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NICKEL-BASE ALLOYS

Walter K. Boyd and Merritt E. Langston, Columbus, Ohio, and Thomas E. Johnson, Milwaukee, Wis.; said Walter K. Boyd and Merritt E. Langston assignors to Battelle Memorial Institute, Columbus, Ohio, a corporation of Ohio; said Johnson assignor to Stainless Foundry & Engineering, Inc., Milwaukee, Wis., a corporation of Wisconsin

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This invention relates to nickel-base alloys. More particularly, the invention relates to nickel-base alloys composed primarily of nickel, but including a substantial amount of chromium and smaller amounts of other elements. These alloys exhibit remarkable resistance to corrosion.

Nickel alloys have been, and are presently, used in the chemical processing industry for corrosion-resistant applications. In this industry, in handling chemicals and solutions of corrosive materials, such as acids, alkalis, and the like, particularly at elevated temperatures, it is highly desirable that equipment in contact with the corrosive environments be of a material possessing a high resistance to corrosion. For example, nickel alloys are used for equipment, such as pumps, impellers, shafts, cellophane hopper lips or blades, valves, pipes, bearings, pipe fittings, vessels, tanks, and the like in this industry. However, the nickel alloys presently employed in these applications have a limited range of practical utility. For example, nickel alloys suitable for use at either a low or a high concentration of acid ordinarily are not satisfactory at an intermediate concentration of acid. Likewise, nickel alloys suitable at low temperatures are not too satisfactory at high temperatures.

It is an object of the invention to provide new nickel-base alloys exhibiting a remarkable resistance to corrosion. It is a further object to provide new nickel-base alloys exhibiting superior corrosion-resistant properties over a broad range of temperature and concentration of corrosive media, which alloys are of great value to the chemical processing industry. It is still a further object to provide alloys, composed primarily of nickel, but including a substantial amount of chromium and smaller amounts of other elements, which alloys are characterized by exceptional corrosion resistance to concentrated acid at elevated temperatures. It is another object to provide alloys of the character described herein, which possess superior corrosion behavior and other desirable properties described herein.

The nickel-base alloys of this invention are of great utility in the chemical-processing industry. These nickel-base alloys possess a unique and remarkable corrosion resistance, generally a corrosion resistance superior to that of presently used nickel alloys. This superior corrosion resistance provides for a longer equipment life, more efficient production, lower production costs, reduced replacements of equipment, and less shutdown time. The nickel-base alloys of the invention also exhibit a low corrosion rate at solution concentrations and temperatures where present nickel alloys find limited application because of the high corrosion rates of the prior art alloys. The nickel-base alloys of the invention also possess other desirable physical characteristics essential to their being used in equipment for the chemical-processing industry.

For their greatest utility, the nickel-base alloys of the invention usually are employed in the cast form. This cast form is capable of being readily machined and welded. Additionally, these nickel-base alloys possess a degree of hot and cold workability that permits at least a limited forgeability, rolling, swaging, and the like.

In accordance with the invention, the nickel-base alloys consist essentially of 26 to 30 percent chromium, 7.5 to 9.0 percent molybdenum, 4 to 6.5 percent copper, and the balance essentially nickel. Generally up to 1.6 percent manganese, up to 2.0 percent iron, up to 2.0 percent silicon, and up to 0.06 percent carbon, also are included in the alloys. Titanium may be added to these nickel-base 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 present. 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 constituents upon analysis (percent by weight) falling within the following broad, preferred, and optimum ranges:

Table I

Composition	Amount, percent by weight		
	Broad Range	Preferred Range	Optimum Range
Chromium	26-30	27.5-30	28.5-29.5.
Molybdenum	7.5-9.0	8.5-9.0	8.5-9.0.
Copper	4-6.5	5-6	5.25-5.75.
Manganese	up to 1.6	1.0-1.5	1.0-1.5.
Iron	up to 2.0	up to 1.5	0.75-1.4.
Silicon	up to 2.0	0.5-1.0	0.5-1.0.
Carbon	up to 0.06	0.04 up to 0.06	0.04-0.05.
Titanium	up to 0.25	up to 0.25	up to 0.15.
Total of Other Elements	up to 0.15	up to 0.10	up to 0.10.
Nickel	balance	balance	balance.

The broad range of compositions in Table I sets forth the alloys 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 corrosion resistance superior to known alloys presently used in the chemical processing industry. The optimum range of compositions in Table I sets forth the alloys providing optimum corrosion resistance to concentrated sulfuric acid at elevated temperatures.

