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## ALLOY STEEL

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4 Claims. (Cl. 75—125)

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The present application is a continuation-in-part of my copending application, Serial No. 768,718, filed August 14, 1947, which in turn is a continuation-in-part of application, Serial No. 705,245, filed October 23, 1946, and the invention relates to high temperature stainless steel and products and articles of the steel.

An object of my invention is the provision of austenitic stainless steel which, in addition to having many useful high temperature properties, has good low-temperature tensile strength and may be satisfactorily worked.

Another object of this invention is that of providing austenitic stainless steel of the character indicated having highly satisfactory and dependable resistance both to creep and stress-rupture under load at elevated temperatures.

A further object of my invention is the provision of austenitic stainless steel of the character indicated which is substantially economical and satisfactory to produce.

A still further object of this invention is the provision of articles and products made of steel of the character hereinbefore set forth.

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

The invention, accordingly, consists in the combination of elements and in the features of composition, articles and products, 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 stainless steels in general, whether they be of a chromium-nickel grade or of straight chromium grade, to some valuable extent possess the property of surface stability at high temperatures and are useful where resistance to corrosive attack in the presence of heat is of importance. Recently, however, demands for high temperature duty is frequently called upon, not only to serve with appreciable immunity from the attack of certain corrosive agents, but to possess great strength and resistance to creep and rupture while under load at high temperatures. There are times, too, where low-temperature strength and other properties of high temperature steels enter as an important consideration, as where the steel is to be used in the form of high temperature turbine parts

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which are intermittently operated so as to expose the metal to hot and cold conditions while under load. These diverse needs are not always fulfilled by stainless steels of specific composition; for example, two alloy steels of different compositions may be equally effective in their resistance to oxidation at high temperatures, yet while heated may display widely different properties, with regard to load-carrying ability at high temperatures.

The conventional austenitic chromium-nickel stainless steels for the most part are seriously limited in their high temperature physical properties. They often creep while heated, creep being a plastic deformation or stretch coupled with loss of strength ultimately leading to rupture of the steel. These steels sometimes also introduce difficulties having to do with tensile strength at low temperatures. In general, it can be said that the chromium-containing martensitic or ferritic stainless steels have greater tensile strength at low temperatures than do those of austenitic grade. It might be expected that this relation of strength would be retained at high temperatures. I find, however, that this does not follow.

Still, it is well recognized that many of the conventional austenitic steels are unsatisfactory, for meeting the standards of high temperature use, particularly where the steels are to be relied upon for withstanding mechanical stress. Engineering requirements have so far exceeded the properties available that other alloys are being sought for use while hot. The known creep-resistant and stress-rupture-resistant alloys in general are notoriously difficult to work or shape. In fact, they may have a variety of properties which promise satisfactory performance at high temperatures, yet do not respond favorably to working operations applied thereto for achieving desired products. The final products often are found to have imperfections resulting from inferior working properties of the metal. Also, where the products are not of a corrosion-resistant grade, high temperature operating conditions often will greatly accelerate the tendency to corrode.

An outstanding object of my invention, accordingly, is the provision of high temperature austenitic stainless steel wrought products and

articles, which are sound and capable of resisting the damaging effects of corrosion and heat and of withstanding creep and rupture while subject to high mechanical stress at elevated temperature, and which have excellent low-temperature tensile strength and many other highly satisfactory low temperature properties.

Referring now more particularly to the practice of my invention, I provide high temperature chromium-nickel stainless steels which importantly contain substantial amounts of phosphorus, molybdenum and copper. These steels, in addition to having excellent high temperature properties including resistance to stress-rupture and creep, have excellent physical properties at relatively low temperatures such as at room temperature. Especially, the steels have excellent low temperature tensile strength and are readily forged and worked such as by hot-cold forging to desired shape. In view of the ability of the steels to resist stretch and other effects of load at high or low temperature, I frequently produce such products as turbine discs thereof, these for operation at different temperatures prevailing in each body such as at relatively low temperatures in the center and at higher temperatures at the edge. The steels also have excellent relaxation properties, relaxation being the ability to maintain a low rate of loss of stress when under a fixed strain at high temperatures. Certain of the products which I produce of the steel, therefore, take the form of bolts and high temperature fastening devices which have the property of remaining firm and tight in the initially seated position.

My stainless steels, or products and articles of the steel, more particularly contain approximately 0.01% to 0.15% carbon, 12% to 22% chromium, 8% to 21% nickel, from 0.05% to 0.5% phosphorus, 1.5% to 4% molybdenum, 2% to 4% copper, 0.10% to 2% manganese, and the remainder substantially all iron. Small amounts of other elements as for special purposes sometimes are present in the steel; however, I find that by avoiding the use of titanium and columbium, not only are savings had in the cost of materials entering the alloy, but considerably better low-temperature strength is had along with improved hot-cold forging properties. Also, in producing the steel substantially free of titanium and columbium, pouring difficulties are lessened. Columbium, and especially titanium, give rise to various difficulties in teeming and in the mold such as segregation and scum formation and tend to give nitride and oxide stringers which, as during or after the steel has been forged or rolled, impair strength and load-carrying ability. I, therefore, keep the steel substantially free of titanium and columbium and of oxides and nitrides of these elements.

