

UNITED STATES PATENT OFFICE

2,432,615

IRON-BASE ALLOYS

Russell Franks and William O. Binder, Niagara Falls, N. Y., assignors to Electro Metallurgical Company, a corporation of West Virginia

No Drawing. Application June 13, 1945,
Serial No. 599,306

14 Claims. (Cl. 75-128)

1

This invention relates to iron-base alloys designed particularly for use in applications where great strength at very high temperatures is required.

The continued development of such devices as superchargers, gas turbines, jet propulsion apparatus and the like depends upon the production of workable metals and alloys that are strong at the high temperatures at which such devices operate. Although several alloys have been proposed for use in high temperature applications, the utility of such alloys has been limited either because they are not hot-workable or machinable or because they become brittle upon continued exposure to elevated temperatures. One characteristic of highly alloyed ferrous metals which complicates the problem considerably is that as the iron-base solid solution is more heavily loaded with alloying materials to increase the high-temperature strength, the high-temperature stability tends to decrease so that upon prolonged heating the material becomes unduly brittle.

There is accordingly a need for hot-workable, machinable alloys having great strength and stability at highly elevated temperatures, and it is the principal object of this invention to satisfy this need.

This object is achieved by the invention which comprises a new iron-base alloy containing certain proportioned quantities of nickel, chromium, cobalt, molybdenum, tungsten, and at least one metal selected from the group consisting of columbium, tantalum, titanium and vanadium, as the principal constituents, together with relatively minor though essential amounts of manganese, silicon, carbon and nitrogen. The impurities commonly present in steels of good quality may also be present in the new alloy.

Specifically, the alloy of the invention contains by weight 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten (usually not over 3% tungsten); an aggregate of 0.5% to 3% of one or more of the elements columbium, tantalum, titanium and vanadium; and up to 2% manganese, up to 1% silicon, up to 0.35% carbon, up to 0.25% nitrogen; and the remainder substantially all iron and incidental impurities. The content of any single element of the columbium, tantalum, titanium, vanadium group should be less than 2%. The titanium content should not exceed 1.5%. Somewhat more of the minor constituents than the upper limits just specified may on occasion be used. For instance, if excellent forge-

2

ability is not essential, the carbon content may be above 0.35%, up to say 1%. Iron is present in a proportion greater than the proportion of any other single element, the iron content being between about 25% and 55% of the alloy.

Alloys within the foregoing composition ranges are readily forged, welded, and machined and, as has been demonstrated by test, have remarkably great strength and stability at high temperatures, for example 1200° F. and upwards. Machine parts of the alloys may be designed to operate at high stress for long periods of time at 1500° F. and at lower stress for moderate periods at somewhat higher temperatures. The invention includes cast or hot-worked articles and welded articles for use at elevated temperatures and composed of such alloys.

A useful test for determining the suitability of metals and alloys for high temperature applications is the so-called "stress-rupture" test. In this test, each of several samples of a given material is subjected to a measured tensile stress at a particular elevated temperature, and the time required for the sample to fail under these conditions of temperature and stress is noted. The data obtained are then plotted, using time and stress as abscissa and ordinate respectively. A curve is thus established for the material tested, showing for the selected temperature the time required to cause failure of the material when a particular stress is applied. Usually curves are established for several different temperatures, and from these curves can be predicted quite accurately the length of time the material can withstand failure at a given stress applied at a given temperature. This information is valuable for design purposes, especially if the material selected may be subjected to overheating, overloading, or both.

In Table I results obtained on testing several alloys typical of the invention are set forth. In this series of tests, all of the specimens except the last were in the as-formed condition. The last was forged, heated one-half hour at 2200° F., quenched in water, reheated four hours at 1500° F. and air cooled. The reported values, stress in pounds per square inch to cause failure in 1000 hours at the indicated temperature, were obtained from curves derived from stress-rupture tests as explained above.

In Table IA are set forth results obtained on testing other alloys typical of the invention at 1500° F. and 20,000 pounds per square inch stress.

Time to failure under these conditions is reported in hours. These results were obtained on specimens in the forged condition. The first was not heat treated after forging, but the second specimen after forging was heated one hour at about 2240° F. and quenched in water.

mens, the yield strength was measured in pounds per square inch at 0.2% offset, tensile strength in pounds per square inch, and percentage elongation (% El.) was measured over a two inch gage length. In the table "% R. A." means