The alloys of the invention may be prepared by present day melt procedures for nickel alloys. 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 furnace is charged and the nickel brought to a molten state, the molten nickel is preferably 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. Preferably the constituents, which are added, are for practical purposes in at least a commercially pure state, to avoid introduction of unwanted constituents or too much of essential constituents. 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, silicon, and titanium to

within the constituent amounts of the composition ranges of the alloys of the invention. Then the molten mass is quickly cast or poured into suitable forms or molds.

As specific examples of alloys of the invention, which have been prepared and which have been shown to provide the advantages of the invention, the following compositions by analysis are illustrative:

Table II

Alloy No.	Composition (percent) [1]						
	Cr	Mo	Cu	Mn	Fe	Si	C
A	27.16	8.60	5.42	1.13	1.20	0.70	0.05
B	27.42	7.60	5.36	1.29	1.68	0.58	0.05
C	29.60	8.60	5.76	1.33	1.43	0.50	0.05
D	27.09	8.30	5.76	0.81	0.79	0.46	0.05
E	27.22	8.45	5.20	0.72	1.32	0.56	0.05
F	26.44	8.40	5.40	0.78	1.43	0.49	0.05
G	29.10	8.00	6.04	1.56	1.98	0.90	0.04

[1] Less than 0.1% titanium, less than 0.005% sulfur, less than 0.005% phosphorus, with the balance essentially nickel.

To evaluate corrosion resistance of the nickel-base alloys, cast and machined samples of various alloys were immersed in aqueous solutions of various acid concentrations at several temperatures. These 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 as the average of replicate samples for three 48-hour periods of immersion. Data are reported as corrosion rate in inches of penetration per year (I.P.Y.), a well-recognized manner of presenting and evaluating corrosion resistance of metals. A corrosion rate of 0.020 I.P.Y. generally is considered the maximum tolerable rate in industrial usage.

Table III represents results of some tests of alloys of this invention upon being exposed to corrosive sulfuric acid media:

Table III

Alloy No.	Loss in inches of penetration per year (I.P.Y.) at 90° C.		
	Sulfuric Acid Concentration		
	65%	78%	93–98%
A	0.015	0.011	0.006
B	0.015	0.014	0.008
C	0.011	0.011	0.007
D	0.017	----------	0.007
E	0.017	----------	0.007
F	0.021	----------	0.008
G	0.010	0.020	0.009

The alloys of the invention upon exposure to sulfuric acid concentrations of less than 65 percent and/or temperatures less than 90° C. exhibit lower corrosion rates (i.e. smaller losses in inches of penetration per year) than obtained at the higher acid concentrations and higher temperatures, illustrated in Table III.

The alloys of the invention also exhibit remarkable corrosion resistance to many other corrosive media at both high and low concentrations and temperatures. For example, alloy No. A of Table II in 25% boiling nitric acid had a loss of 0.010 I.P.Y. (inches of penetration per year). A commercial nickel alloy, presently widely used in the chemical processing industry, for comparison purposes had a corrosion rate of 0.197 I.P.Y. in 25% boiling nitric acid. Equipment made from alloy compositions of the invention has exhibited exceptional utility in corrosive media in the chemical processing industry. While the ultimate service life for equipment made of alloy compositions of the invention has not been completely determined, to date the service life of the alloy compositions of the invention has been found to be at least equal to and in most instances superior to commercially available nickel alloy compositions. With the alloy compositions of the invention there has been obtained a service life of three to four or more times that obtained with many conventionally used nickel alloys.

For comparison purposes, Table IV presents typical results of conventional nickel alloys (alloys No. 607 and No. 593) subjected to the same corrosive media test to which the alloys of the invention were exposed. Table IV also presents a number of illustrative, experimental alloys having amounts of constituents falling outside the constituent ranges of the nickel-base alloys of the invention with results of these corrosive media tests illustrating that these alloys do not possess the superior corrosion resistance found in the alloys of the invention.

Table IV

Alloy No.	Composition (percent)								Loss in inches of penetration per year (I.P.Y.) at 90° C.		
	Cr	Mo	Cu	Mn	Fe	Si	C	Ni	Sulfuric Acid Concentration		
									65%	78%	93–98%
607	22.30	5.40	6.22	1.25	0.98	0.92	0.05	62.70	0.063	0.022	0.012
593	22.38	6.00	6.56	0.99	6.39	0.99	0.25	56.35	0.096	0.051	0.020
501	22.45	3.80	6.18	1.22	1.45	0.73	0.05	balance	0.050	0.019	0.012
502	22.40	5.00	6.20	1.26	1.25	0.72	0.03	balance	0.033	0.018	0.012
506	21.78	5.45	6.25	1.22	1.70	1.86	0.05	balance	0.034	0.013	0.008
503	22.55	7.60	6.20	1.20	1.20	0.05	0.05	balance	0.031	0.016	0.009
511	22.20	12.10	4.28	1.28	1.37	0.60	0.05	58.00	0.022	0.015	0.008
509	22.45	12.10	6.36	1.30	1.45	0.56	0.05	55.60	0.031	0.014	0.008
510	22.63	12.10	7.24	1.29	1.48	0.63	0.05	54.46	0.022	0.014	0.010
508	21.50	13.50	5.76	1.15	1.73	0.70	0.05	55.50	0.029	0.012	0.006

