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CORROSION RESISTANT ALLOY

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8 Claims

ABSTRACT OF THE DISCLOSURE

A highly corrosion-resistant, workable, durable, strong, hardenable, relatively inexpensive nickel-based, high chromium, high iron, austenitic alloy, containing, in approximately the quantities indicated: Ni 26-48 (preferably to 38%) (balance); Cr 30-34%; Mo 4-5.25%; Co 4-7.5%; Fe 3-25% (but preferably 10-25%); Cu 2.5-8%; C .05-.25%; Si to 4%; B to .10%; and with the preferable range of Si about 2-3.5% so that the alloy is age hardenable. All percentages herein are by weight.

SUMMARY OF THE INVENTION

The invention comprises an austenitic nickel base alloy of particular value in handling hot concentrated sulfuric acid (for example, 65% and up). Appropriate uses are for pump and valve components that are subjected to hot concentrated sulfuric acid.

An object is to provide an alloy that has excellent resistance to corrosion, that is less expensive than commonly used materials, and that can be age-hardened. A further object is a metal alloy of sufficient strength and impact resistance to withstand mechanical shock normally experienced in process plant pump and valve service, that is resistant to thermal shock, to galling and wear such as experienced by shafts, that can be hardened to a minimum of ca. 40 Rc (ca. 370 Br), and that is machinable.

Specifically, it is an object to provide improved corrosion-resistance by the inclusion of a high percentage of chromium, without rendering the alloy brittle and of low ductility, this result being obtained by the presence of cobalt and manganese.

A further object is an alloy with the properties recited that can include 2.5-8% copper to improve corrosion rate, but preferably near the lower limit, to assure good castability.

Further, improvement in corrosion resistance comes from the addition of molybdenum within a range of about 4-9%. Molybdenum, when kept below about 9%, does not drive the alloy out of the austenitic phase, which would decrease resistance owing to the possibility of electrolytic action between phases. It is an object to reduce the requirement of the more expensive molybdenum by increasing the percentage of the less expensive chromium.

Another object is to further improve corrosion resistance and at the same time reduce cost of the material. This is done by including up to about 25% iron in the alloy, in place of nickel. Also iron is less costly than nickel. A further advantage of the presence of substantial quantities of iron is that it is not necessary to use pure chromium, molybdenum and other metals for the alloy, which pure metals add to its cost. Less expensive iron compounds of these metals, such as iron chromium alloy or iron molybdenum alloy, can be used to supply the chromium and the molybdenum.

Another object of the invention is to provide an alloy that is subject to being heat treated and can be made

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into an age-hardened alloy. This is particularly valuable where it is to be used for shafting, bearings and the like, as it can be used with a minimum of seizing and galling. A silicon boron type of hardening, for example, can be used. The silicon may make some contribution to corrosion resistance in hot concentrated oxidizing acids such as the 65% and up sulfuric acid.

The alloy of the present invention is a nickel-based alloy in which the nickel percentage to total composition is relatively high and is sufficient to maintain the alloy in the austenitic phase. Chromium is present to add corrosion-resistance and hardness to the alloy. While it is desirable to have the chromium as high as can be, ordinarily chromium above about 28% renders this general type alloy too brittle and weak.

It has been found that the addition of cobalt and manganese to the nickel-chrome alloy enables a substantially higher percentage of chromium to be included without having the alloy too brittle and lacking in strength. To illustrate, a nickel base alloy containing thirty-two parts chromium, cobalt to about six parts, and manganese to about three parts, constitutes a product that is not too brittle, has reasonable strength, and has great resistance to corrosion of the type here involved.

Additional corrosion resistance can result from certain amounts of copper. Above eight percent of copper renders the materials too hot-short, but 2.5-3% copper improves the corrosion resistance without rendering the material too hot-short. The ratio of copper should be kept toward the lower end of the permissible range.

Molybdenum in the range of about 4-9% also increases the corrosion resistance. Above that, it tends to change the material from the austenitic to the ferritic phase. Accordingly, in the alloy, about 4% of molybdenum is desirable.

Another very valuable feature of the present invention is that iron is substituted for a portion of the nickel. Tests have demonstrated that from about 3% up to about 25%, with correspondingly decreased nickel, corrosion resistance is improved. Particular improvement results from iron percentages of about 10% to 25% iron. Iron substituted for a part of the nickel has the advantage of reducing the cost of the alloy and improving its corrosion resistance in the environment here contemplated.

A further advantage of the use of iron in place of part of the nickel is that the less expensive iron forms of chromium, molybdenum and the like can be used in place of the pure metals. When they are so used, their iron content merely adds to the iron content of the alloy.

