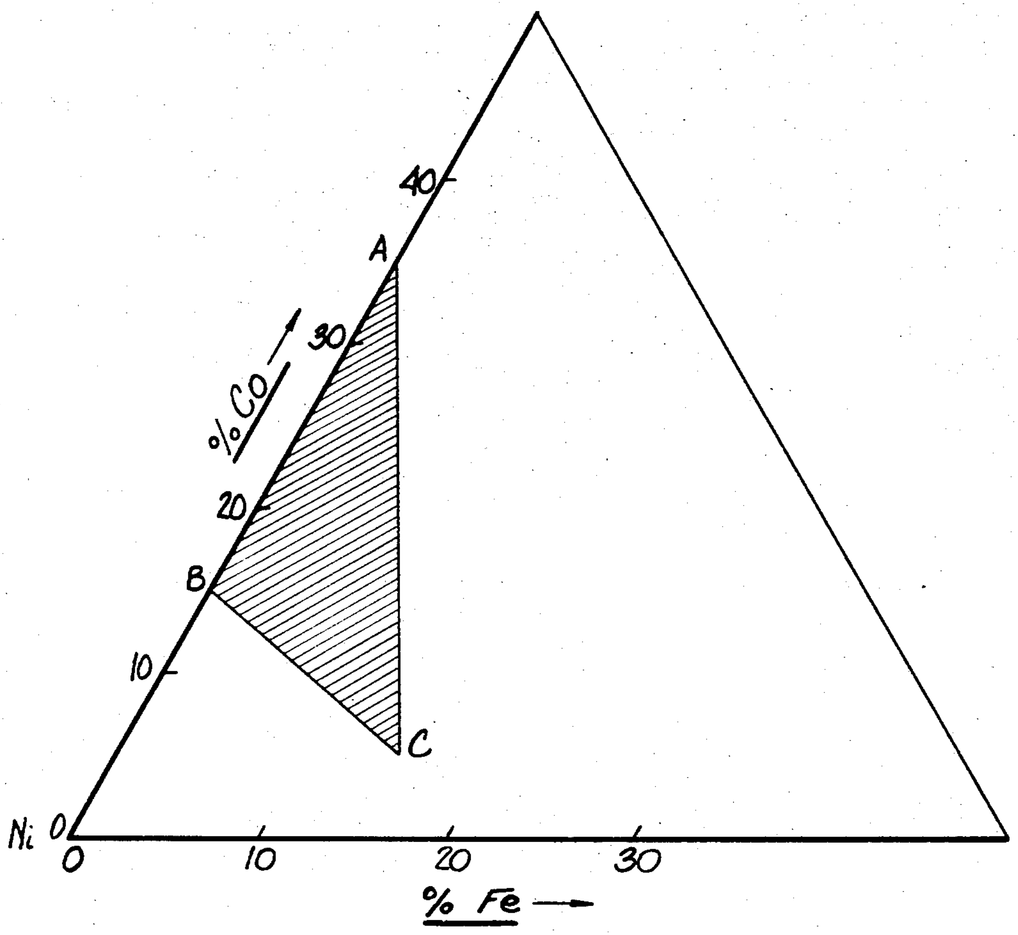
Nov. 19, 1968 E. G. RICHARDS ET AL 3,411,899

NICKEL-CHROMIUM ALLOYS WITH DELAYED AGING CHARACTERISTICS

Filed July 15, 1966



INVENTORS
EDWARD GORDON RICHARDS
BY DAVID MARSHALL WARD

M. L. Pinel
ATTORNEY

United States Patent Office 3,411,899
Patented Nov. 19, 1968

3,411,899

NICKEL-CHROMIUM ALLOYS WITH DELAYED AGING CHARACTERISTICS

Edward Gordon Richards, West Hagley, and David Marshall Ward, Birmingham, England, assignors to The International Nickel Company, Inc., New York, N.Y., a corporation of Delaware

Filed July 15, 1966, Ser. No. 565,476
Claims priority, application Great Britain, July 22, 1965, 31,326/65
7 Claims. (Cl. 75—171)

The present invention relates to nickel-containing alloys and more particularly to precipitation hardening nickel-chromium-cobalt alloys of such composition that the alloys manifest the unique capability to self-retard the onset of precipitation hardening whereby ease in carrying out various processing operations is facilitated.

