

UNITED STATES PATENT OFFICE

2,536,033

HIGH-TEMPERATURE STAINLESS STEEL

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

No Drawing. Application May 14, 1948,
Serial No. 27,152

7 Claims. (Cl. 75-125)

1

2

The present application is a continuation-in-part of my copending application, Serial No. 671,905, filed May 23, 1946, now Patent No. 2,447,897, and entitled High Temperature Stainless Steel, which application in turn is a continuation-in-part of my copending application, Serial No. 645,015, filed February 1, 1946, now Patent No. 2,447,896, and entitled High Temperature Turbine, and the invention relates to high temperature steel and products and articles of the steel.

An object of my invention is the provision of strong and durable high temperature stainless steel, and products and articles of the steel, which are resistant to stress-rupture and creep while under load in the heated condition, and which resist attack of hot corrosive matter and avoid the formation of heat scale up to very high temperatures.

A further object of this invention is the provision of high temperature stainless steel having excellent hot working properties, great physical strength and high resistance to corrosion; another object being that of providing wrought products and articles of the steel.

A still further object is the provision of high temperature stainless steel subjected to heat treatment for enhanced high temperature properties.

Other objects 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, and in the articles, products 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 a great variety of austenitic stainless steels in the prior art, as for example those containing about 10% to 25% chromium, 7% to 15% or more nickel, and the remainder substantially all iron, are useful in the production of low temperature or mildly heat resistant products or articles of manufacture. Among the better known of these steels are the usual 18-8 chromium-nickel steels which are readily worked as by rolling, drawing, spinning, or the like, into such products as trim for house, store, office or restaurant purposes or into vehicle or outdoor trim subjected to the effects of weather. Then too, these steels are very much in demand for the fabrication into products, such as for cooking and table service, receptacles and other appliances

where a metal of enduring brightness is called for even to withstand body salts, fruit acids and other corrosive chemicals.

The austenitic stainless steels of the character just referred to have a relatively high alloy content by virtue of the inclusion of nickel, as compared with straight chromium ferritic stainless steels, and are relatively better suited to resist oxidation when heated to high temperatures, say for example above 1000° F. The nickel, importantly being present as an austenite former, contributes materially to the oxidation resistance. There is still the existing fact, however, that the austenitic stainless steels ordinarily on the market are unsatisfactory for meeting exacting demands at high temperature as in such forms as bolts and fasteners, internal combustion engine valves, gas and steam turbine blades, rotors, buckets, nozzles, supercharger components, or in the form of a host of other products and articles subjected to mechanical stress under temperature conditions of use. Products when made of these steels are too susceptible to creep and stress rupture while hot.

It remains that austenitic stainless steels, as a general class, have a more favorable lattice structure for cohesion under stress or load at high temperatures than do ferritic straight-chromium stainless steels. This alone, however, does not necessarily assure adequate high temperature properties in austenitic steels as an entire class, especially with respect to the considerations of stress rupture and creep. The austenitic steels in most instances do have favorable hot working properties, which so often is not true of certain heretofore known high temperature creep resistant and stress-rupture resistant alloy metals. In this connection, many high temperature steels, for example, are notoriously difficult to hot work.

An outstanding object of my invention, accordingly, is the provision of hot worked austenitic stainless steel articles and products, which are resistant to heat and corrosion at elevated temperatures and are resistant to creep and stress-rupture under mechanical load and severe heat.

Referring now more particularly to the practice of my invention, I find that by correlating proper amounts of the ingredients chromium, nickel, cobalt, manganese, molybdenum, copper, carbon, and either or both titanium and columbium, to provide an austenitic stainless steel, satisfactory hot working properties are had along with excellent high temperature strength and resistance to heat and corrosion. The steel which

3

I provide preferably contains about 12% to 22% chromium, 10% to 22% nickel, cobalt ranging from 5% to 20%, from very small amounts up to 2% manganese, 2% to 4% molybdenum, 2% to 4% copper, from 0.08% to 0.20% carbon, at least one metal of the group consisting of titanium and columbium, the titanium ranging from 0.15% to 0.75%, the columbium from 0.20% to 1.10%, and the remainder substantially all iron. Such elements as sulphur and phosphorus preferably are less than about 0.04% each.

I often form my steel, as by hot working and machining, into any of a host of high temperature products and articles, among which are bolts and fasteners, rivets, high temperature chemical equipment parts, tubes such as seamless tubes formed by piercing and drawing, gas and steam turbine blades, rotors, buckets, nozzles, and supercharger parts for either intermittently or continuously serving under mechanical stress and/or corrosive attack. The high temperature products and articles of manufacture are strong, durable and reliable. They resist creep and stress-rupture while hot.

In certain instances, I provide products of the steel 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, too, I use the sheet, wire, or the like, directly in high temperature applications without appreciable fabrication.

My high temperature stainless steel and articles and products thereof are wholly austenitic. Ferrite, if present at all, is only in traces. This I find is essential to the required stress-rupture properties. Where appreciable amounts of ferrite are present the stress-rupture values fall off; also, the working properties suffer.

