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CORROSION RESISTANT NICKEL-BASE ALLOY

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ABSTRACT OF THE DISCLOSURE

A hot workable, cold workable alloy capable of retaining bend and kink ductility in fine cold drawn wire at a tensile strength level of at least about 300,000 pounds per square inch contains about 10% to about 16% molybdenum, about 17% to about 21% chromium, not more than about 0.5% carbon, up to about 2% columbium, up to about 2% tungsten, up to about 3% tantalum, up to about 2% vanadium, up to about 0.25% manganese, up to about 0.5% silicon, not more than 1% copper, not more than 8% iron, up to about 10% cobalt, at least one deoxidizing element from the group consisting of aluminum, titanium and boron, a desulfurizing amount of magnesium, and the balance essentially nickel.

The present invention is directed to improved corrosion resistant nickel-base alloys, and more particularly, to nickel-base alloys having improved hot workability, having improved strength and ductility in the form of heavily cold worked fine wire, and having outstanding resistance to corrosion in aqueous chloride-containing media and other corrosive media.

The corrosion resistance of many nickel-base alloys in a variety of media is well known and is utilized commercially. For many years, a nickel-base alloy containing approximately 16% molybdenum, 17% chromium and 4% tungsten has been regarded as the standard alloy when resistance to sea water and other chloride-containing media was required. The alloy has been widely used in chemical apparatus and the like in applications in which resistance to chlorides is required. The alloy has always been attended by a difficult hot working characteristic. Thus, the hot working temperature range of the alloy is restricted and it is usually found that a number of reheats are required during the hot working cycle, with only a limited amount of hot reduction being possible after each heating. This characteristic of the alloy has contributed to increasing the cost thereof. Recently, there has been a demand for wire rope or cable which would be inert to sea water so that the cable could be immersed therein for periods of several years without attention. The application also required that the alloy be capable of developing a tensile strength of at least 300,000 pounds per square inch (p.s.i.) in the form of heavily cold worked fine wire. In order that such wire could be stranded into cable, it was required that the wire resist kinking and bending tests at this high strength level. The kinking test involved looping the wire and pulling the ends thereof to close the loop tightly. The bending test involved wrapping the wire tightly about its own diameter ten or more times. It was required that the wire having the aforementioned strength pass both the kinking and the bending test without breaking in order to be considered satisfactory for stranding. It was found that the aforementioned standard corrosion resisting alloy was incapable of passing the kinking and bending tests at a tensile strength level exceeding about 230,000 p.s.i. Accordingly, the art was faced with the problem of satisfying a peculiarly difficult combination of criteria involving hot workability,

cold workability, high strength, ductility and corrosion resistance in a single alloy.

We have now discovered a nickel-base alloy having controlled composition, having outstanding corrosion resistance, having markedly improved workability both hot and cold enabling its production at lower cost than alloys having comparable corrosion resistance, and having improved ductility in the kinking and bending tests at a high strength level when produced as heavily cold worked fine wire.

It is an object of the present invention to provide an improved corrosion resistant nickel-base alloy.

It is a further object of the invention to provide a nickel-base alloy having markedly improved hot and cold workability.

Another object of the invention is to provide heavily cold worked wire having excellent sea water corrosion resistance together with the capability of being stranded into wire rope at a high strength level.

Other objects and advantages of the invention will become apparent from the following description.

Generally speaking, the present invention is directed to a nickel-base alloy characterized by resistance to corrosion in chloride environments such as sea water and by markedly improved workability both hot and cold, comprising, by weight, about 10% to about 16% molybdenum, about 17% to about 21% chromium, with the contents of molybdenum and chromium not exceeding about 36%, not more than about 0.05% carbon, up to about 2% columbium, up to about 2% tungsten, up to about 3% tantalum, up to about 2% vanadium, up to about 0.5% manganese, up to about 0.5% silicon, not more than about 7% or 8%, and, more advantageously, not more than 5%, iron, up to about 10% cobalt, up to about 1% copper, deoxidizing amounts of at least one element from the group consisting of aluminum, titanium and boron, a desulfurizing amount of magnesium, and the balance essentially nickel. Advantageously, in the interests of hot workability, the alloy contains about 18% to about 20% chromium, about 10% to about 15% molybdenum, not more than about 0.05% carbon, not more than about 5% iron, not more than about 2% tungsten, and not more than 1% copper. It is also advantageous that the alloy contain columbium in an amount of at least 10 times the carbon content. This feature of the invention permits welding of the alloy while avoiding the necessity of solution treatment after welding and also contributes to corrosion resistance.