As is generally known to those skilled in the art, nickel-rich alloys of the nickel-chromium-cobalt type, with or without iron, are characterized by high strength at elevated temperatures, i.e., the alloys sustain high stress for prolonged periods before fracture. A useful improvement in high temperature strength is afforded by the addition of certain elements, e.g., molybdenum and tungsten, which enter into solid solution in the basic composition. But the greatest strengthening effect is generally obtained by the incorporation of constituents which produce stable precipitates in the nickel-rich matrix. Titanium, aluminum and columbium, which combine with nickel either individually or in combination to produce very stable precipitates, are notable in this regard and are particularly effective in improving high temperature strength, a property which generally increases with the amount of stable precipitate and, thus, with the contents of the effective addition elements.

As is further known, to promote the precipitation of the stable phases in the most beneficial form and distribution pattern to achieve maximum strength and ductility at high temperatures, the alloys must be suitably heat treated. This generally consists in solution heating at a very high temperature to dissolve the stable phases followed by aging at a lower temperature below the temperature of solubility of the stable phases to cause reprecipitation thereof. The aging temperature is dependent on the alloy composition but generally falls within the range of about 500° C. to 1100° C. At temperatures within the aging range, precipitation commences almost immediately and is manifested by an immediate and progressive increase in alloy hardness. The rate of increase in hardness and the maximum hardness obtained both depend on the aging temperature but usually increase with the content in the alloy of the elements which produce the stable precipitates.

Although the formation of stable precipitates improves the high temperature strength of the alloys, the immediate onset of precipitation and the rapid hardening frequently create difficulties in fabricating components from the alloys. For example, marked hardening may occur in wrought material during cooling from hot working temperatures and during the cooling of castings, thus increasing the difficulty of machining the alloys in these forms, particularly in heavy sections when the cooling rate is low and the amount of precipitation hardening is correspondingly increased. Difficulties also arise when it is necessary to reheat components to relieve internal stresses brought about, for example, by cold working or welding during fabrication. The presence of such stresses increases the rate of hardening of the alloys such that rapid precipitation hardening occurs at temperatures below those necessary to relieve the internal stresses and the ductility of the material may be so far reduced as to cause cracking before the internal stresses are relieved.

This effect is most marked with the strongest alloys containing the largest amounts of elements which produce stable precipitates. At best, therefore, considerable care is necessary during the fabrication of precipitation hardening alloys, especially when they are used in heavy sections and when stress relieving treatments are necessary. Suffice to say, it would be most desirable to obviate or greatly minimize the foregoing drawbacks and the present invention is specifically addressed to this objective.

It has now been discovered that with nickel-chromium-cobalt alloys of certain composition, with or without iron, and containing titanium and metal from the group consisting of columbium and tantalum as hardening constituents in special proportions, the onset of precipitation hardening can be delayed and substantially so. This is accomplished, however, such that the stable phases are still precipitated on more prolonged heating in the aging temperature range to give the desired high strength at elevated temperatures.

It is an object of the invention to provide precipitation hardening nickel-chromium-cobalt alloys in which as a result of the composition thereof the onset of precipitation and hardening is considerably self-delayed.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which there is graphically depicted a relationship among nickel, cobalt and iron as more fully described hereinafter.

Generally speaking, alloys in accordance herewith contain (in percent by weight) from about 16% to 24% chromium, about 5% to 35% cobalt, up to 15% iron, provided that 2×(percent Fe)+(percent Co) does not exceed 35% and that 2×(percent Fe)+3×(percent Co) is not less than 45%, from 1% to about 2.8% titanium, up to 4% columbium, up to 8% tantalum, provided that (percent Cb)+0.5×(percent Ta) is from 2% to 4%, up to 4% molybdenum, up to 8% tungsten, provided that 2×(percent Mo)+(percent W) does not exceed 8.5%, carbon in an amount not exceeding about 0.15%, up to about 0.004% boron, up to 0.05% zirconium and the balance, apart from impurities, being essentially nickel. The contents of the major impurities, silicon and manganese, should not exceed 0.5% each. Silicon impairs weldability and advantageously is kept below 0.3%, and preferably the amounts of both elements present are as low as possible.