The substantial quantity of cobalt present in my stainless steel not only supplements the effect of nickel to assure an austenitic balance, but improves the stress-rupture properties and seems to arrest development of sigma phase. Also, by reason of the cobalt constituent, a steel of relatively high alloy content is had in favor of better scaling resistance under intense heat. With any appreciable lowering of the molybdenum and copper contents to outside the ranges hereinbefore noted, the desired high temperature load-carrying capacity of the steels suffer, and with appreciable increase beyond the ranges workability disappears. The elements titanium or columbium, or preferably both, likewise constitute a desired part of the alloy. Alone or together as the case may be, and especially with proper heat treatment of the steel, they enhance stress-rupture and creep properties and give improvements in the high temperature load-carrying ability.

The particular form of heat treatment which I employ for enhancing the high temperature load-carrying properties of the steel is in the character of an annealing and precipitation treatment. In the preferred embodiment of this practice, I heat up the steel, as for example roughly formed articles of the steel, to within solution temperature range of about 2050° F. to 2250° F. at which temperatures either or both the titanium and columbium go into solution depending upon whether one or both are present. The titanium is quite soluble throughout the heating range. The solubility of columbium increases toward the upper end of the temperature

4

range. Copper also goes into solution. Working operations are achieved on the metal if desired, either before, along with, or following the annealing treatment.

After a suitable period of time, I terminate the treatment at solution temperature and quench the steel as in air, oil or water conveniently to about room temperature. By subsequently heating the quenched metal preferably to within a temperature range of about 1200° F. to 1500° F. and by maintaining the same at temperature for a long enough time, a critically dispersed finely divided precipitate comes out in the metal lattice along the slip planes in the matrix. In this, there is a precipitation of intermetallic compounds including titanium or columbium or both. These come out in fine form, or possibly as an intermetallic compound including such elements as nickel, molybdenum, titanium and/or columbium. Although not immediately visible with the ordinary light microscope, they become visible after considerable time is allowed for coalescing. Some portion of the elements precipitated, such as the titanium and columbium, is in the form of carbides which increase in amount on the higher side of the precipitation treatment temperature range just noted.

I quench the steel from the precipitation heat-treated condition. The quenched metal has a fine grain structure, and is further characterized by enhanced load-carrying capacity in view of atomic slip interference developed by the precipitates. The steel in this condition often is worked, fabricated or finished to give articles or products. During high temperature use of the steel, 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 the solution temperature, of course, tends to put the precipitates back into solution.

A few examples of the austenitic chromium-nickel-cobalt stainless steels which I provide are identified in Table I. These steels in addition to containing the amounts of ingredients noted have a remainder which is substantially all iron.

Table I.—Chromium-nickel-cobalt stainless steels

	Sample X	Sample Y	Sample Z
	Percent	Percent	Percent
Chromium.....	17.28	20.51	15.07
Nickel.....	12.96	13.42	10.47
Cobalt.....	13.01	15.49	16.10
Molybdenum.....	2.77	2.51	3.21
Copper.....	3.10	3.05	3.05
Carbon.....	0.102	0.102	0.117
Titanium.....	0.15	0.19	0.21
Columbium.....	0.43	0.42	0.36
Manganese.....	1.68	0.57	0.64
Silicon.....	0.87	0.55	0.57
Sulphur.....	0.014	0.009	0.009
Phosphorus.....	0.012	0.007	0.019

Several samples of the steel X were prepared, then were given annealing treatment at somewhat different temperatures followed by identical precipitation heat treatment, and then were tested with respect to stress-rupture and the corresponding elongation and reduction in area. Table II gives the results of these tests for the several conditions of heat-treatment.

Table II.—Stress-rupture tests of steel X at 1200° F.

[Condition A, annealed at 2050° F. for ¼ hour and water-quenched plus aging at 1200° F. for 5 hours and water-quenched.]

Load	Time for Rupture	Elongation (2"-%)	Reduction in Area
P. s. i.	Hours		Per cent
43,000	81.6	11.3	13.5
40,000	238.3	12.2	19.8
37,000	786.5	10.0	19.0

[Condition B, annealed at 2250° F. for ¼ hour and water-quenched plus aging at 1200° F. for 5 hours and water-quenched.]

Load	Time for Rupture	Elongation (2"-%)	Reduction in Area
P. s. i.	Hours		Per cent
45,000	19.5	9.7	13.0
43,000	87.9	10.6	11.3
40,000	204.6	8.5	13.0

Upon subjecting samples of the steel Y to stress-rupture tests, the results noted in Table III were had.

Table III.—Stress-rupture tests of steel Y

[Steel annealed at 2250° F. for ¼ hour and water-quenched plus aging at 1350° F. for 5 hours and water-quenched, before testing.]

Load	Time for Rupture	Elongation (2"-%)	Reduction in Area
TESTED AT 1200° F.			
P. s. i.	Hours		Per cent
43,000	337.5	9.4	14.2
37,000	2,548.0	5.1	12.3
TESTED AT 1500° F.			
15,000	172	8.14	11.18
12,000	583	2.72	3.80

Tests also were made on samples of the steel Z, these samples being annealed and precipitation heat-treated according to the schedule in Table IV.

