United States Patent Office

2,695,844

Patented Nov. 30, 1954

2,695,844

HIGH-TEMPERATURE COBALT BASE ALLOYS

William Charles Clarke, Jr., Dundalk, Md., assignor to Armco Steel Corporation, a corporation of Ohio

No Drawing. Application September 28, 1949, Serial No. 118,453

8 Claims. (Cl. 75—134)

This invention relates generally to high temperature alloys, and more particularly to alloys having a high degree of resistance to the combined effects of heat and stress.

An object of my invention is the provision of durable and reliable high temperature alloys.

Another object of my invention is that of providing high temperature alloys which are highly capable of withstanding the combined and continued effects of elevated temperatures and stress.

A further object of this invention is the provision of alloys of the character indicated which are amenable to such operations as forging and hot rolling.

Other objects of my invention in part will be obvious and in part pointed out more fully hereinafter.

The invention, accordingly, consists in the combination of elements, composition of materials, in the products, articles and manufactures, and in the several method steps and the relation of each of the same to one or more of the others as described herein, the scope of the application of which is indicated in the following claims.

As conducive to a clearer understanding of certain features of my invention, it may be noted at this point that many alloys, and articles and products made of alloy metal, are today in demand for high temperature use. It frequently occurs that metal products in this general category are needed for use at temperatures above about 1000° F. which incidentally assure that the metal will be intensely hot, this use sometimes over a long and continued period of time. There are occasions too where the alloy products, in view of the particular use at hand, are subjected to load and stress under the prevailing conditions of intense heat.

A variety of alloys which perhaps rightfully belong in the low temperature class are highly susceptible to the development of surface scale or heat scale when subjected to intense heat. Of even greater consequence in certain instances, heat causes many of these alloys to become so weak that high temperature use is out of the question. The alloys very often are susceptible to creep under load, especially while hot, and are further unreliable for the reason of ensuing rupture.

Even many of the heretofore known high temperature alloys are extremely limited in utility for such reasons as having a very marked tendency toward creep and stress rupture while intensely heated. In other instances, some of the conventional high temperature products are objectionable because of having very low resistance to the development of heat scale while heated in the high temperature range. The alloy metal often is of a kind which affords little if any resistance to corrosion as in hot corrosive atmospheres such as might surround use in certain high temperature equipment.

So many of the conventional high temperature alloys are notoriously difficult to work, as by forging and hot rolling. For this reason, they are less in demand for reduction to particular form for producing wrought products and articles. This condition exists though working is often regarded as being important for producing a high temperature product or article.

An outstanding object of my invention accordingly is the provision of high temperature alloys and wrought products and articles of the same which reliably resist corrosion and the development of heat scale and which have highly favorable creep and stress rupture properties in high temperature use.

Referring now more particularly to the practice of my invention, I provide high temperature cobalt base alloys which in containing certain elements in critical amounts in addition to the cobalt, not only have good hot working properties, high strength, and highly favorable resistance to creep and stress rupture under intense heat, but are further characterized by resistance to corrosion and by substantial freedom from heat scale development when in high temperature use. These alloys in accordance with my invention contain approximately 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, carbon in amounts up to about 0.35%, and the remainder substantially cobalt. Iron usually is an element present in the alloy composition, this being in quantities up to about 10% either as an impurity or otherwise. My alloy composition preferably includes nickel in substantial amounts up to about 16%, but on occasions nickel may be entirely or substantially absent. Among other constituents which preferably are in the alloy are up to about 3% total titanium and/or columbium. I prefer to introduce effective quantities of both of the latter for together they have an especially advantageous effect upon the high temperature properties. There are instances though where I provide the alloys without either titanium or columbium, as where the immediate high temperature needs are successfully satisfied without the addition. Only small quantities of such elements as manganese, silicon, sulphur and phosphorus usually are in the alloys, these preferably being with the manganese in quantities ranging up to about 2%, the silicon ranging up to about 1.5%, and the sulphur and phosphorus each not exceeding about 0.04%.