TABLE I

Composition: 0.5% Si; 1.5% Mn; 3% Mo; 2% W; Rest Fe and—							Stress to Cause Failure at 1000 hours		
% Cr	% Ni	% Co	% Cb	% C	% N	Other	1200° F.	1300° F.	1500° F.
15	15	13	1	0.15	0.10	Nil	47,000	23,000	13,000
18	15	13	1	0.33	0.07	do	40,000	18,000	10,000
21	21	21	1	0.13	0.11	do	48,500	27,000	14,000
21	21	21	1	0.28	0.11	do	46,000	21,000	12,000
21	19	19	1	0.13	0.11	do	(1)	(1)	14,000
21	19	19	Nil	0.16	0.14	1% Ta	(1)	(1)	18,000
21	19	19	0.5	0.15	0.15	0.5% Ta	(1)	(1)	16,000+
21	19	19	1	0.15	0.15	1% Ta	(1)	(1)	17,000
21	19	19	1	0.15	0.15	2% Ta	(1)	(1)	11,000
21	19	19	Nil	0.15	0.15	1% V	(1)	(1)	15,000
21	19	19	Nil	0.15	0.15	2% V	(1)	(1)	13,000
21	19	19	0.5	0.13	0.15	0.5% V	(1)	(1)	14,000
21	19	19	Nil	0.15	0.15	0.5% Ta, 0.5% V	(1)	(1)	16,000
21	21	21	1	0.28	0.11	Nil	(1)	27,500	16,500

¹ No test.

TABLE IA

Composition: 0.5% Si; 1.5% Mn; 3% Mo; 2% W; Rest Fe and—							Hours to fail at 1500° F. and 20,000 lbs./in. ²
% Cr	% Ni	% Co	% Cb	% C	% N	Other	
20	20	20	Nil	0.15	0.12	1% Ti	112
20	20	20	0.5	0.15	0.12	0.25% Ti	160

The data in the above tables illustrate the high strength of the alloys of the invention at elevated temperatures. Previously known alloys used commercially for parts requiring great strength at high temperatures fall far short of the performance indicated by the foregoing data. For instance, a commercial alloy composed of 13.4% chromium, 19.1% nickel, 2.6% tungsten, 0.7% molybdenum, 0.5% carbon, rest iron, when tested at 1200° F. showed a stress to rupture strength in 1000 hours of 21,000 pounds per square inch. A similar alloy, containing however 27.4% nickel, showed a similar strength at 1200° F., a strength of 11,000 pounds per square inch at 1350° F., and 6,000 pounds per square inch at 1500° F.

Proper proportioning of the alloying elements is required to obtain the great strength possessed by the alloys of the invention. Particularly is this so in the case of the elements carbon, nitrogen and columbium, tantalum, titanium and vanadium. If the carbon content is too high or if nitrogen is omitted, the strength of the alloys is impaired.

That the alloys of the invention are strong at ordinary temperatures as well as at elevated temperatures has been demonstrated by tensile tests conducted at ordinary room temperature. The results of such tests are set forth in the following Table II. Different samples of the alloys were tested in the as-forged condition (Condition 1) and after being forged, heated at 2200–2300° F. for one hour and quenched in water (Condition 2). In the tests made on A. S. T. M. standard 0.505 inch diameter tensile test speci-

percentage reduction of area at the breaking point of the specimen.

TABLE II

Composition—remainder Fe and 1.5% Mn and 0.5% Si

Alloy No.	% Cr	% Ni	% Co	% Mo	% W	% Cb	% C	% N
1	15	16	13	3	2	1	0.15	0.10
2	21	21	21	3.2	2.2	1	0.13	0.11

Results of tensile tests

Alloy No.	Condition of Sample	Yield Strength	Tensile Strength	% El.%	% R.A.
1	1	102,000	125,000	18	50
2	2	43,000	102,800	59	71
2	1	116,500	142,700	16	45
2	2	53,400	115,100	58	67

An unusual property of the alloys of this invention in their resistance to both oxidizing and reducing corrosive media. Corrosion-resistant alloys which have heretofore been available have in general been especially suited either for resistance to oxidizing corrosives or reducing corrosives, but not to both types of media. For example, stainless steels of the 18% chromium, 8% nickel type, particularly those modified by the presence of both molybdenum and columbium, have great resistance to oxidizing corrosives but relatively much poorer resistance to reducing corrosives. On the other hand, nickel-base alloys containing substantial quantities of molybdenum exhibit remarkable resistance to reducing corrosives but relatively much poorer resistance to oxidizing corrosives. Thus, articles designed for use where corrosives of the oxidizing type are encountered can not ordinarily be used where corrosives of the reducing type are encountered and vice versa. In strong contrast to this behavior of conventional corrosion-resisting

alloys, the alloys of this invention exhibit very good resistance to corrosives of either oxidizing or reducing media.

In Table III are set forth typical corrosion test results obtained in several different media on specimens of commercial stainless steel, commercial nickel-molybdenum alloy, and an alloy of this invention. In the table, alloy "A" is a commercial 18% chromium, 8% nickel steel of high quality containing both molybdenum and columbium; alloy "B" is an alloy typifying this invention and containing about 21% chromium, 21% nickel, 21% cobalt, 3% molybdenum, 2% tungsten, 1% columbium, 0.5% silicon, 1.5% manganese, 0.1% nitrogen, and 0.1% carbon, remainder iron; alloy "C" is a commercial nickel-base alloy of high quality containing about 15% each of molybdenum and chromium. Corrosion test results in the table are given in inches penetration per month.