It is advantageous that the alloy contain not more than about 0.03% carbon and not more than about 2% iron, e.g., up to about 1% iron. A special alloy in accordance with the invention contains about 18% or 19% to about 20% chromium, about 13% to about 15% molybdenum, along with about 0.5% columbium, not more than about 4% iron, about 0.25% each of aluminum and titanium, about 0.02% carbon, about 0.005% boron, a desulfurizing amount of magnesium, and the balance essentially nickel. Another special alloy in accordance with the invention contains about 18% to about 20% chromium, about 10% to about 12% molybdenum, about 1% columbium, about 0.5% to about 2% vanadium, up to 1% tungsten, not more than about 4% iron, up to about 2% tantalum, about 0.25% each of titanium and aluminum, about 0.02% carbon, about 0.005% boron, a desulfurizing amount of magnesium, and the balance essentially nickel.

In producing the alloy, it is particularly advantageous from the hot working viewpoint, to employ deoxidizing additions of elements from the group consisting of aluminum, titanium and boron and to employ a desulfurizing addition of magnesium. Aluminum and titanium may be added in amounts up to 1% each, e.g., up to about 0.5%

each, with retained aluminum and titanium in the alloy being in the range of about 0.1% to about 0.3% each. Aluminum and titanium in age hardening amounts greatly complicate workability of the alloy both hot and cold and markedly increase the cost of the alloy, especially in wire form. Boron is also a beneficial deoxidant which may be added to the melt in amounts up to about 0.01% with deoxidizing amounts on the order of about 0.004% being retained in the melt. Magnesium is an important desulfurizing element which is added to the melt in amounts up to 0.1% with amounts on the order of 0.02% magnesium being retained in the melt. It is to be appreciated that excessive amounts of chromium or molybdenum or both in the alloy will interfere with the desired good hot workability. Accordingly, the total amount of molybdenum and chromium does not exceed about 36% in the alloy and, more preferably, does not exceed about 35%. Thus, an ingot of a properly deoxidized alloy containing 19% chromium, 19% molybdenum, balance essentially nickel, broke on hot rolling from a heating temperature of about 2200° F. Alloys containing 17% molybdenum and 20% chromium were not commercially malleable. Manganese and silicon are detrimental to hot workability. Accordingly, the alloy does not contain more than about 0.5% silicon and, more advantageously, not more than about 0.2% silicon. Manganese may be present in amounts up to about 0.5% and, more advantageously, does not exceed about 0.25%. Conventional deoxidation with manganese and silicon is not effective in the alloy. Tungsten in the alloy does not appear to improve corrosion resistance, although tungsten may be present in the alloy in amounts not exceeding about 2% for strengthening purposes. Tantalum and vanadium appear to improve corrosion resistance and appear to act synergistically with columbium in improving the resistance to corrosion in chloride environments, and offer a particularly advantageous effect in this connection when the alloy contains molybdenum in amouts of about 10% to about 12%. Accordingly, tantalum may be employed in amounts up to about 3% and vanadium in amounts up to about 2%. As previously noted, the balance of the alloy is essentially nickel and it is advantageous in most cases that the nickel content of the alloy be at least about 65%.

In order to give those skilled in the art a better appreciation of the advantages of the invention, the following illustrative examples are given.

EXAMPLE I

A number of alloy compositions in accordance with the invention were prepared by air melting and casting into ingots. In each instance, the melts were finished with additions of aluminum and titanium amounting up to about 0.25% each, with a magnesium addition of about 0.06% and a boron addition of 0.003%. No intentional additions of manganese or silicon were made. The resulting ingots were soaked at about 2200° F. and were hot rolled to billets. In each case, it was observed that the ingots exhibited good hot working properties, with reductions up to about 85% being readily achieved without reheating and with substantially complete freedom from edge cracking being obtained. Portions of metal from the hot rolled material were annealed at about 2150° F. to 2200° F. for one-half hour and were cold rolled without difficulty from a hot rolled thickness of about one-quarter inch to strip about one-sixteenth inch thick. Specimens having a surface area of 25 square centimeters were prepared from the strip material in the cold rolled condition and in the condition resulting from an anneal at about 2150° F. for one-half hour and were immersed for 72 hours in a 10% ferric chloride solution at room temperature. Crevices were intentionally produced on the specimens by wrapping rubber bands about them. This test procedure is described by M. A. Streicher in Journal of the Electrochemical Society, volume 103, pages 375 to 390, No. 7, July 1956, and is considered equivalent to exposure for one year in sea water. The compositions of the melts and the weight loss in milligrams determined in the ferric chloride test on the materials in the cold rolled condition and in the annealed codition are give in the following Table I.