One of the outstanding advantages provided by the alloys of the invention is a significant superiority at intermediate ranges of acid concentration at elevated temperatures over prior art alloys. A comparison of the corrosion rates of the prior art alloys (No. 607 and No. 593) of Table IV with the corrosion rates of the alloys of the invention of Table III illustrates this advantage. For example, prior art alloys No. 607 and No. 593 (Table IV) had corrosion rates of 0.063 I.P.Y. and 0.096 I.P.Y., respectively, in a 65% sulfuric acid concentration at 90° C. In comparison therewith, alloy A (Table III) of the invention had a corrosion rate of 0.015 I.P.Y. at the same conditions or a superior corrosion rate for the alloy of the invention of about one-fourth to one-sixth that for conventionally employed prior art alloys.

From test data of the nature as reported in Table IV for experimental alloys it has been found that chromium contents of less than 26% generally provide corrosion rates inferior to those exhibited by the alloys of the invention whether the molybdenum contents are above or below or within the contents specified for the alloys

of the invention. Nickel alloys having chromium contents larger than 30% are more difficult to machine and weld than the alloys of the invention. These higher chromium alloys also are more expensive. Any slight benefit in corrosion rates that may be realized from chromium contents in excess of 30% does not offset the increased cost and other resultant disadvantages. Generally it has been found that the chromium content may range from 26 to 30% with advantages and improvements of the invention being obtainable. Within this broad range of chromium, a preferred range of 27.5 to 30% of chromium generally provides a corrosion resistance superior to known alloys at one or more acid concentrations, and an optimum range of 28.5 to 29.5% chromium provides the optimum corrosion resistance to concentrated sulfuric acid at elevated temperatures. It also has been found in nickel-base alloys of a standard chromium content that increasing the molybdenum content generally results in an improvement in corrosion properties. In the alloys of the invention these corrosion resisting benefits are at a maximum over a molybdenum content broad range of 7.5 to 9.0%. Molybdenum contents above and below this broad range provide no appreciable improvement in corrosion resistance. Within this broad range of 7.5 to 9.0% molybdenum; a preferred and superior corrosion resistance is obtained from 8.5 to 9.0% molybdenum, with this range of molybdenum also providing the optimum corrosion resistance to concentrated sulfuric acid at elevated temperatures. Similarly in nickel-base alloys of a standard chromium content it has been found that the copper level may vary from 4 to 6.5% with the improved corrosion benefits of the invention being obtainable. Copper levels above and below this broad range of 4 to 6.5% generally show little or no improvement in corrosion resistance over known alloys. Somewhat narrower ranges of 5 to 6% and 5.25 to 5.75% of copper have been found to provide preferred and optimum benefits respectively. In addition to the principal elements of nickel, chromium, molybdenum, and copper, the alloys of the invention may comprise other elements in limited amounts. Some carbon, iron, silicon and other concomitant impurities (i.e. sulfur, phosphorus, etc.) are residual elements and generally unavoidable, but are kept as low as economically practical within good melting practice and should be within the ranges set forth in Table I if results of the invention are to be obtained. Generally, the lower the level of such elements in the alloys the better the corrosion resistance, with larger amounts being deleterious and not desirable to impart a beneficial corrosion resistance. The inclusion in the alloys of manganese and titanium within the limited amounts specified in Table I has been found to be desirable from a metallurgical standpoint.

From the foregoing description 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 and purview and range of equivalency of these claims.

What is claimed is:

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

Chromium	27.5–30
Molybdenum	8.5–9.0
Copper	5–6
Manganese	1.0–1.5
Iron	Up to 1.5
Silicon	0.5–1.0
Carbon	0.04 up to 0.06
Titanium	Up to 0.25
Nickel	Balance

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

Chromium	28.5–29.5
Molybdenum	8.5–9.0
Copper	5.25–5.75
Manganese	1.0–1.5
Iron	0.75–1.4
Silicon	0.5–1.0
Carbon	0.04–0.05
Titanium	Up to 0.15
Nickel	Balance

References Cited in the file of this patent

UNITED STATES PATENTS

1,115,239	Parr	Oct. 27, 1914
2,597,495	Jackson et al.	May 20, 1952