Alloys within the foregoing ranges exhibit a remarkable ability to resist the immediate onset of precipitation hardening. In this connection, the time to the onset of aging, that is to say, the time before any significant increase in hardness occurs, may be referred to as the incubation period and varies with the aging temperature. Alloys having incubation periods of several hours, to wit, at least five hours and advantageously 25 hours have been developed in reaching the objective, and such alloys are deemed quite beneficial since alloys in which the precipitation hardening response has been thus delayed have marked advantages over existing high temperature alloys for heavy section components and welded or cold worked fabrications. In particular, castings or hot worked parts can be cooled naturally without significantly increasing their hardness, and internally stressed components can be readily reheated to annealing temperatures and stress relieved before precipitation hardening commences. It will be appreciated, however, that the incubation period should not be too long, not greater than about 50 hours, since otherwise the period of heating required to age the alloys satisfactorily would be impracticably long.

In carrying the invention into practice, the alloys can be precipitation hardened by heating at temperatures in the range of 550° C. to 850° C., most advantageously

650° C. to 750° C. Generally speaking, the incubation period should be at least five hours at 750° C. On the other hand, it should not exceed 50 hours. Initial solution heating of the alloys can be carried out at temperatures above about 950° C., e.g., in the range of about 1000° C. to 1100° C.

It is important that the content of each of the constituents of the alloys is within the ranges set out above. Numerous tests have been carried out to show the effects on different properties of varying the composition, and the results of these are set forth in the tables hereinafter. In each case the testpieces were machined from forged bar of the alloy that had been solution heated for one hour at 1000° C. Stress-rupture tests were carried out at 650° C. under a stress of 36 long tons per square inch (t.s.i.) after aging for 16 hours at 700° C., the stress-rupture lives and elongation values being determined at fracture. Impact values were determined at room temperature using a notched impact testpiece that had been heated at 650° C. for 10,000 hours. Incubation periods were determined by hardness measurements on specimens heated at 750° C. for different periods of time and water quenched to room temperature. The shortest time to give an increase in hardness above that of the solution treated and quenched material was taken as a measurement of the incubation period.

If the chromium content is more than 24%, the incubation period is very short. It increases rapidly with decreasing chromium content, becoming very long with chromium content below 16%. The results of tests on a series of alloys of different chromium contents are set out in Table I. Each alloy nominally contained 20% cobalt, 2% tungsten, 1.5% titanium, 3% columbium and 0.05% carbon, the balance, except for the chromium, being nickel. Alloy No. 3 is in accordance with the invention, whereas Alloys Nos. 1, 2 and 4 are not.

TABLE I

Alloy No.	Cr, percent	Stress-rupture		Impact strength, ft./lbs.	Incubation period, hrs.
		Life, hrs.	El, percent		
1	9.3	1	42	90	>100
2	14.9	21	30	53	>100
3	19.9	140	13	31	25
4	24.4	210	4.8	22	0.5

In the absence of iron, the incubation period is too long and the stress-rupture life too low if the cobalt content is less than 15%, while if the cobalt content exceeds 35%, the incubation period is too short and the stress-rupture ductility is too low. Replacement of part of the cobalt by iron reduces the incubation period and for a practically useful incubation period and satisfactory stress-rupture properties the cobalt and iron contents must comply with the relationships

$$2\times(\text{percent Fe})+\text{percent Co}\leqq 35$$

and

$$2\times(\text{percent Fe})+3\times(\text{percent Co})\geqq 45$$

The alloys defined by these relationships lie within the area ABCA in the accompanying drawing, in which contents of nickel, cobalt and iron are plotted in triangular coordinates. Advantageously the alloys contain from 17% to 25% of cobalt and are substantially free from iron except as an impurity, e.g., in amounts up to 1%. The properties of a series of alloys containing different amounts of cobalt, iron (and also tungsten), but otherwise all of the nominal composition 20% chromium, 1.5% titanium, 3% columbium, 0.05% carbon, and the balance nickel, are set out in Table II.

TABLE II

	W, percent	Fe, percent	Co, percent	Stress-rupture		Impact strength, ft./lbs.	Incubation period, hrs.
				Life, hrs.	El., percent		
Alloy No.:							
5	2.50	-------------	10.2	44	38	29	500-100
3	2.0	-------------	20.0	140	13	31	25
6	2.25	-------------	30.6	414	9.3	32	7.5
7	2.26	-------------	39.5	875	1.1	24	<0.5
8	2.19	9.7	9.8	85	8.5	30	7.5
9	2.25	9.4	20.2	455	4.8	26	<0.5
10	2.15	9.1	30.2	765	6.7	24	<0.5
11	2.67	20.9	0.1	71	4.9	13	<0.5
12	2.89	13	10.7	463	5.3	13	<0.5

Of the iron-free alloys in Table II, Alloy No. 5 contains too litttle cobalt and Alloy No. 7 too much, but the cobalt contents of Alloys Nos. 3 and 6 come within the range of 15% to 35% and these alloys have satisfactory incubation periods. Of the iron-containing alloys, only Alloy No. 8 has iron and cobalt contents that satisfy the two relationships given hereinabove. Alloys Nos. 9 to 12 are thus not examples of the invention.

