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HIGH-TEMPERATURE STAINLESS STEEL

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The present application is a continuation in part of my copending application, Serial No. 645,015, filed February 1, 1946, and the invention relates to high temperature steel.

An object of my invention is the provision of hot-workable chromium-nickel stainless steels which are readily suited to high temperature serviceability.

A further object is the provision of a simple, practical and reliable method for conditioning stainless steels to a point of enhanced resistance to high temperature stress-rupture and creep.

A still further object of my invention is the provision of chromium-nickel stainless steels, as for example, wrought and subsequently heat treated articles and products, which are strong, tough and durable under conditions of high temperature use.

Other objects in part will be obvious and in part pointed out hereinafter.

The invention accordingly consists in the combination of elements, composition of ingredients, and in the articles, products and manufactures thereof, also 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 the more commonly known austenitic chromium-nickel stainless steels containing approximately 10% to 25% chromium, 7% to 15% or more nickel, and the remainder substantially all iron are useful in the production of a host of corrosion-resistant and mildly heat-resistant products or articles of manufacture. These alloy steels, particularly those containing 18% chromium, 8% nickel, and the balance substantially iron, are made to fulfill a number of interior and exterior structural uses, as in the form of trim and fixtures, where a pleasantly decorative metal resistant to the corrosive effect of atmospheric conditions is desired. Then, too, these steels are made to serve a variety of restaurant, dairy, kitchen and hospital needs, for example, as cooking and serving utensils, receptacles and numerous other appliances where a metal of enduring brightness is in demand.

It is well recognized, however, that the austenitic chromium-nickel stainless steels just referred to are not satisfactory for duty at extremely high temperatures, especially under high mechanical stress for example. They nevertheless

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have a more favorable lattice structure for cohesion under high stress at temperatures above about 1000° F. than do ferritic straight-chromium stainless steels. Of further significance, the straight-chromium steels have greater strength, in way of comparison with the austenitic steels at lower temperatures. There is still the existing fact, however, that many of the austenitic steels are unsatisfactory, as with respect to stress rupture and creep resistance, for meeting the exacting requirements at high temperature in such forms as bolts and fasteners, internal combustion engine valves, gas and steam turbine blades, rotors, buckets, nozzles, and a host of other products and articles subjected to high mechanical stress under the temperature conditions of use.

Known creep resistant and stress-rupture resistant alloys of the high temperature group, on the other hand, are notoriously difficult to work and therefore the production of wrought articles and products from the same presents no small problem, even on the assumption that the metal possesses sufficient strength for eventual use as a finished product.

An outstanding object of my invention accordingly is in the provision of hot-worked chromium-nickel stainless steel articles and products, which are resistant to heat and corrosion at elevated temperatures and are resistant to creep and rupture under high mechanical load during high temperature conditions of use.

Referring now more particularly to the practice of my invention, I find that by properly selecting and correlating in a steel the ingredients chromium, nickel, molybdenum and copper with additions of manganese, columbium and titanium, the carbon content being kept low, to give a fully austenitic steel, satisfactory hot working properties are had. More specifically, I find that stainless steel containing approximately 0.01% to 0.15% carbon, 12% to 22% chromium, 10% to 21% nickel, from 0.10% to 2.0% manganese, 2% to 4% molybdenum, copper ranging from 2% to 4%, from 0.15% to 0.75% titanium, 0.20% to 1.10% columbium, and the remainder substantially all iron, possesses excellent properties in use. The steel readily is formed into desired high-temperature products and manufactures as for example into bolts and fasteners, rivets, high temperature chemical equipment and parts, heat engine valves including exhaust valves for internal combustion engines, tubes such as seamless tubes formed by drawing, gas and steam turbine blades, rotors, buckets, nozzles, and a

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host of other products of the steel illustratively for serving under mechanical stress and/or corrosive attack either intermittently or continuously during high temperature use. At high temperature, as in the presence of hot corrosive gases and while under prolonged mechanical stress, the products or articles of manufacture are strong, tough and durable.

The steels which I provide are wholly austenitic in structure. Ferrite, if present at all, is only in traces. This I find essential to the required stress-rupture properties. Where appreciable amounts of ferrite are present the stress-rupture values fall off; also the working qualities of the metal suffer.

The composition limits given are considered to be in every sense critical since I find that where they are departed from one or more of the desired qualities suffer. For example, with a higher carbon content the working properties suffer and products of the metal are not so easily produced. To like effect with a manganese content exceeding 2.0%, there is a loss in hot-working properties. With any appreciable lowering of the molybdenum and copper contents the desired high temperature load-carrying characteristics of the steels suffer, and with appreciable increase workability disappears. The elements titanium and columbium in the amounts indicated likewise constitute a desired part of the alloy. In combination, and with proper heat treatment of the steel, they enhance stress-rupture and creep properties and give improvements in the high temperature load-carrying ability by virtue of the precipitation of carbides of columbium and titanium and a precipitation of intermetallic compounds of these elements, the amounts in the form of carbides and of intermetallic compounds depending to an extent upon the temperatures of heat-treatment. Where larger quantities of titanium and columbium are used, however, a loss of load-carrying ability of the steel occurs.