TABLE III

Alloy	Corrosion Rate in Medium Shown				
	Boiling 65% HNO ₃	Room Temp. 10% HCl	70° C. 10% HCl	70° C. 10% HCl Aerated	Wet Cl ₂ Gas
A -----	0.0008	0.0021	(¹)	(¹)	0.09
B -----	0.0014	0.0009	0.075	0.075	0.07
C -----	0.066	0.00026	0.008	0.015	0.003

¹ Dissolved.

It will be seen from the data in Table III that the stainless steel had good resistance to corrosion in nitric acid, an oxidizing medium, but dissolved in warm hydrochloric acid, a reducing medium. The nickel-molybdenum alloy, on the other hand had good resistance to hydrochloric acid but was not nearly so resistant to nitric acid. The alloy of this invention had fair to good resistance to both oxidizing and reducing media. For best corrosion-resistance the carbon and nitrogen contents of the alloys ought to be low. Improved resistance to reducing-type corrosives may be obtained by raising the molybdenum content, say to about 6%, but too high a proportion of molybdenum detrimentally affects hot workability.

The corrosion-resisting properties of the alloys of this invention recommend their use in applications where resistance to either oxidizing or reducing, or both oxidizing and reducing corrosive conditions either alternately or simultaneously, is required. Such last mentioned applications include for example the handling of acetic anhydride or of hydrochloric acid containing ferrous ions.

The alloys of the invention may be forged or otherwise hot-worked without difficulty in the range of 2100° to 1600° F. and are easily machinable. They have good cold or hot bending and forming properties because of their high ductility, and that they have good deep-drawing properties is evidenced by standard Erichsen test values on rolled sheet in the annealed condition (air cooled from 1150° C.) of 11.4. The sheet in these tests was 0.035 inch thick and composed of an alloy containing about 21% chromium; 20% nickel; 20% cobalt; 3% molybdenum; 2% tungsten; 1% columbium; 1.5% manganese; 0.5% silicon; 0.13% nitrogen; 0.13% carbon; rest iron. In the Erichsen test a sheet to be tested is clamped between two dies in such a way that the metal is free to flow while a tool having a rounded end is moved against the steel under the influence of a

ram actuated by a micrometer screw. The depth of impression in millimeters to obtain fracture is the "Erichsen value."

Another important advantage of the alloys of this invention is that they may be welded by ordinary welding methods including the various electric arc and oxyacetylene fusion-deposition methods, submerged-melt electric methods and solid-phase pressure welding methods, the welds produced being sound, tough, and ductile both in the weld zone itself and in areas adjacent to and remote from the weld zone.

Table IV sets forth results of tensile and Charpy impact tests on standard specimens composed entirely of metal deposited by electric arc welding. The metal contained 22% chromium; 19% nickel; 20% cobalt; 3% molybdenum; 2% tungsten; 1% columbium; 0.5% silicon; 0.5% manganese; 0.12% nitrogen; 0.06% carbon; rest iron. In the table the stress at 0.2% offset, yield point (Y. P.) and maximum stress are given in pounds per square inch, elongation in percentage of a one inch gage length (% El.), reduction of area (% R. A.) at the breaking point in percentage of original cross-sectional area, and Charpy impact strength in foot pounds. The first line in the table shows results obtained on a specimen in the as-welded condition, the second, results obtained on a welded specimen heated at 1150° C. for 15 minutes and cooled in still air.

TABLE IV

	Stress @ 0.2% offset	Y. P.	Max. Stress	% El.	% R. A.	Charpy Impact
35	49,800 -----	54,200	102,600	44	45.8	23
	55,200 -----	60,800	104,200	42	34.1	28

To ensure the attainment of the desirable welding characteristics of the alloys of the invention it is most important that the composition limits set forth be adhered to so that the alloying elements are present in the proper proportions. If the proportions of molybdenum, tungsten, columbium, tantalum, titanium, vanadium, and carbon be higher than the ranges given, the alloys suffer in hot-workability and weldability; welds made in such alloys lacking toughness and ductility. The deleterious effects of too high proportions of these elements can not satisfactorily be offset by increasing the proportions of cobalt and nickel in the alloys. Too high a carbon content or too low proportions of columbium, tantalum, titanium, or vanadium, and nitrogen have adverse effects on the high-temperature strength of the alloys. Accordingly, care should be taken that the composition limits described be observed in making these alloys.