My cobalt base alloys derive beneficial high temperature effects from the cobalt constituent. Also, the amounts of chromium and other elements used are regarded as being critical. With any appreciable lowering of the chromium content to outside the range hereinbefore noted, scaling resistance and general corrosion resistance of the alloy suffer, and with appreciable increase beyond the range, hot working difficulties appear, the alloy further tending to lose ductility in high temperature use. In general, I find that carbon in excess of about 0.35% is not favorable. Where the amounts of copper and molybdenum in my alloys are appreciably lowered to outside the low ends of the ranges given hereinbefore for these elements, the high temperature load-carrying capacity decreases, or where the amounts appreciably exceed the upper limits of the ranges, the hot working properties suffer. Too much molybdenum also seems to impair scaling resistance. If nickel is used at all in my alloy, I keep the nickel below about 15% and preferably below about 10% for best stress rupture properties. On those occasions where one or both elements of the group consisting of titanium and columbium are in the alloy, I find that best advantages are had by using about up to 3% total titanium and/or columbium. Larger amounts seem to decrease the stress rupture properties. Where manganese is in excess of about 2% and silicon more than about 1.5%, this is detrimental to the hot working properties.

My high temperature alloys, especially where the manganese, silicon, sulphur and phosphorus are within the percentage ranges just noted, are amenable to hot working as by forging and hot rolling. I, therefore, frequently resort to such operations as hot working in producing wrought products and articles of the alloy metal, as for example turbine parts such as wheels, rotors, blades, buckets or nozzles. Among other high temperature products and articles which I produce of the alloy metal are supercharger parts, chemical equipment parts, tubes for any of a variety of uses such as for carrying high temperature fluids under pressure. Still further examples of my high temperature alloy articles are bolts, rivets and fasteners. The products and articles of manufacture are strong, durable and reliable. They resist creep and stress rupture such as at temperatures ranging from about 1000° F. to 1900° F. and while either intermittently or continuously under mechanical stress or load. The metal resists forming heat scale under the

conditions of intense heat and possesses a valuable degree of corrosion resistance.

In certain instances, I provide products of my cobalt base alloy in such form as sheet, strip, wire, rods, or the like, which are readily useful for fabrication as by cutting, punching or bending into shape, or welding as by means of oxy-acetylene or arc welding equipment. Sometimes I use the sheet, wire, or the like directly in high temperature applications without appreciable fabrication.

The cobalt base alloy articles and products which I provide often are useful without particular heat treatment or after annealing, and thus are often so used. I achieve a remarkable increase though in the high temperature load-carrying ability by employing a heat treatment in the nature of an annealing and precipitation treatment. In the annealing operation, I heat the alloy metal to a sufficiently high temperature and for long enough time to put at least part of the copper, and at least some of the titanium and columbium when present, into solid solution. Where desired, advantage is taken of annealing temperatures to achieve hot working or other operations for producing my products and articles of the metal. A preferred temperature range for annealing is that of about 2050° F. to 2250° F.

After the annealing and before precipitation heat treatment, I quench the cobalt base alloy metal preferably to about room temperature, this, for example, by using air, oil or water as the quenching medium. By subsequently heating the quenched metal preferably to within a temperature range of about 1000° F. to 1400° F. and by maintaining the same at temperature for long enough time, a critically finely divided precipitate is believed to come out in the metal lattice along the slip planes in the matrix. The copper is thought to precipitate in fine form, or possibly as an intermetallic compound including one or more of the group consisting of nickel, titanium or columbium, depending upon which if any of the nickel, titanium and columbium are present in the alloy composition. Although not immediately visible with the ordinary light microscope, the precipitates become visible after a very long period of time at high temperatures is allowed for coalescing. When titanium and/or columbium are present in the alloy, some portion thereof is thought to come out in the form of carbides. Regardless of theory, however, I find that my high temperature alloys, and articles and products thereof, have excellent properties. Upon quenching or cooling the metal as in air from the precipitation treating temperature, I find that it has a fine grain structure and is further characterized by enhanced load-carrying capacity in view of the precipitation treatment. I often work the metal in this heat-treated condition, or subject the same to fabricating and finishing operations, thus providing high temperature products or articles. During high temperature use of the cobalt base alloy, the precipitates remain critically dispersed, uncoalesced and effective against creep and stress rupture, for long periods of time. Any heating of the metal to as high as solution temperature, of course, tends to put the precipitates back into solution.