As a preferred embodiment of my invention, the steel which I provide consists of carbon 0.10% maximum, 17% chromium, 13% nickel, from 1.0% to 1.5% manganese, 3.0% molybdenum, 3% copper, 0.25% titanium, 0.40% columbium and the remainder substantially all iron. Incidental amounts of phosphorus, sulphur and silicon, of course, are present, the latter not exceeding 0.7% and the other two individually not exceeding 0.03%.

The particular form of heat-treatment which I employ for enhancing the load-carrying ability of the steel is of the character of an annealing and precipitation treatment. I heat up the steel to within solution temperature range of about 2050° F. to 2250° F., at which temperatures substantially all titanium goes into solution and also a part of the columbium. The solubility of columbium increases in the higher end of the heating range. With the titanium and a part of the columbium in solution, I quench the steel as in air, oil or water, preferably to room temperature. In a re-heat of the quenched metal for precipitation, which I effect as for example at about 1200° F. to about 1500° F., the temperature range preferred, titanium and columbium, and copper too it is felt, precipitate in the matrix. There is involved a critical dispersion of a finely divided precipitate in the metal lattice along the slip planes. This becomes clearly visible under the microscope after long exposures at high temperatures. In this, there is a precipitation of intermetallic compounds including titanium and co-

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lumbium. The copper too it is believed comes out in fine form, or possibly as an intermetallic compound including titanium, columbium and nickel. A portion of the titanium and columbium precipitate as carbides which increase in amount on the higher side of the precipitation treatment temperature range just noted. I quench the steel from the precipitation 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. These precipitates exist in critically dispersed finely divided condition between slip planes in the matrix, and remain uncoalesced and effective against creep and stress-rupture of the steels for extremely long periods of time in high temperature use of the steel.

As illustrative of the practice of my invention austenitic chromium-nickel stainless steel first is produced, this for example in the form of ingots, in the manner described in Patent No. 1,925,182 of Alexander L. Feild. These ingots are then heated and fashioned into billets by hot-rolling or forging from at temperature of about 2250° F. The billets are then forged into roughly formed gas turbine shafts, bolts, wheels, buckets, and the like. Machining to final size is achieved as desired. Fabrication of certain parts by welding with the oxy-acetylene torch, or electric arc means, employing welding rods preferably of approximately the same analysis as the stock being welded, is undertaken where desired.

As a matter of further preference, subsequent to the rough forging and machining of my turbine parts, I heat the same at a temperature of say 1200° F. for about five hours. These are then quenched as by air-cooling, and then pickled.

The turbine equipment which I provide is corrosion-resistant and heat-resistant. Moreover, it is capable of withstanding the exacting conditions of duty at high temperatures up to about 1500° F. or more, over long periods of continuous use without grain growth, fatigue or failure by creep or stress-rupture. In use, the turbine parts display reliable strength in tension, compression and torsion. They are resistant to warping, and resist harmful scaling and corrosive or scouring attack by oxidizing and reducing gases at high temperatures.

In way of further illustration of properties, a sample of forged and aged metal (forged from 2250° F. and aged at 1200° F. for about five hours followed by air-cooling) taken from my turbine parts and analyzing approximately 0.09% carbon, 16.93% chromium, 13.10% nickel, 1.21% manganese, 2.98% copper, 2.95% molybdenum, 0.21% titanium, 0.43% columbium and the remainder substantially all iron, at the end of a 1000 hour tensile test at 35,000 p. s. i. at 1200° F. had a total extension of 0.60% in a 2-inch gauge length. This represents a rate of elongation of 0.000218% per hour. It therefore can be seen from the present example that the elevated temperature properties of my stainless steel, and products and articles thereof, are of an extremely high order with respect to stress-rupture resistance and creep.

I have exposed other samples of steel of the composition just noted to stress-rupture tests at 1200° F. and found the same to endure a 49,000 pound per square inch stress for 10 hours, and 43,000 p. s. i. for 100 hours, and 38,500 p. s. i. for 1000 hours.

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Still other samples, these analyzing 0.090% carbon, 17.53% chromium, 13.18% nickel, 2.99% molybdenum, 2.99% copper, 0.42% columbium, 0.29% titanium, 1.21% manganese, and the remainder substantially all iron, were prepared and subjected to test with the following results:

TABLE I

Stress-rupture test at 1200° F.

Condition A, annealed at 2050° F. for one-half hour and water quenched, plus aging at 1200° F. for five hours and water quenched:

Stress	Time for Rupture
P. s. i.	Hours
48,000	10
40,250	100
34,500	1,000

Condition B, annealed at 2250° F. for one-half hour and water quenched, plus aging at 1200° F. for five hours and water quenched:

Stress	Time for Rupture
P. s. i.	Hours
60,000	10
48,000	100
38,500	1,000

TABLE II
Creep tests

Condition	Test Temp.	Load	Initial Extension	Extension after 500 hrs.	Rate of Extension, percent in 100,000 hrs. between 900th and 1800th hour
	° F.	P. s. i.			
A	1,200	18,000	0.105	0.140	1.10
B	1,200	20,000	0.145	0.180	0.88
B	1,350	10,000	0.055	0.140	1.07

My austenitic chromium-nickel stainless steel is capable of fabrication in a simple, direct and economical manner by virtue of the comparative ease of working, despite the high temperature properties of the same, as by means of hot-forming operations and through the use of conventional welding methods. The chromium-nickel stainless steel used therefore has by virtue of the particular combination of elements therein the remarkable ability to be worked and subjected to precipitation slip-interference treatment during the product manufacturing operations, and to withstand conditions surrounding the use of the resulting finished products.

