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STAINLESS STEEL

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My invention relates generally to chromium-nickel stainless steels. More particularly, it is directed to preciptation-hardenable chromium-nickel stainless steels and a method for producing the hardened steel. As well, it relates to precipitation-hardened products or manufactures fabricated from such steels, particularly those displaying high resistance to corrosion and retaining high strength qualities when exposed to enduring high temperature duty.

An object of my invention is to provide a stainless steel of the well-known chromium-nickel type which, while hardenable by low temperature treatment in simple, direct and thoroughly effective manner, thereupon displays effective resistance to corrosion and high physical strength, both at room temperature and on subsequent exposure in service to extremely high temperature duty, and which can be effectively worked as by rolling and drawing.

Another object is to provide a steel of the general type described, together with a simple and direct method of producing the same, which steel displays superior forming and machining properties in the pre-hardened condition.

Another object is to provide a precipitation-hardened stainless steel of the chromium-nickel type which displays high values of yield and ultimate strength, is substantially free from objectionable directionality arising from cold-rolling the usual austenitic chromium-nickel steels to the so-called "high tensile" condition, and which exhibits high resistance to corrosion, and high strength properties when exposed to high temperature working conditions.

A still further object of my invention is the provision of hard stainless steel articles of manufacture which are generally of the chromium-nickel type, which may be readily produced from roughly formed castings or wrought products by forming, machining or the like, and subsequently hardened without sacrifice of either shape or surface qualities and without appreciable departure from dimensions imparted thereto.

Other objects and advantages of my invention in part will be obvious and in part more fully pointed out during the course of the following disclosure.

Accordingly, my invention resides in the combination of component elements, the compositions of materials, the several procedural steps and in the relation of composition to procedural steps as described hereinafter, the scope of the application of which is more fully set forth in the claims at the end of this disclosure.

As conducive to a more clear understanding of certain essential features of my invention it may be here noted that in a sense, my invention is an improvement to that of Letters Patent of the United States No. 2,482,096 issued to William C. Clarke, Jr., on September 20, 1949, for "Alloy and Method."

As recited in the aforesaid Clarke patent, a serious problem existed in the field of stainless steels of combining the inherent and advantageous workability of the

stably-austenitic chromium-nickel steels with the high strength properties and hardenability of the martensitic grades of either straight-chromium alloys or chromium steels including relatively small additions of nickel. Moreover, and as described by Clarke, the problem existed in the hardening of articles fashioned from the straight chromium alloys, of retention of the dimensions previously imparted thereto, with alloy in pre-hardened condition, while avoiding the surface discoloration and the heat scale which usually attended quench-hardening treatment from high temperature condition. Departure from dimensions, as by twisting or warping, was particularly noticeable in fabricated elements which were extremely thin, i. e. having large ratio of surface area to volume.

Clarke undertook to provide an unstable austenitic-ferritic alloy transformable above room temperature which (through the addition of copper) and while retaining the advantageous properties of austenitic metals, nevertheless lent itself readily to low temperature age-heating after transformation. By Clarke's teachings consistent results were achieved, with ultimate products displaying superior strength qualities with absence of detrimental directionality, surface discoloration or heat scale. The low temperatures employed in hardening, whereby a copper-rich phase, finely dispersed, was cast down through the metal, ensured that the close tolerances which were readily imparted to the metal, itself freely workable while in its predominantly martensitic-ferritic pre-hardened condition, were effectively retained upon hardening.

I have found, however, that present-day requirements necessitate substantial increase in strength properties of both the steel and the products fabricated therefrom upon prolonged exposure to high temperature duty, such, illustratively, as is encountered in valves handling superheated steam, in jet engines and the like. Increased resistance to corrosion is likewise an objective. The teachings of those heretofore working in the art, including those of Clarke, have for one reason or another fallen short of entirely fulfilling these practical requirements.

An important object of my invention, therefore, is the provision of a basically chromium-nickel type stainless steel, which being first rendered suitable for fabrication in pre-hardened condition, is thereafter and while in fabricated condition age-hardenable at low temperatures, and will thereupon display superior properties of physical strength, coupled with high resistance to corrosion, under extremes of prolonged and enduring high temperature duty.