For optimum results, I provide cobalt base alloys of the character indicated, but which more specifically contain approximately 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, 0.08% to 0.20% carbon, and the remainder substantially cobalt. Should nickel be used in the alloy composition, the amounts of this element preferably range up to about 10% maximum. I prefer to use quantities of both titanium and columbium in the alloy, but, on occasions, either or both are omitted. Where used, the titanium ranges in amount up to about 0.35% and the columbium up to about 0.70%, alone or together. Iron usually is present in the alloy in permissible amounts up to about 10%. Where manganese, silicon, sulphur and phosphorus are in the alloy, as usually is the case, these preferably are with the manganese in quantities ranging up to about 2%, the silicon ranging up to about 1.5%, and the sulphur and phosphorus each not exceeding about 0.04%.

A few examples of the high temperature cobalt base alloys which I provide are noted in Table I. In this, it will be observed that Alloys A, B and C respectively have increased carbon contents within the permissible carbon range. Also, it will be seen that the Alloy B has a higher nickel content and a lower chromium content as compared with either Alloy A or Alloy C.

TABLE I

Cobalt base alloys

	Alloy A, Percent	Alloy B, Percent	Alloy C, Percent
Carbon	0.11	0.23	0.30
Chromium	19.25	16.39	19.00
Molybdenum	1.92	1.90	2.25
Copper	3.19	3.08	3.25
Nickel	5.33	15.40	5.00
Titanium	0.17	0.23	0.20
Columbium	0.56	0.53	0.50
Manganese	0.86	Low	0.50
Silicon	0.31	0.55	0.60
Sulphur	0.029	0.012	Low
Phosphorus	0.02	.018	0.02
Cobalt	58.7	52.8	58.0
Iron	Bal.	Bal.	Bal.

The several alloys identified in Table I all were subjected to annealing at about 2250° F. for one-half hour, followed by quenching in water and precipitation heat treatment at about 1350° F. for five hours. The alloys then were given stress rupture tests, the conditions and results of which appear in Table II.

TABLE II

Stress rupture tests of Alloys A, B and C

Alloy	Test Temp., ° F.	Load (p. s. i.)	Time for Rupture (hrs.)	Elong. (2" per-) cent	Red. of Area (percent)
A	1,500	30,000	40	8.1	26.0
	1,500	25,000	239	6.5	7.0
	1,500	21,500	492	6.0	8.2
	1,500	20,000	1,281	4.0	2.5
	1,700	10,000	183	4.3	3.3
	1,700	7,500	532	2.5	1.0
B	1,500	28,000	44	9.0	13.2
	1,500	25,000	116	4.0	6.0
	1,500	23,000	162	4.3	4.5
C	1,500	30,000	36	2.0	1.0
	1,500	24,000	70	1.0	1.0

My cobalt base alloys have many vaulable high temperature properties, including resistance to stress rupture whether or not the alloys or products and articles thereof are in the precipitation heat-treated condition. The precipitation heat treatment though enhances a number of the properties. Despite the high temperature properties, my cobalt base alloys are capable of reduction as by forging and hot rolling and of fabrication in a simple, direct and economical manner by virtue of the inherent ease of working. In view of the excellent working properties, I often resort to the production of wrought articles and products of the metal. I find too, though, that my high temperature alloys are thoroughly amenable to casting or molding as in a fixed mold or centrifugally to desired form. Because of this, I often provide cast high temperature products and articles of the alloy metal.