Tungsten in the alloys is wholly or partly replaceable by half its weight of molybdenum provided

$$\text{Percent W}+2\times(\text{percent Mo})\text{ is from 0 to 8.5}$$

At values of percent W+2×(percent Mo) above 8.5, the incubation period becomes too short. For the best stress-rupture properties the alloys preferably contain one or both of tungsten and molybdenum so that the value of this expression is at least 1. These effects are shown by the test results in Table III which relates to alloys that contain the indicated amounts of tungsten, molybdenum and cobalt and also (nominally) 20% chromium, 1.5% titanium, 3% columbium and 0.05% carbon, the balance being nickel.

TABLE III

	W, percent	Mo. percent	Co, percent	Stress-rupture		Impact strength, ft./lbs.	Incubation period, hrs.
				Life, hrs.	El., percent		
Alloy No.:							
13	-------------	-------------	20.3	70	34	24	25
3	2.0	-------------	20.0	140	13	31	25
14	5.8	-------------	19.7	470	18	27	7.5
15	2.2	1.2	20.4	260	12	35	25
16	2.1	3.1	20.0	340	5	33	5
17	-------------	1.3	20.1	175	23	38	25
18	-------------	4.7	19.9	450	10	44	1

Alloys Nos. 13, 3, 14, 15, 16, and 17 are in accordance with the invention but Alloy No. 18 with its high molybdenum content is not.

The incubation period decreases with increasing titanium content. If there is less than 1% titanium, it is too long, while if there is more than 2.8%, it is too short and the impact strength is also very poor. These effects are illustrated by the test results in Table IV, which were obtained with alloys containing varying amounts of titanium as shown and also (nominally) 20% chromium, 20% cobalt, 3% columbium, 2% tungsten, and 0.05% carbon, the balance being nickel.

TABLE IV

Alloy No.	Ti, percent	Stress-rupture		Impact strength, ft./lbs.	Incubation period, hrs.
		Life, hrs.	El., percent		
19	0.05	<10	----------	97	>100
3	1.45	140	13	31	25
20	2.73	140	26	24	7.5
21	2.85	380	11	6.5	<0.5

Alloys Nos. 3 and 20 are in accordance with the invention, whereas Alloys Nos. 19 and 21 are outside the scope thereof.

Commercially available sources of columbium are commonly contaminated with tantalum, and small amounts of tantalum will therefore normally be present even in nominally tantalum-free alloys. If desired, columbium, as indicated herein, may be partly or wholly replaced by twice its weight of tantalum, i.e., on an atom-for-atom basis.

The alloys almost inevitably contain small amounts of carbon and preferably at least 0.03% carbon is present to inhibit grain growth. Amounts of carbon in excess of 0.15% drastically reduce the stress-rupture life of the alloys, and preferably the carbon content does not exceed 0.1%. The effect of varying carbon content is shown by the test results in Table V, which relate to alloys that nominally contain, besides carbon, 20% chromium, 20% cobalt, 1.5% titanium, 3% columbium and 2% tungsten, the balance being nickel.

TABLE V

	C, percent	Stress-rupture		Impact strength, ft./lbs.
		Life, hrs.	El., percent	
Alloy No.:				
3	0.055	140	13	31
22	0.137	129	13	38
23	0.258	1	38	42

Alloys Nos. 3 and 22 are in accordance herewith but Alloy No. 23 with its high carbon content is not.

The ductility in stress-rupture tests at 650° C. and the impact strength of the alloys can be somewhat increased by small additions of boron and zirconium, up to 0.004% and 0.05%, respectively. However, the presence of these elements impairs the weldability of the alloys and preferably the boron content does not exceed 0.003% and the zirconium content 0.02%. No additions of boron or zirconium were made to any of the alloys tested in the tables above.

