

1

3,592,632

HIGH TEMPERATURE NICKEL-CHROMIUM-IRON ALLOYS PARTICULARLY SUITABLE FOR STEAM POWER APPLICATIONS

Robert C. Gibson, Ringwood, N.J., and Glenn W. Tuffnell, Warwick, N.Y., assignors to The International Nickel Company, Inc., New York, N.Y.

No Drawing. Filed July 14, 1966, Ser. No. 565,083

Int. Cl. C22c 37/10, 39/02
U.S. Cl. 75-124

11 Claims

ABSTRACT OF THE DISCLOSURE

A nickel-iron-chromium alloy containing molybdenum and/or tungsten and beneficially aluminum, titanium and carbon, the constituents being so correlated as to provide highly useful properties which enable the alloy to be used for such applications as superheater tubes.

The present invention relates to high temperature alloys and, more particularly, to nickel-iron-chromium alloys of novel composition which, because of their high tensile and stress-rupture strengths, good tensile ductility and corrosion resistance, and an unique ability to provide improved high temperature stability upon exposure to elevated temperatures over extended periods, are particularly suited for use as superheater tubes in steam power stations, heat exchangers or for other high temperature applications.

It is generally known that high temperature alloys of the nickel-iron-chromium type are useful for a variety of commercial applications since they manifest a desired combination of metallurgical properties, including good stress-rupture characteristics, tensile ductility, corrosion resistance, etc. It is also well known that certain high temperature applications require alloys which exhibit one or more specific characteristics to an outstanding degree. For example, alloys used in steam power applications, e.g., super-heater tubes, heat exchangers and the like, must be particularly characterized by stability and freedom from embrittlement over long periods at high temperature. Steam temperatures in the neighborhood of 1000° F. to 1100° F., e.g., 1050° F., are in current use and stainless steels such as AISI 304 and 316, among other materials, have proven satisfactory.

The trend, however, seemingly is toward steam temperatures of the order of 1200° F. and higher. At such temperatures, it is considered that the aforementioned stainless steels would be unsuitable since the lower strengths resulting from the temperature increase would necessitate substantial increase in wall thickness. In this connection, alloys suitable for this purpose should manifest the ability to absorb at least 50 foot-pounds of impact energy at room temperature after exposure at 1200° F. for about 1000 hours and at least 20 foot-pounds of impact energy at room temperature after exposure at 1200° F. for about 10,000 hours. In addition to long term stability, it would be a decided advantage if the material to be used for such applications were also capable of withstanding 40,000 pounds per square inch (p.s.i.) stress for at least 1000 hours at 1200° F. Accordingly, there is a need to provide new alloys of relatively low cost capable of meeting the above objectives, but, in so doing, other mechanical characteristics must not be sacrificed.

It has now been discovered that nickel-iron-chromium alloys containing special and correlated amounts of columbium, tungsten, molybdenum, titanium, aluminum and carbon provide outstanding long term stability while concurrently exhibiting good tensile ductility, stress-rupture life, corrosion resistance, etc. Upon exposure to tempera-

2

tures of the order of 1200° F. for at least 1000 hours alloys within the invention not only possess Charpy V-notch impact strengths of at least 50 foot-pounds but many alloys exhibit impact strengths of up to 100 foot-pounds or more.

An object of this invention is to provide novel nickel-iron-chromium alloys possessing a highly satisfactory combination of high strength, toughness, ductility and corrosion resistance after exposure to high temperatures for extended periods.

Another object is to provide nickel-chromium-iron alloys possessing long term stability as evidenced by Charpy V-notch impact strengths greater than 50 foot-pounds and preferably in excess of 75 foot-pounds after exposure to elevated temperatures for prolonged periods.

Another object is to provide nickel-iron-chromium alloys especially adapted to high temperature use as, for example, superheater tubing in steam power stations, heat exchangers and the like.