TABLE I

	Percent							Weight loss, milligrams in ferric chloride test	
Alloy No.	Mo	Cr	Cb	W	V	Other	Ni*	Cold Rolled	Annealed
1	10	21					Bal.	5.7	3.3
2	10	21	1		1		Bal.	0.2	0.1
3	10	21	1		2		Bal.	0.1	0.2
4	10	21	1	1	0.5		Bal.	Nil	0.1
5	10	21	1	1	0.5	2 Ta	Bal.	Nil	Nil
6	12	18					Bal.	Nil	0.1
7	12	20					Bal.	Nil	Nil
8	12	21					Bal.		Nil
9	14	18					Bal.	0.7	0.2
10	14	18			1		Bal.	0.6	0.2
11	14	18				2 Ta	Bal.	2.8	0.8
12	14	18		1	1		Bal.	0.4	0.3
13	14	18		1	2		Bal.	0.5	0.2
14	14	18		1	1	2 Ta	Bal.	0.6	1.0
15	14	18	1		1	2 Ta	Bal.	0.5	0.5
16	14	18	1	1	0.5	2 Ta	Bal.	1.3	1.1
17	14	20	0.5				Bal.	Nil	Nil
18	14	20	0.5				Bal.	0.9	0.5
19	15	20					Bal.	Nil	Nil
20	15	20					Bal.	0.4	
21	16	17					Bal.	0.5	0.1
22	16	17	2				Bal.		1.0
23	14	19				4 Co	Bal.	0.9	0.5

*Including about 0.25% aluminum, about 0.25% titanium, about 0.003% boron and about 0.02% magnesium. The alloys contained less than 0.1% each of manganese and silicon and not more than 0.5% iron.

It was found that in instances in which a weight loss of less than one milligram was determined, there was no evidence of pitting or crevice corrosion. In instances wherein a weight loss in the range of 1 to 5 milligrams was reported, slight etching was found in the crevice areas. The ferric chloride environment is extremely severe and standard grades of stainless steel are avidly attacked therein.

EXAMPLE II

U-bend specimens and crevice specimens of Alloys Nos. 7 and 19 given in Table I were exposed in sea water for 14 months without evidence of stress corrosion cracking, pitting or crevice corrosion.

EXAMPLE III

Metal from Alloys No. 7 and 19 was subjected to the stress corrosion cracking test in a boiling aqueous solution containing 42 weight percent of magnesium chloride for 30 days without evidence of stress corrosion cracking.

EXAMPLE IV

Cold drawn wire prepared as a result of 94% reduction in drawing made from Alloys Nos. 20 and 18 gave tensile strengths of 312,000 p.s.i. and 318,000 p.s.i., re-

spectively, while retaining bend and kink ductility. In the same test, an alloy containing about 16% molybdenum, about 17% chromium, about 4% tungsten, about 5% iron, and the balance essentially nickel could be drawn only to a strength of 230,000 p.s.i. before bend and kink ductility was lost. Annealed strip of this material produced and tested in accordance with the procedures used in Example I had a weight loss of 2.1 milligrams in the ferric chloride test. Again, an alloy containing about 0.12% carbon, about 21.6% chromium, about 9.09% molybdenum, about 0.62% tungsten, about 18.29% iron, about 1.1% cobalt, about 0.54% manganese, about 0.70% silicon, and the balance essentially nickel, could be cold worked in wire form to a tensile strength of only about 249,000 p.s.i. before bend and kink ductility was lost.

