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ALLOY AND METHOD

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9 Claims. (Cl. 75—125)

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This application is a companion to my copending application, Serial No. 546,927, filed of even date herewith and entitled Alloy and method, and the invention relates to chromium-nickel stainless steels and more particularly to a method for hardening the same and preliminarily conditioning the same for hardening as well as both to pre-hardened and to precipitation-hardened products or manufactures thereof.

An object of my invention is the provision of a chromium-nickel stainless steel which is hardened by low temperature treatment and of a simple, direct and thoroughly effective method for hardening the same.

A further object of my invention is the provision of precipitation-hardened chromium-nickel stainless steels which possess high values of yield and ultimate strength both in tension and compression, together with reasonably high ductility, and which are substantially free from the directionality which characterizes the well-known austenitic chromium-nickel stainless steels in the cold-rolled or so-called "high tensile" condition.

A still further object of my invention is the provision of pre-treated chromium-nickel stainless steel products which readily may be worked, formed, machined or the like and subsequently hardened without sacrifice of shape, or surface qualities.

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

The invention accordingly consists in the combination of elements, composition of materials, and conditions of treatment, in the various operational steps, and in 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 stainless steels are defined as steels which comprise 10% to 35% chromium, with or without nickel, and with or without supplemental additions of copper, manganese, silicon, cobalt, molybdenum, tungsten, vanadium, columbium, titanium, sulphur, and the like, for special purposes, and a remainder which is substantially all iron. The carbon content usually is low, this being on the order of 0.03% to 0.20% although it may be higher for special purposes.

There are the straight-chromium hardenable steels such as the 12% to 18% chromium varieties, and chromium steels with small additions of nickel as the 16% chromium-2% nickel grades,

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both of which are hardened directly by quenching, preferably from temperatures in the vicinity of 1800° F. As increasing amounts of nickel are added to the straight-chromium alloys of the general character just mentioned, there is a change from magnetic, hardenable, ferritic-martensitic qualities to the grades, such as 18-8 chromium-nickel, which are stably austenitic, non-magnetic, and non-hardenable by heat treatment.

The predominantly ferritic-martensitic steels have many desirable physical properties in the hardened condition, including high tensile and compressive values, and high yield strength together with good directional properties. Products fabricated from the steels are in considerable demand. Unfortunately, however, the high temperatures required for quench-hardening offer an obstacle to the obtainment of end products which are free of heat-scale and surface discoloration. The hardened products also tend to be distorted as a result of intense heat in the hardening treatment. This tendency of course renders production within close dimensional tolerances time-consuming and costly. The many difficulties in hardening the products stand as noteworthy objections to the steels in commercial hardening practice especially in the case of flat-rolled products such as strip or sheet.

The predominantly austenitic chromium-nickel steels on the other hand are successfully subjected to a number of fabricating operations including hot working, cold forming and machining. They are joined by various methods such as by riveting, soldering or welding. Unfortunately, however, the steels as a result of cold-rolling or drawing have poor yield strength properties especially in compression along the direction of cold-rolling. Another disadvantage of these steels, of course, is their lack of response to hardening heat-treatment.

Some effort has been made in the prior art to provide stainless steels which are hardenable by heating to a temperature low enough to avoid or minimize oxidation and undue distortion. This effort has been to realize a precipitation, at this relatively low temperature, of a critically dispersed phase. An analogy presents itself in the case of the well-known aluminum alloys.

For example, in the prior art, it has been suggested to use titanium or columbium as hardening agents for chromium-nickel stainless steels. Such precipitation hardenable alloys have been disappointing either because the expected results are not actually obtained, or because of difficulties encountered in obtaining products of consistently uniform and reliable properties. Moreover, titanium is difficult to control in amount due to erratic recovery in the steel melting operation, and presents a very serious difficulty in the case of products to be welded because of the loss of titanium during the welding operation.

