

## UNITED STATES PATENT OFFICE

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## FERROUS ALLOYS FOR HIGH-TEMPERATURE USE

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

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This invention relates to ferrous 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 ferrous 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 ferrous alloy containing certain proportioned quantities of nickel, chromium, cobalt, tungsten, at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium and at least one metal selected from the group consisting of boron and aluminum as the principal constituents, together with relatively minor though essential amounts of manganese, silicon, carbon and nitrogen. Molybdenum and 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; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; an aggregate of 0.5% to 3% of one or more of the elements columbium, tantalum, titanium, and vanadium; an aggregate of 0.01% to 3% of at least one metal selected from the group consisting of aluminum and boron, the boron content not exceeding 1% and the aluminum content being not less than 0.5% in the absence of boron; 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

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content of any single element of the columbium, tantalum, titanium, vanadium group should be less than 2%, and titanium preferably does 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 forgeability is not essential, the carbon content may be above 0.35%, up to say 1%. In general, for ease of hot-working the alloys of the invention should contain about 15% to 25% nickel and 10% to 25% cobalt, and iron should be 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. At least 5% and preferably at least 10% iron should be present in any case. Boron preferably does not exceed 0.7%. The tungsten content should be not less than 7.5% in the absence of molybdenum. A preferred range for molybdenum, if molybdenum is present, is 0.5% to 5%.

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 the table results obtained on testing several

alloys typical of the invention are set forth. In this series of tests, all of the specimens were in the cast condition. The reported values were obtained on testing at 1500° F. and the specific stresses reported in the table, the stresses being reported as pounds per square inch and the time in hours.

Table

| % Composition—Remainder Substantially all Fe |    |    |     |    |     |    |      |       | Hours to Fail at 1500° F. and Stress Indicated |        |        |
|----------------------------------------------|----|----|-----|----|-----|----|------|-------|------------------------------------------------|--------|--------|
| Cr                                           | Ni | Co | Mo  | W  | B   | Cb | C    | N     | 20,000                                         | 25,000 | 30,000 |
| 18.5                                         | 4  | 20 | 2   | 2  | 0.4 | 1  | 0.09 | low   | 623                                            | 167    | N. T.  |
| 18.5                                         | 4  | 20 | 4   | 4  | 0.5 | 1  | 0.09 | low   | N. T.                                          | 256    | N. T.  |
| 18.5                                         | 20 | 20 | 4   | 4  | 0.4 | 1  | 0.14 | 0.1   | 2 1344                                         | 324    | 121    |
| 18                                           | 20 | 20 | nil | 15 | 0.5 | 1  | 0.10 | N. D. | N. T.                                          | N. T.  | 2 648  |
| 18                                           | 20 | 20 | 3   | 10 | 0.5 | 1  | 0.10 | N. D. | N. T.                                          | N. T.  | 243    |
| 18                                           | 20 | 35 | nil | 14 | 0.5 | 1  | 0.10 | N. D. | N. T.                                          | N. T.  | 600    |
| 18                                           | 20 | 35 | 3   | 10 | 0.5 | 1  | 0.10 | N. D. | N. T.                                          | N. T.  | 592    |

1 25,500 p. s. i. stress.

N. T.=no test.

N. D.=not determined.

2 No failure.

The data in the above table illustrate the remarkable high-temperature strength of iron-chromium-nickel-cobalt alloys containing properly proportioned quantities of molybdenum, tungsten, columbium and boron. The data also show the strengthening effect of increasing nickel.

In addition to their strength at high temperatures the alloys of the invention possess other desirable properties. They are strong and have good ductility at ordinary room temperature. They may be hot-worked and machined, the alloys containing 10% to 25% nickel and 10% to 25% cobalt being particularly notable in these respects. The same alloys also possess unusual corrosion-resisting properties in that they exhibit substantial resistance to corrosive attack by both oxidizing and reducing media. Additionally, the alloys of the invention are weldable by any of the conventional welding methods including electric arc welding, oxyacetylene welding, submerged-melt electric welding and solid-phase pressure welding.