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

Generally speaking and in accordance with the present invention, alloys contemplated herein characterized by long term stability upon exposure to high temperature for extended periods contain (in percent by weight) about 34% to 40% nickel, about 15% to about 19% chromium, about 0.25% to 2% columbium, at least one metal selected from the group consisting of tungsten and molybdenum in an amount of up to 3.5% each, the sum of the columbium, tungsten and molybdenum being at least 1.25%, advantageously at least 2%, and not greater than about 6%, up to about 0.75% titanium, up to about 0.75% aluminum and, advantageously, from 0.35% to about 0.75% titanium or aluminum or both, up to about 0.08% carbon, up to about 0.015% boron, up to about 0.75%, e.g., up to 0.3%, silicon, up to about 4%, e.g., up to 1%, manganese, and the balance essentially iron. Where long term stability, 50 foot-pounds or more after 1000 hours exposure at 1200° F., in combination with a 1000 hours rupture strength of about 40,000 p.s.i. or higher at 1200° F. is required, the aforescribed alloys should contain from 0.5% to 1.5% columbium and at least 2.5% of metal from the group consisting of tungsten and molybdenum. It is to advantage that both tungsten and molybdenum are present in amounts of at least 0.5% and up to 3% each.

In carrying the invention into practice, it is advantageous that the nickel content not fall below about 34% in order to minimize or preclude formation of sigma phase, a phase which detracts from strength, toughness and stress-rupture properties. Put another way, the other constituents, i.e., chromium, columbium, tungsten, molybdenum, etc., which are useful as strengtheners must be balanced with sufficient nickel, beneficially at least 36% nickel, to avoid poor stability after long time exposure at intermediate temperatures, say, 1200° F. to 1400° F. On the other hand, nickel contents above 40% raise the cost of the alloy without appreciably increasing the strength, toughness or ductility.

Chromium presents a paradox. Increasing chromium enhances corrosion and oxidation resistance, most desirable features. But the higher the chromium the greater is the adverse effect on long term stability. Therefore, the chromium content must be carefully balanced and should not be less than about 15% and beneficially not less than 16%; otherwise, corrosion resistance, particularly in sulfidizing, oxidizing or high temperature steam environments, is unsatisfactory. Chromium appreciably above about 19% is detrimental because of the likelihood of sigma phase formation.

A total of at least 1.25%, preferably 2%, of columbium, tungsten and molybdenum is necessary for sufficient

yield and stress-rupture strengths. In consistently achieving highly satisfactory results, tungsten and molybdenum should be copresent and in this regard the more advantageous alloys contain from 1% to 3% of each. The upper limit of tungsten or molybdenum or any combination thereof should not exceed 3.5%, while columbium should not be present in amounts in excess of 2% and preferably not above 1.5%. These maximum limits should not be exceeded since toughness and corrosion resistance are decreased especially where molybdenum and columbium rather than tungsten are in excess. An amount of columbium plus tungsten plus molybdenum not exceeding 5.5% or 5.25% markedly contributes to retention of a high level of toughness. (Since commercially available columbium contains up to about 10% tantalum, the values reported for columbium include up to about 10% thereof as tantalum.)

It is preferred that the alloys contain at least 0.35% of each of the constituents titanium and aluminum in order to achieve both good room and elevated temperature strength characteristics. The presence of titanium or aluminum in amounts less than 0.35% decreases strength and stress-rupture life. If titanium or aluminum are present in amounts much above 0.75%, toughness is decreased although stress-rupture properties are enhanced. A total of from 0.35% to 1% of titanium and aluminum provides for an excellent combination of strength and toughness.

Carbon should not exceed about 0.08% because of the tendency of the strengthening elements, chromium, tungsten, molybdenum and columbium, to form carbides which adversely affect stress-rupture strength and corrosion resistance. More specifically, with a total columbium plus tungsten plus molybdenum content of about 1.25% to 2.5%, the carbon content advantageously should not exceed about 0.03%. When this sum is from about 2.5% to about 3.5%, carbon can be increased up to 0.06% and when this correlation exceeds 3.5%, from 0.06% to 0.08% can be tolerated; however, it is much preferred to keep the carbon at a level not greater than 0.03%.

A most advantageous alloy range in achieving optimum results in accordance with the invention is as follows: about 36% to about 39% nickel, about 16% to about 18% chromium, about 1% to 2% tungsten, about 1% to 2% molybdenum, about 0.7% to about 1% columbium, about 0.35% to 0.5% titanium, about 0.35% to 0.5% aluminum, carbon in an amount up to about 0.06%, up to 0.01% boron, e.g., from 0.005% to 0.01% boron, up to 0.3% silicon, up to 0.4% manganese, and the balance essentially iron. These alloys show marked ability to retain corrosion resistance, high strength, toughness and ductility after high temperature exposure for prolonged periods of time. Because of such characteristics, the alloys are eminently suitable for superheater tubes. Moreover, these alloys are easily fabricated by conventional methods.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative data are given: Alloys 1 through 4 (within the invention) and Alloys A and B (outside the invention) were vacuum melted (except No. 4 which was air melted), and were then cast into 30 pound ingots, the ingots being then soaked one hour at 2150° F. and thereafter forged to 1½ inch square billets. The billets were then cut into quarters (to minimize the effect of segregation) to produce ¾ inch square bars which were annealed at 2000° F. for one hour and then cold rolled to ½ inch square pieces.