In accordance with the present invention, there is provided a nickel-base, corrosion-resistant alloy consisting of the following in approximately the percentage ranges by weight indicated:

Ni	-----	26-48
Cr	-----	30-34
Mo	-----	4-5.25
Co	-----	4-7.5
Fe	-----	To 25
Mn	-----	1-3.5
Cu	-----	2.5-8.0
C	-----	.05-.25
Si	-----	To 4.0
B	-----	To .10

The alloy can be made by a conventional stainless melting process. The following table shows different exam-

ples of alloys made up in accordance with the present invention.

		6002	6003	6004	6005	6427	6439	6563	6599
Ni-----	{F	48.4	38.4	33.4	28.4	36.25	33.6	42.90	42.
	{A	45.30	35.40	32.85	26.45	35.90	33.6	Bal	43.2
Cr-----	{F	32.00	32.00	32.00	32.00	32.00	30.6	32.00	32.00
	{A	32.82	32.82	32.00	34.01	31.88	30.6	31.40	31.00
Mo-----	{F	4.00	4.00	4.00	4.00	4.00	4.5	4.00	4.00
	{A	5.00	5.00	4.70	4.70	4.20	4.5	5.25	4.5
Co-----	{F	6.00	6.00	6.00	6.00	6.00	5.84	6.00	6.00
	{A	6.12	7.32	6.12	5.84	6.76	5.84	7.10	6.36
Cu-----	{F	3.00	3.00	3.00	3.00	3.00	2.91	4.00	4.00
	{A	2.85	3.10	3.05	2.80	2.08	2.91	4.40	3.85
Mn-----	{F	3.00	3.00	3.00	3.00	3.00	3.10	1.75	1.75
	{A	1.28	1.48	1.44	1.28	2.90	3.10	1.47	1.69
C-----	{F	.05	.05	.05	.05	.08	.11	.07	.07
	{A	.17	.21	.21	.21	.03	.11	.09	.08
Fe-----	{F	Nil	10.00	15.00	20.00	15.00	15.75	8.50	8.50
	{A	2.82	10.90	15.82	20.80	15.18	15.75	8.75	8.00
Si-----	{F	3.50	3.50	3.50	3.50	.65	3.40	.75	.75
	{A	3.47	3.60	3.68	3.77	.94	3.40	.94	1.20
B-----	{F	.05	.05	.05	.05		.08		
	{A	.02	.02	.03	.03		.08		

NOTE.—F=Formula for mix; A=By analysis of alloy.

	Number bars cast ¹			
	6	6	6	4
Hardness as cast-----	286	255	262	286
After age hardening-----	372	437	415	426
Corrosion rate, i.p.y., 98% H ₂ SO ₄ at 120° C-----	.031	.010	.009	.011

¹ 50 pounds.

² Hi cold ductility, some hot ductility.

In the table the compositions are given first by Formula F and thereafter by analysis of alloy (A). The alloying metals may be added in the form of iron compositions; for example: molybdenum as ferro-molybdenum, ferro-boron, ferro-silicon, ferrochromium, etc. Iron added from these compositions is cumulative with the iron added specifically to increase iron content.

The alloys were cast into bars and given an initial heat treatment of six hours at 2100° F. followed by rapid air quench. Thereafter some were given an age-hardening treatment.

In comparing melts 6002, 6003, 6004 and 6005, it can be seen that the total nickel and iron content remains about constant. As the nickel content decreases in formula value from 48.4% to 28.4% in successive increments of 10%, 5% and 5%, the iron percentage increases from nil, to 10%, 15% and 20%. All of the other components were held at fixed percentages. (The melt analysis shows substantially the same ratios.)

These samples, 6002-6005, showed Brinell hardness as cast of about 286, 255, 262 and 286, respectively. After solution heat treatment and age hardening, they had Brinell hardness of 372, 437, 415 and 426, respectively. It is, of course, understood that the silicon and boron addition to the original mix have been included for the primary purpose of providing for the age-hardening. The age-hardening, sometimes called "precipitation hardening," is known in the art and comprises usually a two-step process involving a solution of homogenizing heat-treatment followed by rapid quenching, and a precipitation or aging treatment to cause separation of a second phase from solid solution and hardening.

Thus it appears that there is a significant increase in hardness when the proportion of iron is brought up to 10% and above.

The samples were also subjected to corrosion tests in 98% sulfuric acid for forty-eight hours at 120° C. The results in terms of milligrams per square centimeter per day of loss by corrosion were for the four melts, respectively, 1.87, .625, .520 and .628. Assuming a density of .31 lb. per cubic inch, these quantities can be converted to inches per year (i.p.y.) by multiplying by .01675. The

resulting i.p.y. amounts for the four samples, respectively, are .031, .010, .009 and .011.

The foregoing, when plotted in a curve, demonstrates that there is a very marked reduction in corrosion in this test when the iron content is raised and that the corrosion resistance remains relatively constant with the iron content from about 10% to 20%.