Referring now more particularly to the practice of my invention, I find that the replacement of a part of the chromium of the precipitation-hardenable 17–4PH steel of Clarke (analyzing approximately 17% chromium, 4% nickel and 3% copper and remainder iron) with a related quantity of the element molybdenum results in the production of an age-hardenable steel which displays all of the desirable work-properties of the copper-rich steel of Clarke when in pre-hardened condition. Moreover, following age-hardening, at a low temperature, my steel displays equal or even better strength and better corrosion resistance at room temperatures. Of particular importance, under enduring high temperatures, my steel possesses the additional important advantage of actually enjoying superior mechanical properties. The comparatively low temperatures at which the age-hardening treatment is carried out insure that the close dimensioning imparted during pre-hardened fabrication will be nicely retained, while surface stain and discoloration are effectively avoided.

Apparently the initial, transforming or solution-treatment of the steel produces an unstable austenite at high temperatures. And when this steel is cooled, as by quenching to room temperature, the copper remains in solid solution. During the age-hardening process following fabrication, the copper is precipitated out of solution in finely dispersed form. The copper acts to impart physical strength to the steel, while the molybdenum serves the function of insuring that these high strength properties are retained under high temperature operating duty. While the copper-rich Clarke steel displays good mechanical properties under normal atmospheric operating temperatures, detrimental loss of these qualities is observed when the working temperatures increase. Moreover, the steel of my invention possesses excellent mechanical properties at high temperatures as well as at room temperature. Striking improvement in the corrosion-resisting qualities is noted when the molybdenum is included in the metal.

Thus, in accordance with my invention, I provide a steel wherein by weight chromium ranges from about 12% to about 18%; nickel ranges from about 3.0% to about 5.0%; copper from about 2.25% to about 5.00%; molybdenum from about 1.00% to about 3.50%; manganese up to 1.00%; silicon up to 1.00%; phosphorus and sulphur up to 0.050%; and remainder iron.

Where advantage attends reduction in hardness of the metal in its pre-hardened condition, thereby increasing its workability, I may add either titanium or columbium, or both. These additives serve to tie up the carbon present in the metal, so that the latter cannot act as a hardening agent. To that end, the titanium, when present, is included in an amount up to about 5 times the carbon as a maximum. When columbium is employed it is used up to a maximum of about 8 times the carbon. By controlling the titanium and the columbium, I achieve a nice control over the hardness of the pre-hardened alloy without appreciable sacrifice of strength qualities in the subsequent hardened condition.

According to the practice of my invention I can achieve some saving in the quantity of nickel employed by adding to the steel, as a replacement for part of the nickel which otherwise would be included, a substantial quantity of manganese. With additional manganese present, that is, up to about 2.5%, I find it entirely reasonable to bring the nickel content to as low as about 2.25%. I do not completely remove nickel from the alloy, however, since nickel has the definite benefit of suppressing delta-ferrite. Manganese does not do this. Where I employ manganese as a nickel substitute, I preferably include nitrogen from, say, about .06% up to about .14%.

Not only does the inclusion of molybdenum in my steel bring about marked improvements in high temperature strength, but also increased corrosion resistance (all in hardened condition). I find that the steel is admirably suited for the production of castings. Moreover, it lends itself equally to working, as by rolling or drawing. Plate, sheet, strip, bar, rod, wire and the like are readily obtained.

With its superior hot duty corrosion resistance and high strength properties I am enabled to fashion my new steels into a host of ultimate articles of use by bending, pressing, stamping, machining and like operations. These include the stems of steam valves as well as other valve parts. It is suitable for pump shafting, bolts and pump impellers. Corrosion-resisting characteristics of the steel enable it to be fashioned into cutlery of enduring quality. By way of example, other articles for high temperature duty include high temperature fastening devices on jet engines such as bolts, screws, washers, nuts and the like. It admirably serves for the production of frames for jet engines and for fasteners for the skin of planes.

I find that in the general analysis hereinbefore recited I advantageously include boron up to 0.005% maximum where some improvement is desired in the hot-working properties of the steel in the pre-hardened condition. Illustratively, boron additives are of advantage when hot-working the steel into plate, sheet, strip, bar, rod, wire and the like. Boron serves the further useful purpose of improving the fluidity of the molten metal in the furnace, and in teeming. Where desired, vanadium may be added up to 1.0% maximum and tungsten up to 3.0% maximum to further improve high temperature strength.