An outstanding object of my invention accordingly is the provision of a method wherein certain stainless steels comprising chromium, and nickel are rendered suitable for fabrication in relatively soft condition, and by which the steels are subsequently precipitation-hardened in the fabricated condition by treatment at temperatures sufficiently low to avoid substantial scaling, discoloration and distortion due to heat effects.

Referring now more particularly to the practice of my invention, I find that certain chromium-nickel stainless steels may be rendered suitable for low temperature hardening by closely correlating the amounts of chromium and nickel and introducing a critical amount of the ingredient copper. In accordance with my invention, I make up a stainless steel containing about 15.5% to approximately 18.5% chromium, nickel in an approximate range of 3.5% to 5.5%, copper in amounts between about 3.2% to 5.0%, carbon preferably not exceeding 0.10% and the balance iron. As an alternate embodiment of my invention, I find that certain desirable properties are had by including in the composition of the steel one or more metals of the group consisting of beryllium from traces up to about 0.25%. As another embodiment, I may include in the composition of the chromium-nickel-copper steel either titanium or columbium, the titanum preferably being not more than about 5 times the carbon content, and the columbium preferably not exceeding about 8 times the carbon.

My stainless steel, either in wrought or cast form, is then conditioned for subsequent forming and fabrication, and final hardening of the formed and fabricated product, by heating in a temperature range not lower than about 1550° F. and extending up to about 2000° F. depending upon specific composition of the metal for such time as to provide an unstable austenitic or austenitic-ferritic structure, with copper in solid solution, which is transformable above room temperature without substantial precipitation of the copper from solid solution. This is in the nature of an annealing treatment.

When the austenite-formers, particularly nickel, tend toward the low side in the general alloy composition range given, illustratively when nickel is present in amounts between about 3.5% and approximately 4.5%, I usually employ high temperatures of heating, as between about 1800° F. and approximately 2000° F., within the temperature range specified, to ensure maximum solubility of copper and subsequent transformation of the metal on quenching.

From the unstable condition had in heating, in which copper is held in solid solution, I quench the steel to low temperature, preferably to room temperature, whereby transformation of the austenitic constituent is effected without substantial precipitation of the copper. As quenched, the steel has gone through phase transformation. The steel is reasonably ductile and has a hardness of approximately Rockwell 20C to 33C. It is substantially free from directional properties as hitherto defined. It is readily formable and machinable, one or more of which properties contribute in making it possible to fabricate the steel at this point into any of a wide variety of pre-hardened products, if desired.

From the transformed or pre-hardened chromium-nickel-copper stainless steels which now are precipitation hardenable by a single heat treatment. I provide products in such forms as sheet strip, plates, bars, wire, rounds. As desired I provide shapes which are more intricate, illustratively trim, structural members and the like, as for the aircraft industries. Also I provide cold-headed bolts and screws requiring hard shanks, shafting, surgical instruments, valves and valve seats. In these articles and products I take advantage of the excellent forming properties of the pre-hardened metal such as cold-forming, upsetting, drawing, machining, stamping, punching, or other steps which are consistent with the properties of the metal.

After the transformation by annealing and fabricating steps to be performed are achieved, I harden the alloys by an age-hardening or precipitation-hardening treatment at a temperature of about 850° F. to approximately 950° F., preferably at about 900° F. This precipitation-hardening is had without substantial danger of distortion, heat-scaling or discoloration from high temperature effects. An annealing furnace will do for the age-hardening operation. The steel, as in the form of the fabricated products, is held at hardening heat in the furnace preferably for about half an hour, although the time of treatment may vary from approximately 15 minutes to 2 hours without resultant excessive under-aging or over-aging. The treatment serves to precipitate a copper-rich phase in the metal grains. This is not visible under an ordinary light microscope, but I find that it can be photographed with the aid of an electron microscope. It is this precipitated copper-rich phase which gives the hardness.