Samples 6002, 6003 and 6004 were compared in corrosion resistance rates (i.p.y.) to presently marketed alloys. Alloy 6002 was found to be comparable and slightly better than the first of the commercial alloys, although not as good as the second one. Heat melts 6002, 6003 and 6004 of the present invention all proved superior to both of the presently commercial alloys. These comparative tests were plotted from tests run at 98% H₂SO₄ at different temperatures ranging from 80-120° C.

A special low-silicon sample 6427 was made with about 15% iron, and was tested for corrosion by a somewhat different method. In this case, the bars were not given a heat-treatment, and were subjected to two tests, one a 15% H₂SO₄, the other 25% H₂SO₄, for two days at boiling temperature. In this test, the alloy 6427 showed about 5.58 milligrams per square centimeter per day and at 25% showed about 5.67 milligrams per square centimeter per day. These become about .094 i.p.y. This shows a higher corrosion rate of the untreated alloy at high temperature, low concentration of sulfuric acid. This alloy did prove very ductile, which is desirable for certain uses.

Tests were run on melt 6439 or its substantial equivalent. The first tests were run to determine whether the alloy is hardenable by solution and by aging treatment. The second tests were to determine whether it is age hardenable.

In the first tests, bars of the alloy were gradient heated in a 2200° F.-1100° F. range. A bar was withdrawn after the lapse of each of time intervals of two, four and eight hours at the gradient temperatures, and was air-quenched. Flat surfaces were machined and hardness tests made. Metallographic microstructure studies were made also for the time-temperature conditions. The bars were solution treated, three each at upper and lower bounds dictated by hardness and microstructure, as will appear.

Thereafter, for an aging study, the six solution treated bars were heated in a gradient of about 1700° F. to about 1100 F. One bar each of a higher and lower solution treatment temperature was withdrawn after each time interval of four, eight and sixteen hours at gradient temperature of 1100°-1700° F. and air-cooled. Hardness tests were made and metallographic microstructure examination.

Solution gradient hardness data on as cast bars indicate that the alloy is hardenable in a low temperature range extending from about 1400° to 1750° F. with a peak hardness of 352-369 BHN occurring at about 1625° F. Hardness drops progressively as the temperature rises from about 1625° F. to a maximum temperature used of 2200° F. Metallographic studies show that at 1170° F. the microstructure is essentially that of a cast alloy. At 1550° F. the microstructure is altered by the development of a needle-like precipitate in an orientation with primary directions at 90°. The precipitate extends over the aging range of 1400° to 1750° F. At 1700° F. the needle-like precipitate agglomerates into rod-like shapes. At 1800° F. the agglomeration is climaxed and solution effects are definitely under way by 1950° F. At 1950° F., increase of time at temperature from two to eight hours is accompanied by a progressive solution of rod-like and globular precipitates and by gradual solution of the large irregular precipitate. At 2050° F., increase of time at temperature from two to eight hours is accompanied by a continuous solution by precipitated phases. After eight hours, rod-like precipitates are scattered and both globular and irregular shapes are breaking up. At 2115° F., the rod-like precipitates have vanished, the globular precipitates are

smaller and less frequent, whereas the irregular masses have become somewhat discontinuous. However, incipient grain boundary fusion appears evident as small black patches. At 2150° F., the incipient eutectic formation has progressed and boundaries are rimmed completely with the eutectic phase. Precipitates within the grain are isolated and globular.

Aging test hardness data were obtained as noted above. A lower bound solution temperature range of 1950° F.—1975° F. with four hours at temperature and air-quenched was selected. Three gradient bars were solution treated at an actual mean temperature of 1960° F. for four hours at that temperature, followed by air-quenching. An upper bound solution temperature range of 2050° to 2075° F. with four hours at temperature and air-quenched was also selected and three such bars so treated. All the bars were then heated in a gradient temperature range of 1125° to 1680° F. One bar after each of four, eight and sixteen hours exposure to the 1125°–1680° F. gradient range.

All of the bars from the aging gradient treatments were hardness tested. Higher hardnesses were developed upon aging from the higher solution treatment. The effective aging range extends from about 1425° to 1600° F. for the particular alloy solution treated at 2050° to 2075° F., held four hours, and air-quenched. Maximum hardness obtained was 358 BHN, reached after 1555° F. aging treatment for sixteen hours. In all cases the hardness is definitely better with the temperature of aging above about 1425° F. and in general appears to be optimum at around 1500° to 1600° F.