Typically and according to the practice of my invention my new steel, either in the form of a casting or as worked from the ingot into plate, sheet, strip, bars, rods and wire, is solution-treated at a temperature ranging from about 1700° to about 2000° F. It is quenched in air or in oil at about 400° F. per minute, to room temperature, or down to about —100° F. This conditions the steel for subsequent forming and fabrication; also for final hardening of the product which is thus formed and fabricated.

The precise temperature employed during solution treatment depends, of course, upon the specific composition of the metal. The temperature selected and the duration of the solution-treatment are sufficient, however, and are so correlated to provide a structure which is either unstable austenite or austenite-ferrite. In either case, the copper and molybdenum are in solid solution. After the steel is brought to temperature, it is quenched, either in oil or in air, and the austenite is transformed to an unstable martensite-ferrite, with copper trapped in solution. That is, with the quenching step in the solution-treatment, I achieve transformation of the austenitic constituent. But this phase transformation takes place so rapidly that the copper remains in solution, without any substantial precipitation thereof. Usually I find that when the quantity of nickel and/or manganese or other austenite formers in the material fall on the low side the temperature of heating should be on the high side, this to an extent sufficient to carry the maximum quantities of copper into solution during the heating stage, with subsequent transformation of the material upon quenching. Where desired, any residual austenite may be transformed by quenching down to —100° F. Of course, this sub-room temperature cooling treatment is optional. Generally, this solution-treatment may be likened to an annealing treatment.

The transformed steels display reasonable ductility with hardness, in the pre-hardened condition, of approximately the range given in Clarke. Moreover, and just as observed in Clarke, the steel is free of detrimental directionality. The steels are then formed and fabricated into desired articles of manufacture as noted.

After forming the material into desired products, I achieve successful hardening, in simple and direct manner and without specialized equipment, by reheating the metal to a temperature range from about 800° F. to about 1200° F. and then cooling. Ordinarily and preferably I hold the steel in the furnace for about one hour, although this ageing time may endure up to about eight hours without appreciable over-ageing. A conventional annealing furnace may be advantageously used for this low-temperature hardening treatment, if desired. This low-temperature age-hardening is conducted without appreciable danger of distortion, discoloration, or heat-scaling commonly resulting from exposure to high temperature.

While prolonged ageing treatment may be employed without detrimental over-ageing, I do not resort to such treatment except when increased toughness in the resulting product is sought, perhaps at some sacrifice of hardness and yield strength. Typically, where toughness at the expense of hardness is sought, I preferably conduct the ageing treatment at a temperature somewhat above 875° F. for a period in excess of say four hours.

As specific examples of the practice of my invention two

heats of steel responding in analysis to the general composition heretofore given are given in Table I below:

TABLE I

Specific examples of 17–4PH and Mo *steel*

Heat	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Cb	V	W
A	.041	.72	.019	.014	.69	14.78	4.02	2.35	3.49	.34	.33	------
B	.037	.75	.018	.014	.64	15.54	3.99	1.34	3.54	.34	.33	------
C	.048	.68	.011	.010	.50	15.26	4.05	1.55	3.41	.34	.46	1.62

I subjected the steels of Table I to solution-treatment at 1900° F. for one-half hour and then quenched the same in oil at room temperature. Certain specimens were retained in pre-hardened condition, for comparison as to physical properties. Other specimens, thus obtained, were reheated to 900° F. for one hour and then air-cooled to room temperature. A comparison of important physical properties between annealed and hardened conditions is disclosed in the following Table II.

TABLE II

Physical properties of the steel in (A) *the transformed condition and in* (B) *the transformed and hardened condition.*

(A)

Heat	Treatment	Ult. Tens. Str., p. s. i.	.2% Yld. Str., p. s. i.	Percent Elong.	Percent Red.	Rockwell Hardness
A	1,900° F.—½ hr.—oil quench.	152,500	101,000	16.0	55.0	C31
B	----do----	153,000	102,000	15.5	52.0	C31
C	----do----	149,000	108,000	16.0	54.0	C27

(B)

A	1,900° F.—½ hr. +900° F.—1 hr.—air cool.	192,800	169,800	16.0	56.5	C43
B	----do----	195,200	173,800	14.5	55.9	C43
C	----do----	196,000	183,000	14.0	53.0	C44

From the foregoing it is apparent that in the pre-hardened condition the metal is relatively ductile, with only moderate hardness. It is readily workable. When subsequently hardened, however, the metal displays great strength.

