 percent molybdenum with this range of molybdenum also providing the optimum corrosion resistance to concentrated sulfuric acid at elevated temperatures. Similarly, it has been found that the copper content may vary from 4 to 6.5 percent with the improvements of the invention being obtainable. Copper contents above this 4 to 6 percent afford little or no improvement in corrosion resistance over known nickel alloys. Somewhat narrower ranges of 5 to 6 percent copper provide optimum benefits.

The inclusion of boron and silicon in the amounts set forth in Table I is essential, if the superior alloys of the invention are to be obtained. It has been found, if the alloys of the invention were to contain less than 1.5 percent silicon and less than 0.025 percent boron, that inferior alloys result. Such inferior alloys have significantly lower hardness numbers and inferior corrosion resistance. If boron additions are made to these inferior alloys and the boron content increased stepwise, in amounts up to about 0.75 percent with the low silicon level unchanged, although hardness increases, there is noted an increasing deleterious effect on the corrosion resistance. This deleterious effect is readily apparent in corrosive environments of 50 to 98 percent sulfuric acid concentrations at an elevated temperature of 100° C. If the silicon content also is increased along with the increases in boron content, general increases in hardness and a lessening of the deleterious effect on the corrosion resistance from the boron content result. This improvement in corrosion resistance begins to be noticeable at about 1.5 percent silicon and about 0.025 percent boron contents. With about 2 percent silicon and 0.05 percent boron contents, a corrosion resistance is obtained substantially equivalent to the alloy containing no boron and less than 0.5 percent silicon. At the 2 percent silicon and 0.2 percent boron level, the resulting alloy has increased significantly in hardness in excess of about 30 B.H.N. points. This hardness increase appears to be due partly to a solid-solution hardening of the matrix, which strengthens the matrix, and partly to an increase from a second phase. This increased hardness from the second phase may be occasioned by a reduction in the solubility of carbon in the matrix from the increased silicon and is accompanied by a formation of a mottled second phase. A further increase in boron content to about 0.55 percent in these 2 percent-silicon nickel-base alloys results in an additional marked increase in hardness, but slightly reduced resistance to corrosion. This reduction in corrosion can be overcome by increasing silicon contents to 4 to 6.5 percent. Thus, in the nickel-base alloys containing 1.5 to 6.5 percent silicon and 0.025 to 0.55 percent boron significantly increased hardnesses are obtained. At the higher silicon levels of 4.5 to 6.0 percent and boron levels of 0.025 to 0.20 percent, within these ranges, the corrosion resist-

ance is superior to the nickel-base alloys containing no boron and less than 0.5 percent silicon. At still higher boron and silicon contents (i.e. boron greater than about 0.55 percent and silicon greater than about 6.5 percent), somewhat higher hardness numbers are obtained. However, at these high boron and silicon contents, the nickel-base alloys have an excessive brittleness, as evidenced by a heat checking or cracking tendency upon cutting with an abrasive saw and by a cracking or fracturing of specimens subjected to the Brinell hardness test. Alloys with these high boron and silicon contents, because of excessive brittleness, are of extremely limited utility and generally are not satisfactory for most applications in the chemical processing industry.

In addition to the principal elements of nickel, chromium, molybdenum, copper, silicon, and boron, the alloys of the invention may comprise other elements in limited amounts. The inclusion of manganese and titanium within the amounts set forth in Table I has been found to be desirable from a metallurgical standpoint. Some iron, carbon, and other concomitant impurities (i.e. sulfur, phosphorous, etc.) are residual elements and generally unavoidable, but are kept as low as economically practicable within good melting practice and should be within the ranges specified in Table I to obtain the results of the invention. Generally, the lower the level of such elements in the alloys, the better the corrosion resistance, with larger amounts being deleterious and not desirable.

A corrosion rate of 0.020 i.p.y generally is considered the maximum tolerable rate for industrial usage. This maximum tolerable rate may be obtained by the alloys of the invention. The drawing illustrates corrosion rate and hardness data for a number of alloys with varied silicon contents and a relatively constant boron content of 0.05 to 0.055 percent by weight. At this boron level, increasing the silicon provides marked decreases in corrosion rates in 93 percent H_2SO_4 at 100° C. and marked increases in hardness. The hardness increases from about 200 BHN to 400 BHN upon increasing the silicon content from 1.5 to about 6.5 percent with corrosion rates approximating the tolerable rate and lower than the tolerable rate with silicon in excess of about 2 percent by weight. The alloys of the invention also possess tensile strengths of about 65,000 to 75,000 p.s.i. and other desirable properties for application in the chemical process industry. At about 6.5 percent silicon, hardnesses in excess of about 400 BHN and excessively brittle alloys are obtained. Alloys containing no boron and such high silicon contents become excessively brittle at somewhat lower hardnesses, as illustrated by alloy No. 17873 in Table II.

If plots are made of data on alloys containing a somewhat higher relatively constant boron content and increasing silicon contents, graphical relationships of the nature illustrated in the drawing are observed. Thus, there may be obtained alloys of a given hardness between 200 to 400 BHN by selection of other combinations of certain amounts of boron and silicon within the ranges for these elements as set forth in Table I.

From the foregoing description of the invention and specific embodiments thereof, it is believed apparent that the invention may be embodied in other specific forms without departing from the true spirit, scope, and essential characteristics of the invention. Hence, in the present invention it is intended to be limited only to the extent as set forth in the appended claims, and it is intended to embrace within these claims all modifications and variations as fall within the meaning, purview, and range of equivalency of these claims.

What is claimed is:

1. A hard, corrosion-resisting alloy consisting essentially of 26 to 30 percent by weight of chromium, 7.5 to 9.0 percent by weight of molybdenum, 4.0 to 6.5 percent by weight copper, 1.5 to 6.5 percent by weight silicon, 0.025 to 0.55 percent by weight boron, and the balance essentially nickel.

2. An alloy characterized by hardness and exceptional corrosion resistance to acid at elevated temperatures, the alloy in percent by weight consisting essentially of:

Chromium	26– 30
Molybdenum	7.5– 9.0
Copper	4– 6.5
Silicon	1.5– 6.5
Boron	0.025–0.55
Manganese	Up to 1.6
Iron	Up to 3.5
Carbon	Up to 0.12
Titanium	Up to 0.25
Nickel	Balance

3. An alloy characterized by hardness and exceptional corrosion resistance to high concentration of sulfuric acid at elevated temperatures, the alloy, in percent by weight, consisting essentially of:

Chromium	27– 29
Molybdenum	8.5– 9.0
Copper	5– 6
Silicon	4.5– 6
Boron	0.025–0.20
Manganese	1– 1.5
Iron	Up to 2.0
Carbon	Up to 0.06
Titanium	Up to 0.10
Nickel	Balance

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