Metallographic studies after aging showed that at 1250° microstructure is essentially that of a solution treated alloy with incipient particles of a precipitated phase appearing. The irregular massive precipitate is somewhat heavier than in the solution treated series. Hardness is about 270 BHN. At 1300° F. the precipitate is somewhat more advanced with some increased concentration of the rod-like precipitate and the hardness is about 285 BHN. At 1400° F., more precipitation has occurred and includes a dense, but fine, precipitate with definite agglomeration evident. Hardness is about 325 BHN. At 1550° F., there is a uniform and dense precipitation of globular and rod-like phases. Hardness is about 360 BHN. Higher aging temperatures of 1600° F. to 1650° F. show continued agglomeration of globular and rod-like phases as hardness drops progressively to 345 and 330 BHN.

In summary, the gradient solution treatment and aging studies conducted upon the alloy indicate that it may be solution treated at temperatures above 1950° F. and that solution treatment at 2050°–2075° F. is effective in this regard. Above 2100° F. and at about 2115° F. for the particular composition noted, incipient fusion of an eutectic phase is noted.

Hardening by way of an aging mechanism, probably involving phases rich in silicon or boron or both, occurs after reheating a solution treated structure. The useful hardness occurring by such aging treatment occurs at higher temperatures than those normally encountered which is valuable particularly for uses where high temperatures will be met.

This same alloy was submitted to tests of impact properties and corrosion characteristics. The impact tests on the alloy, both in the as cast and solution treated states, showed more impact resistance than the solution treated and aged alloy, thus indicating the use of a solution treated alloy where impact is a factor. Hardness tests were run. In the as cast condition, the BHN ran from 235 to 240; in the solution treated specimens, it ran from 189 to 204; and in the solution treated and aged specimens, from 310 to 358. The difference in these values from the one previously recited is thought to result from some difference in temperature control in the test procedures.

Corrosion tests were run. In the as cast condition, the corrosion rate varied from .0098 i.p.y. at 80° to .0214

i.p.y. at 120° C., in 98% sulfuric acid. The solution treated samples varied from .0108 to .0202 as the temperature rose from 80° C. to 120° C. with 98% sulfuric acid. The solution treated and aged sample varied from .0113 to .0222 i.p.y. as the temperature rose from 80° to 120° C., 98% sulfuric acid. These corrosion rates are calculated by multiplying the loss in weight in milligrams per square centimeter per day by .01675.

These tests show that the solution treated alloy has higher impact strength than that developed after solution treating and aging. The results also indicate that there is a reasonable similarity in corrosion rates between solution treated and aged alloy with corrosion rate at 120° C., about double that at 80° C.

Samples from melt 6427 were given ductility tests. These showed a high degree of cold ductility. A one-fourth inch rod was coiled into a two-loop coil of about an inch in diameter without fracturing. The hammer-forging of a hot specimen indicated adequate hot ductility.

The foregoing shows that higher ratios of chromium can be incorporated in nickel-base alloys where manganese and cobalt are also included, as the resulting product is not excessively brittle and hard, but to the contrary, is adequately ductile and can be machined. It shows that the quantity of nickel can be reduced and a corresponding quantity of iron added, which not only does not reduce, but actually enhances corrosion resistance and hardness. Further, it reduces cost both in saving nickel and in enabling other alloys to be provided in the cheaper form of iron composition.

Various changes and modifications may be within the purview of this invention as will be readily apparent to those skilled in the art. Such changes and modifications are within the scope and teaching of this invention as defined by the claims appended hereto.

What is claimed is:

1. A nickel-base, corrosion-resistant alloy consisting of the following in approximately the percentage ranges by weight indicated:

Ni	26–48
Cr	30–34
Mo	4–5.25
Co	4–7.5
Fe	To 25
Mn	1–3.5
Cu	2.5–8.0
C	.05–.25
Si	To 4.0
B	To .10

2. The alloy of claim 1 wherein the concentration of chromium in said alloy is from about 32 to about 34 weight percent.

3. A nickel-base, corrosion-resistant alloy consisting of the following in approximately the percentage ranges by weight indicated:

Ni	26–38
Cr	30–34
Mo	4–5.25
Co	4–7
Fe	10–25
Mn	1–3.5
Cu	2.5–8.0
C	.05–.25
Si	2–4.0
B	To .10

4. The alloy of claim 3 wherein the concentration of chromium in said alloy is from about 32 to about 34 weight percent.

5. The alloy of claim 3 wherein the concentration range of copper in said alloy is from about 2.5–4 weight percent.

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6. A nickel-base, corrosion-resistant alloy consisting of the following in approximately the percentage ranges by weight indicated:

Ni	34-38
Cr	32-34
Mo	4-5
Co	5-7
Fe	10-20
Mn	1-3
Cu	2.5-4
C	.05-.25
Si	2-4
B	To .10

7. The alloy of claim 1 wherein the concentration of

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iron in said alloy is from about 10 to about 25 weight percent.

8. The alloy of claim 7 age-hardened.

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10 RICHARD O. DEAN, Primary Examiner

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