To ensure the attainment of the desirable 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. For example, nitrogen is beneficial to high temperature properties in the range given, but too high a nitrogen content is detrimental. Similarly, if the proportions of molybdenum, tungsten, 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. For the best combination of workability and high temperature strength the proportion of any single element of the group columbium, tantalum, titanium and vanadium should be less than 2% of the alloy. 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, compo-

sitions near the upper limits of the ranges given should be employed. For the fabrication of wrought articles for use at the latter temperatures an alloy containing 15% to 25% chromium, 15% to 25% nickel, 10% to 25% cobalt, 0.5% to 5% molybdenum, 0.5% to 15% tungsten, 0.5% to less than 2% columbium, not over 0.35% carbon,

and 0.01% to 0.7% boron, remainder substantially all iron is preferred.

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.

This application is in part a continuation of our copending application Serial No. 599,310, filed June 13, 1945, which is in part a continuation of our application Serial No. 540,313, filed June 14, 1944, which is in turn in part a continuation of our application Serial No. 511,318, filed November 22, 1943.

We claim:

1. A hot-workable alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2% and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 1% of the alloy and the aluminum content being not less than 0.5% in the absence of boron; up to 0.25% nitrogen; the remainder substantially all iron.

2. A hot-workable alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; 7.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01 to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 1% of the alloy and the aluminum content being not less than 0.5% in the absence of boron; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

3. A hot-workable alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 0.5% to 5% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not ex-

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ceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 0.7% of the alloy, and the aluminum content being not less than 0.5% in the absence of boron; 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%; up 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 alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 0.7% of the alloy, and the aluminum content being not less than 0.5% in the absence of boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

5. A hot-worked article which in its normal use is exposed to elevated temperatures, said article being composed of an alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; 7.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 0.7% of the alloy and the aluminum content not less than 0.5% in the absence of boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen, the remainder substantially all iron and incidental impurities.

6. A hot-worked article which in its normal use is exposed to elevated temperatures, said article being composed of an alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; 0.5% to 5% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 0.7% of the alloy, and the aluminum content being not less than 0.5% in the absence of boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

7. A welded article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, tita-

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nium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 0.7% of the alloy and the aluminum content being not less than 0.5% in the absence of boron; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

8. A cast article which in its normal use is exposed to elevated temperatures, said article being composed of an alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 1% of the alloy and the aluminum content being not less than 0.5% in the absence of boron; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

9. An alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2% and titanium not exceeding 1.5%; 0.01% to 0.7% boron; 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%; up to 0.25% nitrogen; remainder substantially all iron.

10. An alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; 7.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2% and titanium not exceeding 1.5%; 0.01% to 0.7% boron; 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%; up to 0.25% nitrogen; remainder substantially all iron.

11. An alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2% and titanium not exceeding 1.5%; 0.5% to 3% aluminum; 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%; up to 0.25% nitrogen; remainder substantially all iron.

12. A hot-worked article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 0.7% boron; carbon in a proportion not greater than 0.35%;

up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

13. A hot-worked article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 7.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 0.7% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

14. A hot-worked article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 0.5% to 5% molybdenum; 0.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 0.7% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

15. A welded article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 0.7% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

16. A welded article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 7.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 0.7% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

17. A welded article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; 0.5% to 5% molyb-

denum; 0.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 0.7% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

18. A cast article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 1% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

19. A cast article which in its normal use is exposed to elevated temperatures upwards of 1200° F., said article being composed of an alloy containing 15% to 25% chromium; 2% to 25% nickel; 10% to 40% cobalt; 7.5% to 15% tungsten; 0.5% to less than 2% columbium; 0.01% to 1% boron; carbon in a proportion not greater than 0.35%; up to 0.25% nitrogen; the remainder substantially all iron and incidental impurities.

20. An article required to withstand corrosion in both oxidizing and reducing media, which article is composed of an alloy containing 15% to 25% chromium; 15% to 25% nickel; 10% to 25% cobalt; up to 8% molybdenum; 0.5% to 15% tungsten; 0.5% to 3% in the aggregate of at least one metal selected from the group consisting of columbium, tantalum, titanium, and vanadium, the content of any single element of said group being less than 2%, and titanium not exceeding 1.5%; 0.01% to 3% in the aggregate of at least one element selected from the group consisting of aluminum and boron, the boron content not exceeding 0.7% of the alloy and the aluminum content being not less than 0.5% in the absence of boron; up 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.