Following the hardening treatment, the products are taken from the furnace and to advantage are quenched to room temperature. In hardened condition, particularly after quenching, the products display high values both with respect to tension, and compression, high yield strength, good directional qualities, a reasonable degree of ductility, and hardness values which usually fall in or near the range of Rockwell C37 to C45. The alloy steel and products thereof also are quite resistant to salt spray and to corrosion in ordinary atmosphere, both before and after hardening.

As a further feature of my invention, I provide welded joints and welded products from the chromium-nickel-copper stainless steels disclosed herein and treat the metal, including the weld, in accordance with my annealing and hardening treatments. In order to afford a beneficial source of weld addition metal, I also provide weld rods which include as filler or deposit metal the chromium-nickel-copper alloy steel disclosed.

The steels which I treat are weldable by arc, gas, spot, or other welding methods without substantial loss of copper. This is an important advantage, remembering that alloys which contain aluminum, titanium, or the like, to promote the precipitation-hardening effect, suffer a loss of the hardening material due to welding.

As illustrative of the practice of my invention, I process one of the chromium-nickel-copper stainless steels in the composition ranges mentioned hereinbefore, with nickel on the high side, for example, one of the alloys including about 4.5% to approximately 5.5% nickel, as in the form of wrought or cast metal stock, in a suitable heat-treating furnace at approximately 1550° F. up to about 1700° F., preferably at about 1600° F. This heating is had for a not too critical period of time, say for 15 minutes up to an hour or more at temperature, to obtain an off-balance austenitic or austenitic-ferritic structure with substantially all of the copper in solution. The metal then is quenched as in air, oil or water to room temperature at a quenching rate of, for example, about 400° F. per minute.

In the quenching from high temperature the metal is transformed to a structure which includes chromium-nickel martensite, but most of the copper still remains in solution. In this condition the metal, if desired, is subjected to forming machining or other fabricating operations. Subsequently the metal is precipitation-hardened in the manner described hereinbefore.

In this relatively low-temperature annealing form of treatment a chromium-nickel-copper stainless steel which I condition with exceptionally good results contains the following: approximately, 16% to 17% chromium, 4.25% to 5.25% nickel, 3.25% to 4.25% copper, carbon up to 0.07% maximum, with or without small additions of beryllium to increase the precipitation hardening effect obtainable with copper alone, and with or without titanium and/or columbium and when present not more than about that needed to tie up the carbon, and with the remainder substantially all iron.

Certain physical properties of the alloys, within the more specific composition range just given, and containing chromium, nickel, copper, carbon, and iron in the amounts specified, but no appreciable amounts of beryllium, titanium or columbium, are given below in Table I:

Table I.—Straight chromium-nickel-copper alloys

	Rockwell Hardness	Brinell Hardness	Ult. Tens. Str., p. s. i.	0.2% Yield Str., p. s. i.	Elong. 2", Per Cent	Reduction of Area, Per Cent
Annealed	28C–33C	270–300	150,000 to 165,000	85,000 to 95,000	8 to 12	45 to 55
Hardened	38C–43C	350–400	180,000 to 190,000	165,000 to 175,000	8 to 12	45 to 60

When the more specific group of alloys of the 16% to 17% chromium, 4.25% to 5.25% nickel, 3.25% to 4.25% copper varieties contain small amounts of titanium or columbium a somewhat different set of physical properties may be expected, as compared with those of the straight chromium-nickel-copper grades. For purposes of comparison, certain properties of the columbium or titanium grades are approximate in Table II.