The presence of aluminum in the alloys is highly detrimental since even small amounts of aluminum drastically reduce the incubation time. Thus, the incubation time of Alloy No. 3 was reduced from 25 hours to less than one half hour by the addition of only 0.5% aluminum.

It will be appreciated that the incubation period for a given alloy will vary somewhat with the temperature within the range of possible aging temperatures. For example, the incubation period of Alloy No. 3 varied with temperature as shown in Table VI.

TABLE IV

Temperature, ° C.	Incubation period, hrs.
600	50
650	16
750	25
850	50

Nevertheless, the alloys of the invention have incubation periods very much greater than those of nickel-chromium-base high temperature alloys hitherto used which are typically only a few seconds. A particularly advantageous alloy range is as follows: about 17% to 23% chromium, about 17% to 25% cobalt, up to 1% iron, about 1.25% to 2.75% titanium, up to 4% columbium, up to 6% tantalum with the sum of the percent columbium plus one half the percent tantalum not exceeding 6%, up to 6% tungsten, up to 3% molybdenum, the sum of the percent tungsten plus two times the percent molybdenum being from 1 to 8.5, up to 0.1% carbon, up to 0.003% boron, up to 0.02% zirconium and the balance essentially nickel. Alloy containings 18% to 22% chromium, 18% to 24% cobalt, 1.4% to 2.75% titanium, 2% to 4% columbium, 2% to 6% tungsten, up to 3% molybdenum with the sum of the tungsten plus twice the molybdenum not exceeding 8%, 0.03% to 0.1% carbon and the balance essentially nickel are quite satisfactory.

The alloys of the invention are resistant to corrosive attack by a molten mixture consisting of 25% sodium chloride and 75% sodium sulfate at 900° C. which simulates the cororsive effects of coal ash. They are therefore suitable for other parts, such as superheater tubes, which are exposed to these conditions.

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.

We claim:

1. A preciptation-hardenable nickel-chrominum-cobalt alloy adapted for elevated temperature use and characterized by the unique capability of delaying the onset of precipitation hardening whereby ease in processing the alloys is facilitated, said alloy consisting essentially of from about 16% to 24% chromium, about 5% to 35% cobalt, up to 15% iron with the cobalt and iron being correlated such that the following relationships are satisfied:

2×(percent Fe)+(percent Co) does not exceed 35% and

2×(percent Fe)+3×(percent Co) is not less than 45%

from 1% to about 2.8% titanium, up to 4% columbian, up to 8% tantalum, the sum of the columbian plus one-half the tantalum being from 2% to 4%, up to 4% molybdenum, up to 8% tungsten, the sum of twice the molybdenum plus the tungsten not exceeding about 8.5%, carbon in an amount not exceeding about 0.15%, up to about 0.004% boron, up to 0.05% zirconium up to 0.5% silicon, up to 0.5% manganese and the balance essentially nickel.

2. The alloy set forth in claim **1** in which the cobalt content is from 17% to 25%.

3. The alloy set forth in claim **2** in which the iron content does not exceed 1%.

4. The alloy set forth in claim **1** in which the sum of twice the molybdenum plus the tungsten is at least 1%.

5. The alloy set forth in claim **1** in which the carbon content does not exceed 0.1%.

6. The alloy set forth in claim **1** and containing about 17% to 23% chromium, about 17% to 25% cobalt, up to 1% iron, about 1.25% to 2.75 titanium, up to 4% columbian, up to 6% tantalum with the columbian plus one-half the tantalum not exceeding about 6%, up to 6% tungsten, up to 3% molybdenum, the sum of the tungsten plus twice the molybdenum being from 1% to 8.5%, up to 0.1% carbon, up to 0.003% boron, up to 0.02% zirconium, up to 0.3% silicon and up to 0.3% manganese.

7. The alloy set forth in claim **1** and containing about 18% to 22% chromium, about 18% to 24% cobalt, about 1.4% to 2.75% titanium, about 2% to 4% columbian, about 2% to 6% tungsten, up to 3% molybdenum with the sum of the tungsten plus twice the molybdenum not exceeding about 8%, about 0.03% to 0.1% carbon and the balance essentially nickel.

References Cited

UNITED STATES PATENTS

2,981,621	4/1961	Thielemann	75—171
3,046,108	7/1962	Eiselstein	75—171
3,151,981	10/1964	Smith et al.	75—171
3,222,165	12/1965	Bird et al.	75—171

RICHARD O. DEAN, *Primary Examiner.*