My chromium-nickel-phosphorus stainless steel importantly is substantially wholly austenitic. Ferrite, if present at all, is only in traces preferably not exceeding about 1.5% to 2% by volume. This virtual exclusion of ferrite, and the inclusion of critical amounts of carbon, phosphorus, copper, molybdenum and manganese in the steel, I find enables high temperature use at temperatures even so high as 1200° F. to 1700° F. or more, and for resisting creep, relaxation and stress rupture. With a higher carbon content than within the composition limits of my steel, the working properties suffer and products of the metal are not so easily produced. Likewise, with a manganese content substantially exceeding 2% there is a loss in hot-working properties. With appreciable lowering of the phosphorus, molybdenum and copper content, the high temperature load-carrying characteristics of the steel suffer, and with appreciable increase, workability disappears.

The stainless steel and articles and products which I provide often are useful without particular heat treatment or after annealing. I achieve a remarkable increase though in the high temperature load-carrying ability, and also better low-temperature properties, by employing heat treatment in the nature of an annealing and precipitation treatment. In the annealing operation, I heat the steel to a sufficiently high temperature and for long enough time to put at least part of the copper into solid solution. When desired, advantage is taken of the annealing temperatures to hot-work the steel. A preferred temperature range for this purpose is that of about 2050° F. to 2250° F.

After the heating for solubility, I quench the steel preferably at about room temperature, for example, while using air, oil or water as the quenching medium. This annealed and quenched steel is substantially wholly austenitic. It is formable and machinable, and, illustratively by these measures, I readily produce such products as turbine blades, rotors, nozzles, turbo-supercharger parts, heat engine valves as for internal combustion engines, high-temperature chemical equipment parts for example to use under high pressure conditions, or rivets, bolts and fasteners, and numerous other products which are subjected to high mechanical stress both while hot and cold in corrosive surroundings. Not only do the products have high temperature properties, but they have high tensile strength at low temperatures. They are resistant to creep and stress-rupture and are highly resistant to corrosion in either the hot or cold condition. The low-temperature strength of the steel is good, and I often enhance this as by subjecting the steel to hot-cold forging or working as in producing the products.

To achieve precipitation heat treatment of the annealed steel, I reheat the metal, this time preferably to within an approximate temperature range of 1200° F. to 1500° F. and quench. Upon holding the steel at temperature for a sufficient period of time, the desired precipitation hardened properties are had. These highly desirable results had may be due to various carbides and phosphides precipitated within the mixture in finely divided form. Or they may be due to the precipitation of some intermetallic compound of copper and nickel, and possibly iron, in critically dispersed form in the metal lattice along the atomic slip planes. Or the copper present may remain in solution and inhibit coalescence. Regardless of theory, however, I find that my steel has excellent properties. The quenched metal has a fine grain structure and is further improved in load-carrying capacity and creep-resistance. The precipitated material remains uncoalesced between the atomic slip planes and effective against creep and stress-rupture of the steel for extremely long periods of time at high temperatures.

The austenitic phosphorus-containing steel which I provide thus has, by virtue of the particular combination of elements therein, the remarkable ability to be worked and fabricated into products and articles having high-temperature properties which are readily enhanced, if desired, by precipitation slip-interference

treatment of the metal as during the product manufacturing operations. The comparative ease of working the high-temperature metal, as by means of hot-forming or hot-cold forming operations, is a valuable and practical aspect from the standpoint of achieving the products and articles.

My turbine equipment, or other products of the steel, are very satisfactory for withstanding the vigorous effects of high temperatures, this for example over long periods of use under stress and without difficulty from grain growth or creep or failure by fatigue or rupture. Further, the equipment resists warping and hurtful scaling and corrosive or scouring attack by gases at high temperatures.

In a more specific preferred composition, my steel and the products made thereof contain, in approximate percentages, 0.08% to 0.15% carbon, 15% to 17.5% chromium, 12% to 15% nickel, 0.075% to 0.15% phosphorus, 2.75% to 3.50% copper, 1.75% to 2.75% molybdenum, anywhere up to 1.25% manganese, and the remainder substantially all iron. Such elements as silicon and sulphur, while usually present, preferably are small in amount.

As illustrative of the practice of my invention, I provide austenitic chromium-nickel-phosphorus stainless steel having the preferred composition just noted, as by producing a melt of the same in a conventional electric steel making furnace of the Heroult type in accordance with any one of several well-known melting processes having general applicability to the production of stainless steel such, for example, as the process generally described in the United States Letters Patent 1,925,182 issued to Alexander L. Feild on September 5, 1933, or the United States Letters Patent 2,056,162 issued to William B. Arness on October 6, 1936, or in the Patent 2,455,073 issued to Donald L. Loveless on November 30, 1948. I work the austenitic steel from ingots into billets by hot-rolling or forging at a temperature of about 2250° F. I work the billets into the rough form of such products as rotor blades and blade supports for gas turbines, ending, for example, with hot-cold forging or rolling operations. Cutting and machining to size are achieved where desired. Also, fabrication by welding with an oxy-acetylene torch, or by electric arc means, employing weld rods for giving a deposit preferably of the same composition as the parent metal, is undertaken if desired. Following the working and fabricating operations, for example, I anneal the steel so as to put the copper in solution, quench the metal, and thereafter reheat the same to achieve precipitation heat treatment. The reheating illustratively is at approximately 1200° F. in a conventional heat-treating furnace, say for about five hours at temperature to achieve precipitation hardening. I quench the precipitation-heat-treated articles or products as by cooling in air. Slip interference, accordingly, prevails in the chromium-nickel-phosphorus steel to enhance the load-carrying capacity.