Table II.—Chromium-nickel-copper-titanium or columbium alloys

	Rockwell Hardness	Brinell Hardness	Ult. Tens. Str., p. s. i.	0.2% Yield Str., p. s. i.	Elong. 2", Per Cent	Reduction of Area, Per Cent
Annealed	20C–30C	230–280	120,000 to 140,000	100,000 to 120,000	8 to 12	45 to 75
Hardened	37C–42C	350–390	170,000 to 185,000	160,000 to 180,000	8 to 12	40 to 60

As indicated at the outset, another group of stainless steels having the broad composition ranges specified hereinbefore but low percentages of austenitic-forming materials, nickel ranging between about 3.5% and approximately 4.5%, respond to heating between temperatures of about 1800° F. to approximately 2000° F. and quenching. In this relatively high-temperature annealing form of treatment the chromium-nickel-copper steels which I condition with exceptionally good results contain the following in approximate amounts: 15.75% to 16.75% chromium, 3.75% to 4.50% nickel, 3.50% to 4.25% copper, up to 0.07% carbon, and the remainder substantially all iron. The properties of this grade, and the modified types including titanium and columbium, are given in Table III below:

Table III

	Rockwell Hardness	Brinell Hardness	Ult. Tens. Str., p. s. i.	0.2% Yield Str., p. s. i.	Elong. 2", Per Cent	Reduction of Area, Per Cent
A. CR-NI-CU TYPE						
Annealed	28C–33C	270–310	150,000 to 165,000	95,000 to 120,000	5 to 12	5 to 55
Hardened	40C–45C	372–426	185,000 to 210,000	175,000 to 200,000	5 to 15	35 to 55
B. CR-NI-CU-CB TYPE						
Annealed	24C–31C	250–290	135,000 to 155,000	100,000 to 125,000	6 to 12	40 to 60
Hardened	40C–45C	370–430	195,000 to 215,000	175,000 to 200,000	6 to 12	25 to 60
C. CR-NI-CU-TI TYPE						
Annealed	28C–32C	270–300	130,000 to 155,000	100,000 to 120,000	6 to 12	35 to 55
Hardened	40C–45C	370–430	195,000 to 215,000	175,000 to 200,000	6 to 12	20 to 45

The chromium-nickel-copper steels described herein which comprise columbium or titanium, as compared with those which do not include these elements, display improved ductility in the pre-hardened or annealed condition. They tend to have lower initial hardnesses as well as improved corrosion resistance under certain conditions. I prefer to introduce titanium and/or columbium in amounts just sufficient to tie up the carbon present, although the use of any smaller quantities, or amounts which are slightly more, also are contemplated.

The hardened chromium-nickel-copper stainless steels which include beryllium, as in amounts from traces up to around 0.25%, are characterized by higher ultimate tensile strength, greater yield strength and high final hardness. They are particularly suitable for use in such forms as cutting tools, dies, hard balls, and the like. The beryllium apparently contributes as a second precipitation-hardening agent to the hardening effect of the copper.

Thus it will be seen that there is provided in this invention, a stainless steel which is suited to low temperature hardening as well as a method of precipitation-hardening such steels in which the various objects hereinbefore noted together with many thoroughly practical advantages are successfully achieved. It will be seen that my novel steel and method makes possible the provision, from alloys which can be cast, wrought, or welded, or subjected to a number of other forming, machining or fabricating operations, products which are precipitation-hardened at low temperatures without substantially distorting, scaling, or discoloring the metal by heat effects. Also it will be seen that the resultant hardened products have high yield and ultimate strength, both in tension and in compression, comparative freedom from directional qualities, and a reasonable amount of ductility. In addition it will be noted that the process is practiced with expediency, enables the production of hardened products with a minimum of supplemental treatments such as pickling, and otherwise is quite suitable for commercial use.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiments 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. A chromium-nickel stainless steel having precipitation-hardenable properties, said steel containing about 15.5% to approximately 18.5% chromium, about 3.5% to approximately 5.5% nickel, copper in amounts between about 3.2% and approximately 5.0%, carbon not exceeding about 0.1%, and the remainder substantially all iron.