TABLE I.—PERCENTAGES

Alloy	Ni	Cr	W	Mo	Cb	Ti	Al	B	C	Fe
1-----	38.6	14.8	1.38	1.48	1.10	0.41	0.59	0.0048	0.009	Bal.
2-----	37.8	17.9	1.35	1.48	1.17	0.42	0.53	0.0048	0.012	Bal.
3-----	37.4	17.7	1.54	1.50	1.05	0.53	0.48	0.0050	0.026	Bal.
4-----	38.8	18.6	1.54	1.51	1.05	0.50	0.50	0.0050	0.029	Bal.
A-----	37.8	14.3	2.50	2.75	1.05	0.36	0.48	0.0062	0.01	Bal.
B-----	37.7	17.6	2.75	2.92	1.15	0.38	0.47	0.0050	0.008	Bal.

In addition to impurities, the alloys contained less than 0.4% of each of silicon and manganese.

The alloys given in Table I were subjected to a series of tests to ascertain both room and elevated temperature characteristics. In Table II tensile data are set forth for each of the alloys, the alloys having been subjected to each of the following treatments:

Treatment I: solution annealing at 1800° F. for about one hour followed by air cooling,

Treatment II: solution heating at 1800° F. for about one hour, air cooling, and then exposing the alloys for 1000 hours at 1200° F. followed by air cooling.

In Table II, the yield (Y.S., 0.2% offset) and ultimate tensile strengths (U.T.S.) are given in pounds per square inch (p.s.i.), the tensile elongation (Elong.) and reduction in area (R.A.) are given in percent (%) and the test temperature was about 70° F.

TABLE II

Alloy	Treat- ment	Y.S., 0.2% offset, p.s.i.	U.T.S., p.s.i.	Elong., percent	R.A., percent	C.V.N., ft.-lbs.
1-----	I	47,200	114,700	46.0	70.5	-----
	II	114,300	166,700	22.0	44.5	95.7
2-----	I	43,000	102,400	46.0	73.5	-----
	II	86,400	155,100	24.0	52.0	97.3
3-----	I	36,100	95,800	45.0	71.5	-----
	II	76,500	138,300	29.0	55.5	108.8
4-----	I	37,000	99,400	46.0	71.0	-----
	II	84,700	154,800	29.0	54.0	97.8
A-----	I	63,300	116,800	40.0	67.0	-----
	II	103,100	160,100	22.0	45.0	41.7
B-----	I	76,000	127,800	35.0	61.5	-----
	II	115,100	168,800	21.0	44.0	29.5

The data in Table II illustrate the superior stability characteristics of the alloys within the invention in comparison with those outside the scope thereof. This is evident from the fact that the impact resistance characteristics of Alloys A and B were below the 50 foot-pounds criterion as determined by the Charpy V-notch test. This is in sharp contrast with the values of about 100 foot-pounds obtained for Alloys Nos. 1 to 4 of the invention.

Elevated temperature properties for the alloys within the invention (treatment I) are reported in Table III.

TABLE III

Alloy	Test temp., ° F.	Stress, p.s.i.	Life, hrs.	Elong., percent	R.A., percent	Min. creep rate ¹
45	1,100	65,000	193.6	37.0	44.2	0.120
	1,200	55,000	101.4	28.0	32.4	0.156
	1,300	35,000	121.9	40.0	47.3	-----
2-----	1,100	65,000	344.1	45.0	46.5	0.046
	1,200	55,000	129.1	31.0	44.3	0.108
	1,300	35,000	173.9	46.0	51.0	-----
3-----	1,200	55,000	81.5	31.0	37.1	-----
	1,200	40,000	2,210.2	37.0	53.2	-----
50	1,200	55,000	141.2	35.0	33.0	-----
4-----	1,200	40,000	3,692.1	37.0	53.8	-----

¹ Percent/hour.