Thus it will be seen that there are provided in my invention cobalt base alloys, and products and articles thereof, in which the various objects noted together with many thoroughly practical advantages are successfully achieved. It will be seen that the metal is strong, durable and tough, corrosion-resistant and heat-resistant and serves well at high temperatures over long periods of time under any of many conditions of actual practical use.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiment hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative and not as a limitation.

I claim:

1. High temperature cobalt alloy having good hot working properties and great high temperature strength and resistance to creep, consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, manganese up to about 2%, silicon up to 1.5%, carbon up to about 0.35%, and the remainder cobalt.

2. High temperature cobalt alloy having good hot working properties and great high temperature strength and resistance to creep, consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, nickel up to about 16%, carbon up to about

0.35%, up to about 3% in total amount of at least one element of the group consisting of titanium and columbium, manganese in quantities up to about 2%, silicon in quantities up to 1.5%, and the remainder cobalt.

3. High temperature cobalt alloy having good hot working properties and great high temperature strength and resistance to creep, consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, manganese up to about 2%, silicon up to about 1.5%, from about 0.08% to 0.20% carbon, at least one element of the group consisting of titanium up to about 0.35% and columbium up to about 0.70%, and the remainder cobalt.

4. High temperature cobalt alloy having good hot working properties and great high temperature strength and resistance to creep, consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, nickel 5% up to about 16%, manganese up to about 2%, silicon up to about 1.5%, from about 0.08% to 0.20% carbon, at least one element of the group consisting of titanium up to about 0.35% and columbium up to about 0.70%, and the remainder cobalt.

5. High temperature cobalt alloy having good hot working properties and great strength and great resistance to creep at high temperatures, consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, manganese up to about 2%, silicon up to about 1.5%, from 0.08% to 0.20% carbon, up to about 0.35% titanium, columbium up to 0.70%, up to about 10% iron, and the remainder cobalt.

6. High temperature cobalt alloy having good hot working properties and great strength and great resistance to creep at high temperatures, consisting of in approximate amount 0.08% to 0.20% carbon, 19% chromium, 2.25% molybdenum, 3.25% copper, 5% nickel, manganese up to about 2%, silicon up to about 1.5%, titanium up to about 0.35%, columbium up to about 0.70%, and the remainder cobalt.

7. High temperature cobalt alloy wrought metal articles or products having great strength and great resistance to creep while hot, said articles or products consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, manganese up to 2%, silicon up to 1.5%, carbon up to about 0.35%, nickel up to about 16%, iron up to about 10%, and the remainder at least about 52.8% cobalt.

8. High temperature cobalt base alloy wrought metal articles or products having great strength and great resistance to creep while hot, said articles or products consisting of about 12% to 25% chromium, 1.5% to 3.5% molybdenum, 2.5% to 4.0% copper, manganese up to 2%, silicon up to 1.5%, carbon up to about 0.35%, titanium and columbium up to 3% total, nickel up to about 16%, iron up to about 10%, and the remainder at least about 52.8% cobalt.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,115,239	Parr	Oct. 27, 1914
1,587,992	Apotzley et al.	June 8, 1926
1,685,570	Masing et al.	Sept. 25, 1928
1,945,679	Corson	Feb. 6, 1934
2,072,911	Touceda	Mar. 9, 1937
2,081,392	Touceda	May 25, 1937
2,108,051	Egeberg et al.	Feb. 15, 1938
2,246,078	Rohn et al.	June 17, 1941
2,309,136	Neiman	Jan. 26, 1943
2,495,063	Hood et al.	Jan. 17, 1950
2,509,800	Blackwood	May 30, 1950
2,509,801	Blackwood	May 30, 1950
2,536,034	Clarke	Jan. 2, 1951

FOREIGN PATENTS

Number	Country	Date
832,391	France	June 27, 1938