Table I is presented below to illustrate the highly satisfactory low-temperature tensile properties, and the high temperature creep and stress-rupture properties of my austenitic chromium-nickel-phosphorus stainless steels. The tabulated results relate more particularly to one of my steels which contains about 0.098% carbon, 16.44% chromium, 13.88% nickel, 0.103% phosphorus, 2.44% molybdenum, 3.22% copper, 0.46% manganese, 0.39% silicon, 0.013% sulphur, and the remainder substantially all iron. This steel was annealed at about 2250° F. for one-half hour, water-quenched, then precipitation-heat-treated at approximately 1350° F. for five hours and cooled in air. With the steel in this annealed and precipitation-heat-treated condition, the following room temperature tensile properties and high temperature stress-rupture properties were noted:



TABLE I

*Physical properties of Cr-Ni-P stainless steel*

A. ROOM TEMPERATURE TENSILE PROPERTIES

| Ult. Tens. Str. p. s. i. | 0.2% Yld. Str., p. s. i. | Elong. 2", per cent | Red. of Area, per cent |
|---|---|---|---|
| 102,000 | 57,000 | 32.5 | 50.0 |

B. STRESS-RUPTURE PROPERTIES

| Temp., °F. | Load, p. s. i. | Fracture Time, Hrs. | Elong. 2", per cent | Red. of Area, per cent |
|---|---|---|---|---|
| 1,200 | 48,000 | 30 | 20.0 | 29.0 |
| 1,200 | 46,000 | 99 | 15.5 | 25.0 |
| 1,200 | 44,000 | 450 | 9.5 | 17.3 |
| 1,500 | 18,000 | 38 | 5.0 | 4.2 |
| 1,500 | 15,000 | 215 | 5.0 | 6.0 |
| 1,500 | 13,000 | 442 | 3.5 | 4.2 |

Thus, it will be seen that there are provided in this invention, austenitic chromium-nickel-phosphorus stainless steels and products and articles of the steel, in which the various objects noted herein, together with many thoroughly practical advantages are successfully achieved. It will be seen that the steel, products and articles are tough, strong and durable, corrosion-resistant and heat-resistant, and are thoroughly capable of withstanding the effects of high temperatures and load over long periods of time. It will also be seen that the steels have great physical strength at low temperatures and are highly useful under either high or low temperature conditions.

It will be appreciated that in certain high temperature uses or articles and products of the steel, reliance may be had upon the prevailing high temperature to achieve precipitation for enhancing the load-carrying capacity and resistance to creep.

While the annealed and precipitation-heat-treated products offer improved resistance to creep and stress-rupture, as compared with products of the steel which have not been subjected to the heat treatment, either the treated or untrated products have useful high temperature and low temperature properties which may be availed upon in the light of immediate needs.

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

I claim:

1. Austenitic chromium - nickel - phosphorus stainless steel of good high temperature properties and good low temperature strength and working properties as well containing approximately 0.01% to 0.15% carbon, 12% to 22% chromium, 8% to 21% nickel,, from 0.05% to 0.5% phosphorus, 1.5% to 4% molybdenum, 2% to 4% copper, 0.10% to 2% manganese, and the remainder iron.

2. Austenitic chromium - nickel - phosphorus stainless steel of good high temperature properties and good low temperature strength and working properties as well containing approximately 0.08% to 0.15% carbon, 15% to 17.5% chromium, 12% to 15% nickel, 0.075% to 0.15% phosphorus, 2.75% to 3.50% copper, 1.75% to 2.75% molybdenum, up to 1.25% manganese, and the remainder iron.

3. Age-hardened austenitic chromium-nickel-phosphorus stainless steel articles of good high temperature properties, containing approximately 0.01% to 0.15% carbon, 12% to 22% chromium, 8% to 21% nickel, from 0.05% to 0.5% phosphorus, 1.5% to 4% molybdenum, 2% to 4% copper, 0.10% to 2% manganese, and the remainder iron, the structure of said steel including a dispersed finely divided precipitate derived by annealing and precipitation heat-treatment.

4. Hot cold-worked austenitic chromium-nickel-phosphorus stainless steel articles of good high temperature properties containing approximately 0.01% to 0.15% carbon, 12% to 22% chromium, 8% to 21% nickel, from 0.05% to 0.5% phosphorus, 1.5% to 4% molybdenum, 2% to 4% copper, 0.10% to 2% manganese, and the remainder iron.



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