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GALL RESISTANT NICKEL-COPPER ALLOY

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The present invention relates to a nickel-copper alloy of special composition and, more particularly, to such a special nickel-copper alloy having a high combination of mechanical properties and superior resistance to steam erosion.

It has been found that the handling of wet steam at high pressures and temperatures, e.g., about 600 p.s.i. to about 1500 psi and about 400° to about 1100° F, has posed severe metallurgical problems due to the corrosive and erosive nature of the steam. For example, valves and particularly seats and gates thereof used in steam service have been subject to a phenomenon called "wire drawing" which involved severe erosion of the valve parts by the passage of steam to the point where the valve became useless. This problem was particularly severe in instances where the valve was only partly open as, for example, in a safety valve. Those skilled in the art know that one type of safety valve is of the poppet type having a circular seat closed by a cylindrical plunger or "feather." In use, the feather is loaded, e.g., by means of a spring, and the load is adjusted such that the valve will open when the pressure in the unit to which the safety valve is attached exceeds the safety limit. When boilers, etc., provided with such a safety valve are operating at maximum capacity and close to the safe maximum working pressure, the valve feather tends to "float" such that small quantities of steam at high pressure are enabled to pass the valve at frequent intervals. Such a condition represents extremely severe service which leads to undesirably rapid erosion of the valve feather and/or seat. It has been established that alloys which can be used in service where steam erosion is encountered must have high gall resistance combined with relatively high strength and hardness as well as resistance to steam erosion. This combination of properties has been difficult of attainment and a demand has existed for an alloy which would resist the erosive action of high pressure steam and which would have other required properties in such service.

Although attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as I am aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that a nickel-copper alloy having a special critical composition is characterized by superior resistance to steam erosion and has a very high combination of mechanical properties and gall resistance.

It is an object of the present invention to provide an improved nickel alloy having superior resistance to erosion by high pressure steam.

Another object of the invention is to provide a nickel alloy having a high combination of mechanical properties and gall resistance.

The invention also contemplates providing a special heat treating method which in combination with the special alloy contemplated in accordance with the invention provides an unusual improvement in the mechanical properties of the alloy.

It is a further object of the invention to provide an improved steam valve having the steam-handling parts thereof manufactured of a special alloy having a critical composition and having greatly improved resistance to steam erosion.

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

Broadly stated, the present invention contemplates a nickel alloy containing about 0.5% to 4.5% silicon, about 3% to 12% chromium, about 0.02% to 0.75% carbon, up to about 1.5% manganese, up to about 10% iron, up to about 4% molybdenum, the balance essentially nickel and copper in a nickel-copper ratio of about 1.5:1 to about 2.5:1. The nickel content of the alloy is usually between about 40% and about 65% and the copper content of the alloy is usually between about 20% and about 35%.

It is important that silicon, chromium, copper and nickel all be present in the alloy in the foregoing amounts to provide the improved combination of mechanical properties and other properties which characterize the alloy contemplated in accordance with the invention. Thus, silicon must be present in an amount of at least about 0.5% as otherwise the alloy becomes difficult to cast and the ductility of the material in the "as-cast" condition is quite low and the silicon must not exceed about 4.5% as otherwise the alloy is susceptible to thermal cracking. In applications requiring particularly improved resistance to galling, the silicon should be at least about 2%. When the chromium content is less than about 3%, the resistance to corrosion by steam diminishes; and when the chromium content exceeds about 12%, no further gain in properties is secured and melting becomes more difficult. Copper and nickel likewise are essential ingredients in the composition and must be present within the foregoing ranges in order to obtain general corrosion resistance. Carbon is an important constituent of the alloy and should be present in the range set forth hereinbefore. Thus, when the carbon content is less than about 0.02%, the alloy is difficult to produce; and when the carbon exceeds about 0.75%, an excessive amount of free carbide is formed that decreases the ductility. Iron and manganese are usually present in an amount of at least about 0.2%, respectively. The manganese contributes castability to the alloy and hence is a desirable constituent. Iron present in substantial amounts, e.g., about 2%, tends to diminish the grain size and to increase the resistance of the alloy to steam penetration. Molybdenum improves the resistance to pitting of the alloy in the presence of steam.

The alloy may contain small amounts of impurities and minor constituents such as sulfur, phosphorus, boron and titanium without affecting the basic and novel characteristics thereof. Such minor constituents and impurities should not be present in amounts exceeding a total of about 0.20%.