Table IV.—Stress-rupture tests of steel Z

[Steel annealed at 2250° F. for ¼ hour and water-quenched plus aging at 1350° F. for 5 hours and water-quenched, before testing.]

Load	Time for Rupture	Elongation (2"-%)	Reduction in Area
TESTED AT 1200° F.			
P. s. i.	Hours		Per cent
50,000	145.7	13.0	20.0
48,000	231.9	11.2	15.5
46,000	454	8.3	19.3
TESTED AT 1500° F.			
16,000	280	4.07	13.05
14,000	400	4.07	13.20
11,000	2,600+	-----	-----

My austenitic chromium-nickel-cobalt stainless steels have many valuable high temperature properties, including resistance to stress-rupture and resistance to creep whether or not the steels and products and articles thereof are in

the precipitation heat-treated condition. The precipitation heat treatment enhances a number of the properties by the development of atomic slip-interference. My austenitic steels despite the high temperature properties of the same are capable of fabrication in a simple, direct and economical manner by virtue of the ease of working. While the carbon content of my steel preferably is on the order of 0.08% to 0.20%, many desirable properties nevertheless are had where the carbon content is as low as 0.03%, or even lower.

Thus it will be seen that there are provided in my invention austenitic chromium-nickel-cobalt alloy stainless steel and products thereof in which the various objects noted together with many thoroughly satisfactory results are successfully achieved. It will be seen that the products are tough, strong and durable, corrosion-resistant and heat-resistant and serve well at high temperatures over long periods of time under 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. Austenitic chromium-nickel-cobalt stainless steel having good hot-working properties and good life and strength at high temperatures, containing about 0.03% to 0.20% carbon, 12% to 22% chromium, 10% to 22% nickel, from 5% to 20% cobalt, not more than about 2% manganese, 2% to 4% molybdenum, 2% to 4% copper, at least one metal of the group consisting of titanium and columbium, the titanium ranging from 0.15% to 0.75% in amount, and the columbium from 0.20% to 1.10%, and the remainder substantially all iron.

2. Austenitic high temperature precipitation-hardened stainless steel having great strength and great resistance to creep at high temperatures, containing about 0.08% to 0.20% carbon, 12% to 22% chromium, 10% to 22% nickel, from 5% to 20% cobalt, 2% to 4% molybdenum, 2% to 4% copper, not more than about 2% manganese, 0.15% to 0.75% titanium, 0.20% to 1.10% columbium, and the remainder substantially all iron, said nickel, molybdenum, titanium and columbium being at least partially precipitated in critically dispersed form for slip-interference.

3. Austenitic high temperature precipitation-hardened stainless steel having great strength and great resistance to creep at high temperatures, containing about 12% to 22% chromium, 10% to 22% nickel, from 5% to 20% cobalt, 2% to 4% molybdenum, 2% to 4% copper, 0.03% to 0.20% carbon, not more than about 2% manganese, from 0.15% to 0.75% titanium, and the remainder substantially all iron, said titanium being at least partially precipitated in critically dispersed form for slip-interference.

4. Austenitic high temperature precipitation-hardened stainless steel having great strength and great resistance to creep at high temperatures, containing about 12% to 22% chromium, 10% to 22% nickel, from 5% to 20% cobalt, 2% to 4% molybdenum, 2% to 4% copper, 0.03% to 0.20% carbon, not more than about 2% manganese, from 0.20% to 1.10% columbium, and the remainder substantially all iron, said columbium being at least partially precipitated in critically dispersed form for slip-interference.

5. Austenitic chromium-nickel-cobalt stainless

7

steel having good hot working properties and good life and strength at high temperatures, containing about 16% to 18% chromium, 12% to 14% nickel, 12% to 14% cobalt, 2.5% to 3.5% molybdenum, 2.5% to 3.5% copper, at least one of the group consisting of .15% to .75% titanium and .20% to 1.10% columbium, 0.08% to 0.20% carbon, and the remainder substantially all iron.

6. Austenitic chromium-nickel-cobalt stainless steel having good hot working properties and good life and strength at high temperatures, containing about 20% to 22% chromium, 13% to 15% nickel, 15% to 17% cobalt, 2.5% to 3.5% molybdenum, 2.5% to 3.5% copper, at least one of the group consisting of .15% to .75% titanium and .20% to 1.10% columbium, 0.08% to 0.20% carbon, and the remainder substantially all iron.

7. Austenitic chromium-nickel-cobalt stainless steel having good hot working properties and

8

good life and strength at high temperatures, containing about 14% to 16% chromium, 10% to 12% nickel, 15% to 17% cobalt, 2.5% to 3.5% molybdenum, 2.5% to 3.5% copper, at least one of the group consisting of .15% to .75% titanium and .20% to 1.10% columbium, 0.08% to 0.20% carbon, and the remainder substantially all iron.

WILLIAM CHARLES CLARKE, Jr.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,397,034	Mohling	Mar. 19, 1946
2,447,896	Clarke	Aug. 24, 1948
2,447,897	Clarke	Aug. 24, 1948