If the alloys are intended for uses in which they will be exposed to temperatures not in excess of about 1350° F., compositions near the lower limits of the ranges given may be used, but if the alloys will be used where exposure to temperatures above 1350° F. is probable, compositions near the upper limits of the ranges given should be employed.

Typical of articles for which the alloy of the invention is well suited are blades, wheels and other parts of turbines. Such articles may be either cast or wrought.

Although particular emphasis has been laid on the hot working properties of the alloys of the invention and the use of the alloys for wrought articles, castings of these alloys also possess very useful properties at high temperatures.

7

This application is in part a continuation of our copending application, Serial No. 540,313, filed June 14, 1944, which in turn is in part a continuation of our application Serial No. 511,318, filed November 22, 1943. Related subject matter is described and claimed in our copending applications, Serial No. 599,310, filed June 13, 1945, and Serial No. 599,307, filed June 13, 1945.

We claim:

1. An iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

2. A hot-workable iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1 to 3.5% molybdenum; 0.5% to 3% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy and titanium not exceeding 1.5%; manganese in an effective proportion up to 2%; silicon in an effective proportion up to 1%; carbon in an effective proportion not exceeding 0.35%; 0.05% to 0.25% nitrogen; the remainder iron.

3. A hot-workable iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy, and titanium not exceeding 1.5%; manganese in an effective proportion up to 2%; silicon in an effective proportion up to 1%; carbon in an effective proportion not exceeding 0.35%; 0.05% to 0.25% nitrogen; the remainder substantially all iron, the iron content being between 25% and 55%.

4. A hot-worked article which in its normal use is exposed to elevated temperatures, said article being composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy, titanium not exceeding 1.5%; carbon in a proportion not greater than 0.35%; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities, the iron being present in a proportion greater than any other single element.

5. A welded article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy and titanium not exceeding 1.5%; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

8

6. A cast article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy, and titanium not exceeding 1.5%; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

7. An iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to less than 2% columbium; manganese in an effective proportion up to 2%; silicon in an effective proportion up to 1%; carbon in an effective proportion not exceeding 0.35%; 0.05% to 0.25% nitrogen; the remainder substantially all iron, the iron content being between 25% and 55%.

8. A hot-worked article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to less than 2% columbium; carbon in a proportion not greater than 0.35%; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

9. A welded article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to less than 2% columbium; carbon in a proportion not greater than 0.35%; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

10. A cast article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to less than 2% columbium; carbon in a proportion not greater than 0.35%; 0.05% to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

11. Article which in its normal use is subject to mechanical stress at elevated temperatures between about 1200° F. and about 1500° F., said article being composed of a hot-worked iron-base alloy capable in the hot-worked condition of withstanding a tensile stress of at least 10,000 pounds per square inch for at least 1000 hours at 1500° F. and comprising 15% to 21% chromium; 15% to 21% nickel; 13% to 21% cobalt; about 3% molybdenum; about 2% tungsten; about 1% columbium; carbon in a proportion between 0.1% and 0.3%; about 0.1% nitrogen; the remainder substantially all iron and incidental impurities, the iron being present in a proportion greater than 25%.

12. A hot-worked article which in its normal use is subject to mechanical stress at elevated temperatures upwards of 1200° F., said article being composed of an iron-base alloy which persistently maintains great strength at such temperatures and comprises substantially 21% chromium; 21% nickel; 21% cobalt; 2% tungsten;

9

3% molybdenum; 1% columbium; 0.2% carbon; 0.1% nitrogen; the remainder substantially all iron and incidental impurities.

13. An article required to withstand corrosion in both oxidizing and reducing media, which article is composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 6% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2% of the alloy; 0.05% to 0.25% nitrogen; carbon in an effective proportion not exceeding 0.35%; the remainder substantially all iron and incidental impurities.

14. A deep-drawn article which in its normal use is exposed to elevated temperatures, which article is composed of an iron-base alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 1% to 3.5% molybdenum; 0.5% to 7.5% tungsten; 0.5% to 3% in the aggregate of at least one element selected from the group consisting of columbium, tantalum, titanium and vanadium, the content of any single element of said group being less than 2%

10

of the alloy and titanium not exceeding 1.5%; 0.05% to 0.25% nitrogen; carbon in an effective proportion not exceeding 0.35%; the remainder substantially all iron and incidental impurities.

RUSSELL FRANKS.
WILLIAM O. BINDER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,227,065	Charlton	Dec. 31, 1940
2,397,034	Mohling	Mar. 19, 1946
2,191,790	Franks	Feb. 27, 1940

OTHER REFERENCES

Pamphlet by Electro Metallurgical Co. of Union Carbide and Carbon Corp., Nitrogen in Chromium Steels, 1941, New York. (Copy in Div. 3, in 75-126.)

The Iron Age, Nitrogen in Chrome-Nickel Steels, March 29, 1945, pages 56 to 60. (Copy in Div. 3, in 75-128.)