It is to be noted that the objective of a 1000 hours rupture strength of at least 40,000 p.s.i. is readily achieved with alloys contemplated in accordance herewith as is evident from Alloys Nos. 3 and 4.

In view of the fact that the alloys of the present invention are characterized by substantial freedom from severe embrittlement upon long time exposure to elevated temperatures, they are particularly suitable as superheater tubes, heat exchangers, components, etc.

The use of the expression "balance" or "balance essentially" in referring to the iron content of the alloys, as will be understood by those skilled in the art, does not exclude the presence of other elements commonly present as incidental elements, e.g., deoxidizing and cleansing elements, and impurities normally associated therewith in small amounts which do not adversely affect the basic characteristics of the alloys.

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 un-

derstand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims:

We claim:

1. A nickel-chromium-iron alloy having an impact strength of at least 50 ft.-lbs. after exposure to a temperature of 1200° F. for about 1000 hours and a 1000 hour stress rupture strength of at least 40,000 p.s.i. at 1200° F. together with good ductility and corrosion and oxidation resistance, said alloy consisting essentially of about 34% to about 40% nickel, about 15% to 19% chromium, about 0.5% to 2% columbium, about 0.5% to 3% of tungsten, about 0.5% to 3% molybdenum, the sum of the columbium, tungsten and molybdenum being at least about 2.5% and not greater than about 6%, titanium and aluminum each being present in an amount up to 0.75% with the total percentage of titanium and aluminum being at least 0.35%, up to about 0.06% carbon, up to about 0.015% boron, up to about 0.75% silicon, up to about 4% manganese, and the balance essentially iron.

2. The alloy set forth in claim 1 in which the carbon content does not exceed 0.03% and manganese does not exceed about 1%.

3. The alloy set forth in claim 1 and containing about 36% to 39% nickel, about 16% to 18% chromium, about 1% to 2% tungsten, about 1% to 2% molybdenum, about 0.7% to 1% columbium, about 0.35% to 0.5% titanium, about 0.35% to 0.5% aluminum, carbon in an amount up to 0.03%, up to 0.01% boron and up to 1% manganese.

4. The alloy set forth in claim 3 and containing up to 0.4% manganese and up to 0.3% silicon.

5. A novel nickel-chromium-iron alloy adapted for elevated temperature use having an impact strength of at least 50 ft.-lbs. after exposure to a temperature of 1200° F. for about 1000 hours and a 1000 hour stress rupture strength of at least 40,000 p.s.i. at 1200° F. and consisting essentially of about 34% to about 40% nickel, about 15% to 19% chromium, about 0.25% to 2% columbium, at least one metal from the group consisting of tungsten and molybdenum in an amount up to 3.5% tungsten and up to 3.5% molybdenum, the sum of the columbium,

tungsten and molybdenum being at least 2.5% but not greater than about 6%, titanium and aluminum each being present in an amount up to 0.75% with the total percentage of titanium and aluminum being at least 0.35%, up to about 0.06% carbon, up to about 0.015% boron, up to 0.75% silicon, up to about 4% manganese, and the balance essentially iron.

6. The alloy set forth in claim 5 in which boron is present up to 0.01%, the columbium content is at least about 0.5% but not greater than 1.5% and which contains up to 1% manganese.

7. The alloy set forth in claim 5 and containing about 0.35% to 0.75% of titanium and about 0.3% to 0.75% aluminum.

8. The alloy set forth in claim 6 in which titanium and aluminum are copresent in a total amount of from 0.35% to about 1% and which contains up to 0.3% silicon and up to 0.4% manganese.

9. The alloys set forth in claim 7 in which the carbon content does not exceed about 0.03%.

10. The alloy as set forth in claim 5 and which consists essentially of 34% to 39% nickel, 15% to 19% chromium, at least 0.5% and up to 1.5% columbium, and from 1% to 3% molybdenum, the sum of the columbium plus molybdenum not exceeding 3.5%.

11. The alloy as set forth in claim 10 and containing at least 0.35% each of aluminum and titanium, up to 0.4% silicon and up to 1% manganese.

References Cited

UNITED STATES PATENTS

2,432,617	12/1947	Franks	75—128.4
3,243,287	3/1966	Lillys	75—128.9
3,384,476	5/1968	Eggnell	75—128
2,451,547	10/1948	German	75—128
2,894,833	7/1959	Linnert	75—128
3,495,977	2/1970	Denhard	75—128

HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

75—128G, 128T, 182W