The addition of molybdenum vastly improves the high temperature duty characteristics of my new steel as contrasted with the regular grade of 17–4PH. This is conclusively established by the comparative tests presented in the following Table III. There I disclose the results of stress rupture tests conducted at 900° F., using test specimens of the regular 17–4PH steel as compared with the 17–4PH+Mo steel of my invention, these latter being formed from heat A in Table I.

TABLE III

*Comparative stress rupture tests on regular 17–4PH steel and 17—4PH+*Mo *steel (heat A)*

	Load, p. s. i.	Temp., ° F.	Time to Fracture in Hrs.
Regular 17-4PH	90,000	900	68.
A(17-4PH+Mo)	90,000	900	1,750 (in progress).
Regular 17-4PH	85,000	900	85.
A(17-4PH+Mo)	85,000	900	3,100 (in progress).

It will be seen from the foregoing that when subjected to 90,000 lbs. unit load at 900° F. the regular 17–4PH steel failed after 68 hours. As contrasted with this, after 1750 hours the speciments formed of 17–4PH+Mo steel displayed no signs of failure, and the tests are still in progress. With somewhat lower stressing, 85,000 lbs. per square inch, and at the same temperature of 900° F., the regular 17–4PH steel failed in 85 hours, while the molybdenum-containing steel successfully sustained 3100 hours of loading, with tests still in progress.

I have found that some criticality attends the chromium and molybdenum contents of the steel of my invention. Where optimum high temperature properties are sought, as for example wrought steels designed for high temperature applications, the following analysis is preferable: Carbon about 0.04%, chromium about 15.0%, nickel about 4.0%, copper about 3.5%, molybdenum about 2.2%, columbium about 0.3%, manganese about 0.6% to .7%, silicon about 0.5%, and remainder iron.

When, however, I seek superior corrosion-resisting properties, perhaps with some slight sacrifice of physical properties under high temperature duty, I increase both the chromium and the molybdenum, to the following preferred analysis: Carbon about 0.04%, chromium about 17.0%, nickel about 4.0%, copper about 3.5%, molybdenum about 3.0%, columbium about 0.3%, manganese about 0.6% to .7%, silicon about 0.5%, and remainder iron.

I find, however, that no change need be made in the composition of the preferred steels to adapt them for casting or for working into various articles of ultimate use. I find them to be equally suitable for either practice.

Thus in the practice of my invention I provide a stainless steel which not only is well suited to low temperature hardening but retains the properties thus imparted thereto, i. e., superior physical properties under prolonged high temperature duty and important resistance to corrosion. As well, I disclose a method of precipitation-hardening such steels. I accomplish these objects as well as many other objects hereinbefore noted, along with many thoroughly practical advantages.

My new steel and method of producing the same makes it possible to produce various articles of manufacture which are precipitation-hardenable at low temperature, and this without substantial detrimental effect upon the steel from heating. The new pre-hardenable alloys can be cast, wrought or welded. They may be subjected to a number of forming, machining or fabricating operations to achieve a host of articles of ultimate use. Uniformly, the resulting products display both at normal and high temperature duty high yield strength and ultimate strength. The products are free from directionality. Adequate ductility is evidenced.

All of the results noted are achieved by what may properly be termed a single treatment alloy. That is, I produce an alloy which, following transformation treatment whereby the unstable austenite is transformed to a structure which includes chromium-nickel martensite, with copper, however, remaining captured in solution, is thereafter hardened in a single heat-treatment operation. And that heat-treatment is at comparatively low temperature so that heat-tint or heat discoloration is effectively avoided.

Since many possible embodiments may be made of my invention, and many changes in the embodiments hereinbefore set forth, it will be understood that the foregoing disclosure is to be interpreted as illustrative and not by way of limitation.