The alloy contemplated in accordance with the present invention is age hardenable in the temperature range of about 1050° to about 1150° F. when heated for time periods of at least about 1 hour and up to about 10 hours. If desired, castings produced in the alloy contemplated in accordance with the invention may be softened for machining by a treatment comprising heating to a temperature in the range of about 1550° to about 1650° F. followed by quenching in oil or water. In some instances, it may be desirable to cool the alloy from the temperature range of about 1550° to about 1650° F. to a temperature not substantially exceeding about 1200° F. prior to quenching in order to minimize or obviate cracking on quenching. In the age-hardened condition, alloys contemplated in accordance with the invention will exhibit

mechanical properties within the ranges shown in the following table:

Yield strength, 0.5% offset, p.s.i.	50,000–100,000
Tensile strength, p.s.i.	75,000–130,000
Brinell Hardness	150–340

Preferably, alloys produced in accordance with the invention will contain about 1% to 3.0% silicon, about 4% to 7% chromium, about 0.05% to 0.25% carbon, about 0.5% to 1% manganese, about 1% to 3% iron, up to about 1% molybdenum, with the balance essentially nickel and copper in the ratio of about 2 parts nickel to each part of copper, and with nickel being present in the range of about 56% to about 62% and copper being present in the range of about 27% to about 32%. The preferred compositions exhibit an improved combination of mechanical properties together with superior resistance to steam erosion. In addition, compositions containing this relatively low silicon content exhibit a surprising response to aging heat treatment characterized by an increase in both tensile strength and ductility. Thus, a series of alloys containing about 6% chromium, about 2.2% iron, about 0.06% carbon, about 0.6% manganese and about 0.1% magnesium, with the balance nickel and copper in a 2:1 ratio, were made up which contained silicon in varying amounts from 1% to 3%. Castings from these alloys were subjected to a tensile test, both in the as-cast condition and in the heat treated condition after treatment of the castings by heating to 1600° F. for one hour, cooling to 1200° F., oil quenching, and aging at 1100° F. for four hours. The as-cast and heat treated castings exhibited the following mechanical properties at each silicon level:

Silicon	Condition	Ultimate Strength, p.s.i.	Elongation, Percent
1	As Cast	52,000	3
	Heat Treated	98,000	16
1.5	As Cast	61,000	4
	Heat Treated	105,000	12
2	As Cast	73,000	5
	Heat Treated	113,000	8
2.5	As Cast	103,000	7
	Heat Treated	119,000	7
3	As Cast	122,000	7
	Heat Treated	125,000	4

In order to give those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Example I

A series of melts having varying chromium contents were made in a magnesia-lined induction furnace. After each of the melts had been prepared and brought to casting temperature, it was deoxidized with about 0.1% magnesium and cast into castings, including valve feather seats for incorporation into steam safety valves. The castings were annealed at 1600° F., cooled to about 1200° F., oil quenched, and aged at 1100° F. for 4 hours. The three valve feather seat castings had the following compositions:

Alloy No.	Percent Si	Percent Cr	Percent Fe	Percent C	Percent Mn	Percent Ni	Percent Cu
1	3.66	2.87	2.2	0.06	0.6	61.4	29.3
5	2.51	5.96	2.2	0.06	0.6	59.4	28.3
8	3.64	8.60	2.2	0.06	0.6	57.4	27.3

In the heat treated condition, the valve feather castings exhibited a Brinell hardness, respectively, of 321, 262 and 319. The valve feather castings were made up into steam safety valves. The valves embodying the first two castings were placed in service in a steam plant at 1200 pounds' gauge pressure. These valves gave satisfactory service for a period of about 8 months whereas the prior valve feather material employed in the same application (a 14% chromium-iron) had given a maximum life of only three months. Stellite valve feathers (containing about 55% cobalt, about 30% chromium and about 5% tungsten) also were unsatisfactory in this plant. The third valve was placed in service in a steam plant at 800 pounds' gauge pressure. The steam in this plant contained some hydrochloric acid vapor. This valve gave satisfactory service for a period of over about 4 months whereas 14% chromium-iron valves had given a maximum service of about three weeks.

Example II

A series of test castings was prepared from alloys within the invention to examine the resistance of these alloys to steam erosion. These castings were produced in the form of a disc about 1¾ inches in diameter and about ⅝ of an inch thick. In performing the test, the procedure described by Venton in the magazine Heating, Piping and Air Conditioning, January 7, 1937, volume 9, pages 34 to 38, was employed. In the test, a steam pressure of 600 pounds per square inch gauge was employed and the test was conducted for 400 hours. In the test, high pressure steam was admitted through a nozzle having a 1/16 inch diameter orifice held at right angles to the face of the test disc and with the nozzle being rigidly held at a distance of 0.005 inch from the test disc. On completion of the test, the test discs were examined to determine the depth of penetration made by the steam and were weighed to determine the weight loss resulting from the steam erosion. Test castings were prepared having the following compositions:

Alloy No.	Percent Cr	Percent Si	Percent Mo	Percent Cu	Percent Ni	Percent C
1	2.87	3.66		29.3	61.4	
2	5.86	0.96		29.1	61.1	
3	6.32	1.84		28.4	59.7	0.10
4	5.77	1.46	3.01	27.5	57.7	0.10
5	5.96	2.51		28.3	59.4	
6	6.29	2.44	1	27.0	56.7	0.23
7	8.6	3.64		27.3	57.4	
8	8.55	3.63	0.85	27	56.7	
9	12.05	2.02		26.7	55.7	
10	11.69	3.61		26.4	55.3	
11	11.85	4.25	0.92	26	54.7	
12	11.48	2.63	3.01	25.8	53.6	
13	11.66	3.81	2.80	25.4	53.3	
14	11.52	3.53	2.99	25.17	53.32	0.06
15	11.03	3.61	2.71	24.3	50.7	
16	11.18	3.46	2.61	24.2	50.5	0.26

Upon completion of the Venton test, test discs were examined for steam penetration and weight loss with the following results:

Alloy No.	Penetration, inches	Weight Loss, grams	BHN
1	.0030	.017	321
2	.0060	.0065	
3	.0020	.0100	228
4	.0015	.0250	228
5	.0020	.0140	262
6	.0025	.0071	
7	.0030	.0170	319
8	.0030	.0120	302
9	.0040	.0200	207
10	.0040	.0150	293
11	.0055	.0160	321
12	.0030	.0061	255
13	.0050	.0150	282
14	.0014	.0150	286
15	.0045	.0100	277
16	.0015	.0170	286

All of the test castings in the foregoing example were subjected to a heat treatment comprising heating to 1600° F. for one hour, cooling to 1200° F., oil quenching, and aging at 1100° F. for 4 hours.

The alloy produced in accordance with the invention develops particularly high gall resistance in the as-cast condition. It has been found that alloys within the invention containing a maximum of 3% silicon, e.g., about

0.5% to about 3% silicon, and containing carbon in the range of about 0.2% to about 0.6% are forgeable. The common composition and properties of a forgeable alloy in accordance with the invention are given in the following example:

Example III

The alloy produced in accordance with the invention has been found to be malleable and develops a high combination of mechanical properties after hot working. Thus, in one instance, an alloy within the invention containing about 5.7% chromium, about 2.8% silicon and about 0.51% carbon was melted in an induction furnace, deoxidized with magnesium and cast into ingots. The ingots were forged at about 1900° F., the forgings were subjected to various heat treatments, including an anneal at 1650° F. followed by an oil quench and an aging treatment at 1100° F. for two hours. It was found that the annealed and oil quenched forging had a hardness of 217 Brinell with a tensile strength of 117,750 pounds per square inch and an elongation of 32.5%. The age-hardened forging developed a hardness of 324 Brinell and had a tensile strength of 168,200 pounds per square inch with an elongation of 13.5%.

Alloys contemplated in accordance with the present invention may be produced in the usual melting furnaces employed for melting nickel and nickel-base alloys. Thus, the inluction furnace, the direct or indirect arc furnace, etc., may be employed. It has been found desirable to thoroughly deoxidize the alloys just prior to casting.

The alloy contemplated in accordance with the invention can be employed either in the form of castings or as forgings for steam valves and parts thereof such as plungers, seats, feathers, gates, etc., and in other applications involving handling of high pressure steam, such as gaskets, nozzles and castings. Because of the superior combination of properties possessed by the alloy, parts made thereof may be used as propellers, pumps, impellers, pistons and elbows.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A nickel-base alloy characterized by a high resistance to galling and by an improved combination of mechanical properties and containing about 0.5% to 4.5% silicon, about 3% to about 12% chromium, about 0.02% to about 0.75% carbon, up to about 1.5% manganese, up to about 10% iron, up to about 4% molybdenum and the balance essentially nickel and copper wherein the nickel to copper ratio is about 1.5:1 to about 2.5:1.

2. A nickel-base alloy characterized by a high resistance to galling and by an improved combination of mechanical properties and containing about 0.5% to 4.5% silicon, about 3% to about 12% chromium, about 0.02% to about 0.75% carbon, about 0.2% to 1.5% manganese, about 0.2% to about 10% iron, up to about 4% molybdenum and the balance essentially nickel and copper wherein the nickel to copper ratio is about 1.5:1 to about 2.5:1.

3. The alloy according to claim 2 wherein the silicon content is at least about 2%.

4. A nickel-base alloy characterized by a high resistance to galling and by an improved combination of mechanical properties and containing about 1% to about 3% silicon, about 4% to about 7% chromium, about 0.05% to about 0.25% carbon, about 0.5% to about 1% manganese, about 1% to about 3% iron, up to about 1% molybdenum, about 27% to about 32% copper and about 56% to about 62% nickel.

5. A forgeable nickel-base alloy characterized by a high resistance to galling and by an improved combination of mechanical properties which comprises about 0.2% to about 0.6% carbon, about 0.5% to about 3% silicon, about 3% to about 12% chromium, about 0.2% to about 1.5% manganese, about 0.2% to about 10% iron, up to about 4% molybdenum, about 20% to about 35% copper and the balance essentially nickel, with the ratio of nickel to copper in the alloy being between about 1.5:1 and 2.5:1.

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