Thus, it will be seen that there is provided in this invention austenitic chromium-nickel alloy stainless steel and products thereof in which the various objects noted, together with many thoroughly practical advantages are successfully achieved. It will be seen that the products are tough, strong and durable, corrosion-resistant and heat-resistant and are well adapted to withstand continuous high temperature duty over long periods of time and under the many variable 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 is to be understood that all matter described

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herein is to be interpreted as illustrative and not as a limitation.

I claim:

1. Hot workable chromium-nickel stainless steel, essentially consisting of 12% to 22% chromium, 10% to 21% nickel, 0.10% to 2% manganese, 2% to 4% molybdenum and 2% to 4% copper, 0.01% to 0.15% carbon, 0.15% to 0.75% titanium, 0.20% to 1.10% columbium and the remainder substantially all iron, said steel being substantially fully austenitic and susceptible to precipitation and critical dispersion of a finely divided precipitate, including columbium and titanium from solution to enhance load-carrying capacity for high temperature duty.

2. In a method of conditioning austenitic chromium-nickel stainless steel for high temperature duty, providing a steel essentially consisting of about 12% to 22% chromium, with about 10% to 21% nickel, manganese in amounts between about 0.10% to 2%, approximately 2% to 4% each of molybdenum and copper, between 0.01% to 0.15% carbon, and 0.15% to 0.75% titanium, 0.20% to 1.10% columbium, and the remainder substantially all iron; then heating the steel at such temperature as to provide said titanium and part of the columbium in solid solution; and reheating said steel within the approximate range of 1200° F. to 1500° F. to achieve precipitation and critical dispersion of a finely divided precipitate including columbium and titanium from solution and increased high temperature load-carrying capacity of the metal.

3. In a method of producing high-temperature-duty austenitic chromium-nickel stainless steel articles, the art which comprises providing a steel essentially consisting of about 12% to 22% chromium, with about 10% to 21% nickel, manganese in amounts between about 0.10% to 2%, approximately 2% to 4% each of molybdenum and copper, between 0.01% to 0.15% carbon, and 0.15% to 0.75% titanium, 0.20% to 1.10% columbium, and the remainder substantially all iron; then heating the articles within the approximate temperature range of 2050° F. to 2250° F. to provide said titanium and part of the columbium in solid solution; working the same to desired shape and size; and re-heating said articles at temperatures sufficiently high to achieve precipitation and critical dispersion of a finely divided precipitate including columbium and titanium from solution and increased high temperature load-carrying capacity of the metal.

4. Chromium-nickel stainless steel for high temperature duty, essentially consisting of 12% to 22% chromium, 10% to 21% nickel, 0.10% to 2% manganese, 2% to 4% molybdenum and 2% to 4% copper, 0.01% to 0.15% carbon, 0.15% to 0.75% titanium, 0.20% to 1.10% columbium, and the remainder substantially all iron, said steel being austenitic, with any ferrite only in traces, and having a finely divided precipitate in critically dispersed form for slip-interference.

5. Chromium-nickel stainless steel for high temperature duty, essentially austenitic in structure, with any ferrite only in traces, and essentially consisting of approximately 17% chromium, 13% nickel, 1% manganese, 3% molybdenum, 3% copper, 0.2% titanium, 0.4% columbium, 0.1% carbon and remainder substantially all iron, at least said titanium and columbium being partially precipitated in critically dispersed form for slip-interference.

6. Wrought austenitic stainless steel articles for high temperature duty characterized by great

strength and great resistance to creep at high temperatures, said articles essentially consisting of about 12% to 22% chromium, 10% to 21% nickel, 0.10% to 2% manganese, 2% to 4% molybdenum and 2% to 4% copper, 0.01% to 0.15% carbon, 0.15% to 0.75% titanium, 0.20% to 1.10% columbium and the remainder substantially all iron, said titanium and columbium being partially precipitated in critically dispersed form for slip-interference.

7. In a method of producing high-temperature-duty austenitic chromium-nickel stainless steel in which any ferrite is present only in traces, the art which comprises providing a steel essentially consisting of about 12% to 22% chromium, about 10% to 21% nickel, manganese in amounts between 0.10% to 2%, approximately 2% to 4% each of molybdenum and copper, about 0.01% to 0.15% carbon, about 0.15% to 0.75% titanium, about 0.20% to 1.10% columbium and remainder substantially all iron; heating the steel within

the approximate temperature range of 2050° F. to 2250° F.; cooling the same; and re-heating the steel within the approximate temperature range of 1200° F. to 1500° F.

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