I claim as my invention:

1. A chromium-nickel stainless steel capable of being age-hardened at but moderately elevated temperatures and displaying in hardened condition, excellent strength and corrosion-resistant properties, along with freedom from directionality under enduring high temperature duty, essentially consisting of chromium about 12% to 18%, nickel about 2.25% to 5.0%, copper about 2.25% to 5.00%, molybdenum about 1.00% to 3.50%, boron up to 0.005% maximum, vanadium up to 1.0% maximum, tungsten up to 3.0% maximum, columbium up to about 0.80%, manganese up to about 2.5% maximum, nitrogen up to about 0.14%, carbon up to about 0.10% maximum, silicon up to about 1.00% maximum, phosphorus and sulphur each up to about 0.050% maximum, and remainder iron.

2. A precipitation-hardenable chromium-nickel stainless steel essentially consisting of chromium about 12% to about 18%, nickel about 3.0% to about 5.0%, copper about 2.25% to about 5.00%, molybdenum about 1.00% to about 3.50%, carbon up to about 0.10%, and the remainder substantially all iron.

3. In the production of precipitation-hardened chromium-nickel stainless steel, the art which comprises providing a steel analyzing about 12% to about 18% chromium, about 3.0% to about 5.0% nickel, about 2.25% to about 5.00% copper, about 1.00% to about 3.50% molybdenum, carbon not exceeding about 0.10%, and the remainder substantially all iron; heating the alloy at approximately 1700° to 2000° F. for a period of time sufficient to provide an unstable austenitic-ferritic structure which is copper and molybdenum-soluble and is transformable above room temperature without substantial precipitation of the copper; thereafter quenching the alloy to transform the same; and thereafter precipitating the copper, with substantial increase in hardness of the alloy, by reheating the alloy within a temperature range of about 800° F. to about 1200° F.

4. A precipitation-hardened chromium-nickel stainless steel essentially consisting of chromium about 12% to about 18%, nickel about 2.25% to about 5.0%, copper about 2.25% to about 5.00%, molybdenum about 1.00% to about 3.50%, carbon up to about 0.10%, manganese up to about 2.25%, nitrogen up to about 0.14%, silicon up to about 1.00%, phosphorus and sulphur each up to about 0.050%, and the balance substantially all iron.

5. A precipitation-hardened stainless steel displaying superior physical properties under enduring high temperature operating duty, and essentially consisting of carbon about 0.04%, chromium about 15.0%, nickel about 4.0%, copper about 3.5%, molybdenum about 2.2%, columbium about 0.3%, manganese about 0.6% to 0.7%, silicon about 0.5%, and remainder iron.

6. A precipitation-hardened stainless steel displaying superior corrosion-resisting properties and essentially consisting of carbon about 0.04%, chromium about 17.0%, nickel about 4.0%, copper about 3.5%, molybdenum about 3.0%, columbium about 0.3%, manganese about 0.6% to 0.7%, silicon about 0.5%, and remainder iron.

7. Precipitation-hardened chromium-nickel stainless steel castings essentially consisting of approximately 12% to about 18% chromium, about 3.0% to about 5.0% nickel, about 2.25% to about 5.00% copper, molybdenum ranging from about 1.00% to about 3.50%, and the remainder substantially all iron, said castings having a phase precipitated through the grains of the steel, which phase is rich in copper.

8. Precipitation-hardened chromium-nickel stainless steel high temperature-duty articles of manufacture such as valves, valve parts, nuts, bolts and washers essentially consisting of approximately 12% to about 18% chromium, about 3.0% to about 5.0% nickel, about 2.25% to about 5.00% copper, molybdenum in amounts between 1.00% to about 3.50%, columbium up to about 0.80%, vanadium up to about 1.00%, tungsten up to about 3.00%, carbon up to about 0.10% maximum, and the remainder substantially all iron.

9. Precipitation-hardened chromium-nickel stainless steel corrosion-resisting articles of manufacture such as cutlery, essentially consisting of chromium from about 12% to about 18%, about 3.0% to 5.0% nickel, about 2.25% to 5.00% copper, molybdenum from about 1.25% to about 3.50%, up to about 0.80% columbium, up to about 1.0% vanadium, up to about 0.10% carbon, and the remainder substantially all iron.

No references cited.