EXAMPLE V

In order to check the effect of welding upon the corrosion resistance of alloys within the invention as reflected by the ferric chloride corrosion test described in conjunction wtih Example I, a number of alloys within the invention (Alloys Nos. 24, 25 and 26) containing nominally 10% chromium and 14% molybdenum, balance essentially nickel, were prepared in strip form using the melting and working procedures described in Example I with the exception that no boron was employed in deoxidation The alloys contained, respectively, about 0.02%, 0.2% and 0.4% silicon and not more than 0.1% manganese. Some difficulty was encountered in hot rolling Alloy No. 26 which contained 0.4% silicon. Three additional alloys outside the invention containing nominally 24% chromium, 14% molybdenum, 0.8% manganese, balance essentially nickel, with 0.02%, 0.2% and 0.4% silicon (Alloys A, B and C, respectively) were prepared in the same way. No useful material was obtained from Alloy C since the ingot thereof broke in hot rolling. Alloy B cracked on hot rolling and Alloy A was difficult to hot roll. Material from Alloys A and B edge cracked during cold rolling. Strip material was also prepared in the same manner from a standard alloy composition, Alloy D, containing about 16% molybdenum, about 17% chromium, about 4% tungsten, and the balance essentially nickel. Autogeneous gas-shielded tungsten arc weld beads were laid across each of the strips and the strips were then ground flush. The treated strips were then subjected to the ferric chloride test as described in Example I along with as-cold rolled and as-annealed strips of the same materials, with the results set forth in the following Table II.

TABLE II

	Weight loss, milligrams in ferric chloride test		
Alloy No.	As-rolled	Annealed	Welded and Ground
24	1.1	0.2	3.7
25	1.7	0.2	9.8
26	54.4	3.7	6.1
A	2.5	0.5	10.1
B	22	nil	18.1
D			4.9

Alloys provided in accordance with the invention are useful not only in the form of heavily cold worked wire which can be stranded into marine cables but also in conventional forms such as sheet, strip, rod, bar, tubing, etc., for the manufacture of chemical equipment, including tanks, pipes, valves, etc. The excellent hot workability which characterizes alloys in accordance with the invention makes them particularly suitable for conversion into standard mill forms and low cost factors attributable to the hot working operations. The alloys are weldable by conventional arc-welding techniques.

We claim:

1. A nickel-base alloy characterized by resistance to corrosion in chloride environments and by improved hot workability consisting essentially of about 10% to about 16% molybdenum, about 17% to about 21% chromium, with the contents of molybdenum and chromium not exceeding about 36%, not more than 0.05% carbon, 0.5 to about 2% columbium, up to about 2% tungsten, up to about 3% tantalum, up to about 2% vanadium, up to about 0.25 manganese, up to about 0.5% silicon, not more than about 1% copper, not more than about 8% iron, up to about 10% cobalt, about 0.1% to about 0.3% aluminum, about 0.1% to about 0.3% titanium and up to about 0.005% boron, a small desulfurizing amount up to about 0.02% magnesium, and the balance essentially nickel.

2. An alloy in accordance with claim **1** containing about 10% to about 15% molybdenum, and about 18% to about 20% chromium.

3. An alloy in accordance with claim **1** containing not more than about 5% iron.

4. An alloy in accordance with claim **1** containing not more than about 2% iron.

5. An alloy in accordance with claim **1** containing not more than about 0.03% carbon.

6. An alloy in accordance with claim **1** containing about 13% to about 15% molybdenum.

7. An alloy in accordance with claim **5** containing about 19% to about 20% chromium and about 15% molybdenum.

8. An alloy in accordance with claim **5** containing about 10% to about 12% molybdenum, about 1% columbium, about 0.5% to about 2% vanadium, up to about 1% tungsten, not more than 2% iron and up to about 2% tantalum.

9. An alloy in accordance with claim **2** containing about 13% to 15% molybdenum capable in the form of cold worked wire of developing a tensile strength of at least about 300,000 pounds per square inch while retaining kink and bend ductility at the said strength level.

10. An alloy in accordance with claim **1** containing at least about 65% nickel.

References Cited

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,510,294 Dated May 5, 1970

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4, line 27, correct the spelling of "condition".

Table I, 6th column (under "V"), for Alloy #9 put "1" and for Alloy #10 change "1" to --2--.

Col. 5, line 25, change "10%" to --19%--. Same column, line 29, after "oxidation" add a period (.).

Signed and sealed this 29th day of June 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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