2. In a method of precipitation-hardening low-carbon chromium-nickel stainless steel, providing a steel comprising about 15.5% to approximately 18.5% chromium, with about 3.5% to approximately 5.5% nickel, and including the ingredient copper in amounts between about 3.2% and approximately 5.0%, with the remainder substantially all iron; then heating this steel within a temperature range sufficiently high and for such period of time as to provide an unstable austenitic-ferritic copper-soluble structure transformable above room temperature without substantial precipitation of the copper; quenching the steel to transform the same; and reheating the steel to a temperature below that of the initial heating but sufficiently high and for such period of time as to obtain precipitation of copper and a substantial increase in the alloy hardness.

3. In a method of precipitation-hardening chromium-nickel stainless steel, providing a steel comprising about 15.5% to approximately 18.5% chromium, about 4.5% to approximately 5.5% nickel, copper between about 3.2% and approximately 5.0%, carbon not exceeding about 0.1%, and the remainder substantially all iron; heating said alloy within a temperature range of about 1550° F. to about 1650° F. for such period of time as to provide an unstable austenitic-ferritic copper-soluble structure transformable above room temperature without substantial precipitation of the copper; quenching said alloy to transform the same; and reheating the alloy within a temperature range of about 850° F. to about 950° F. for such period of time as to obtain precipitation of copper and a substantial increase in the alloy hardness.

4. In a method of precipitation-hardening chromium-nickel stainless steel, providing a steel comprising about 15.5% to approximately 18.5% chromium, about 3.5% to approximately 4.5% nickel, copper between about 3.2% and approximately 5.0%, carbon not exceeding about 0.1%, and the remainder substantially all iron; heating said alloy within a temperature range of about 1800° F. to about 2000° F. for such period of time as to provide an unstable austenitic-ferritic copper-soluble structure transformable above room temperature without substantial precipitation of the copper; quenching said alloy to transform the same; and reheating the alloy within a temperature range of about 850° F. to 950° F. for such period of time so as to obtain precipitation of copper and a substantial increase in the alloy hardness.

5. A precipitation-hardened chromium-nickel stainless steel comprising approximately 15.5% to about 18.5% chromium, about 3.5% to approximately 5.5% nickel, copper in amounts ranging between about 3.2% and approximately 5.0%, carbon not exceeding about 0.1%, and the remainder substantially all iron; said alloy including through the grains a precipitated copper-rich phase invisible under an ordinary light microscope but visible under an electron microscope.

6. A precipitation-hardened chromium-nickel stainless steel comprising approximately 15.5% to about 18.5% chromium, about 3.5% to approximately 5.5% nickel, copper in amounts between about 3.2% and approximately 5.0%, carbon not exceeding about 0.1%, and the remainder substantially all iron.

7. A precipitation-hardened chromium-nickel stainless steel containing approximately 15.5% to about 18.5% chromium, about 3.5% to approximately 5.5% nickel, copper in amounts between about 3.2% and approximately 5.0%, carbon not exceeding about 0.1%, at least one of the metals of the group consisting of columbium up to 8 times the carbon content, titanium up to 5 times the carbon content, and beryllium up to 0.25%, and the remainder substantially all iron.

8. In a method of providing pre-hardened fabricated chromium-nickel stainless steel articles and products comprising about 15.5% to 18.5% chromium, about 3.5% to 5.5% nickel, copper between about 3.2% and approximately 5.0%, and the remainder iron, the art which includes heating said alloy steel within a temperature range of approximately 1800° F. to about 2000° F. and quenching the same to provide an austenitic structure at about room temperature with a substantial amount of the copper in solution, and

fabricating the quenched steel into articles and products.

9. Pre-hardened chromium-nickel stainless steel in the wrought or cast condition, comprising, about 15.5% to 18.5% chromium, 3.5% to 5.50% nickel, copper between about 3.2% and 5.0%, carbon not exceeding about 0.1%, and the remainder substantially all iron, said product being characterized by a predominantly austenitic structure down to at least about room temperature in which copper is present in solution.

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