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HARDENABLE IRON ALLOY

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This invention relates to chromium-nickel stainless steels, more especially to a method for conditioning the same for hardening as well as to the resulting pre-hardened and precipitation-hardened stainless steel products or manufactures.

An object of my invention is the provision of chromium-nickel stainless steels which respond from the annealed condition to low temperature hardening treatment.

A further object is the provision of a highly effective and industrially feasible method for conditioning stainless steels of the character referred to, wherein, the metal is readily treated to a soft, formable and machinable quality and subsequently is exposed to a reliable sequence of operations for achieving phase transformation and precipitation-hardening of the same.

A still further object of my invention is the provision of precipitation-hardened stainless steels which display high yield strength and high ultimate strength values both in tension and compression together with a reasonable amount of ductility, and which are substantially free of directional effects so common to work-hardened austenitic chromium-nickel stainless steels.

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 by definition the stainless steels comprise 10% to 35% chromium, quite frequently nickel, often one or more such special purpose elements as copper, manganese, silicon, cobalt, molybdenum, tungsten, vanadium, titanium, columbium, sulphur, phosphorus, or the like, and a remainder which is substantially all iron. The carbon content of these steels usually is low, that is, on the order of 0.03% to 0.20%, but for certain purposes the amount may be higher.

In the category of stainless steels, there are chromium-nickel austenitic steels, for example, the well known 18% chromium-8% nickel varie-

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ties, which are amenable to fabrication by such physical measures as cold forming, hot working, or machining, and to welding, soldering, riveting, or other joining treatments. The austenitic stainless steels are hardenable to some extent by mechanical working, but retain the soft austenitic phase through heating and quenching in accordance with conventional heat treatment hardening methods. In rolling or drawing the metal, directionality develops which results in a loss of strength particularly strength in compression along the direction of working. The austenitic stainless steels, therefore, usually are put into use in soft-strain-relieved condition, or in the work-hardened condition when feasible.

The stainless steels which are hardenable by heat treatment, such as the 12% to 18% straight-chromium varieties and those with relatively small nickel contents, for example, the 16% chromium-2% nickel grades, have many desirable physical properties in the hardened condition including high tensile strength, great strength in compression, and high yield strength together with good directional properties after working. These steels, however, require quenching from high temperatures, usually in the vicinity 1800° F. or even more, to achieve hardness at room temperature. The high hardening temperatures lend to the accumulation of surface scale and tend to distort the products under treatment to such extent as to destroy desired dimensions in the hardened condition. The many difficulties in hardening the products stand as noteworthy objections to the steels especially those steels in the form of flat rolled products such as sheet or strip.

The provision of stainless steels which are hardenable by heating to a temperature sufficiently low to avoid or minimize oxidation and undue distortion heretofore has been attempted, as through efforts to realize at this relatively low temperature a critically disbursed phase. As a prior art development, it has been suggested to use columbium or titanium hardening agents in chromium-nickel stainless steels. The precipitation hardenable alloys so provided, however, are not so easily produced in the hardened condition, especially considering difficulties which frequently prevent the achievement of products of consistently uniform and reliable properties. The titanium addition, for example, is particularly

difficult to control. In steel melting operations the recovery of the addition element is erratic. The titanium once recovered is subject to loss such as during welding treatment of the steel at the localized points of welding, often in amounts which destroy the precipitation hardenability of the welded joints.

An outstanding object of my invention accordingly is the provision of chromium-nickel stainless steels which lend themselves to ready fabrication into sheet, strip, bars, wire, and the like, and into a wide variety of more complex products, for subsequent hardening at low temperatures with minimum scaling and discoloration and without warping, which steels and products fashioned thereof are also characterized by highly desirable properties in both the pre-hardened and hardened conditions.

Referring now more particularly to the practice of my invention, I find that by closely correlating the chromium and nickel contents of the steels, and by including certain critical amounts of the ingredient copper, and critical amounts of carbon and nitrogen for supplementing the effect of the nickel, a relatively low-alloy content chromium-nickel-copper stainless steel is had which with special treatment retains a copper soluble austenitic structure down to about room temperature and is hardenable by transformation and the precipitation of copper from solid solution. This result is both new and startling. My stainless steel includes by correlation about 16.5% to approximately 18.5% chromium, nickel in the approximate range of 2.85% to 4.85%, copper in amounts between about 3% and approximately 5%, from about 0.14% to approximately 0.21% carbon and nitrogen in sum total, with at least one of the elements further being in the respective approximate ranges of 0.10% to 0.16% carbon and 0.05% to 0.13% nitrogen, and the remainder substantially all iron. At times, and for special purposes, I also include in the steel composition just defined, such elements as beryllium from traces up to 0.25% and/or other special purpose elements. In any event, the steel which I provide has a balanced composition which remains soft, ductile and workable after annealing, yet is precipitation hardenable by special treatment forming a part of my invention.

In the broad group of chromium-nickel-copper stainless steels noted hereinbefore which comprise relatively large amounts of nitrogen, I prefer those which include 0.08% to 0.10% nitrogen, up to 0.10% carbon, 16.5% to 18.5% chromium, 3.25% to 4.85% nickel and from 3% to 5% copper; the percentages given being approximate. Likewise, of the higher-carbon steels disclosed herein, I prefer those comprising, in approximate percentages, 0.10% to 0.12% carbon, up to 0.05% nitrogen, 16.5% to 18.5% chromium, 3.25% to 4.85% nickel and 3% to 5% copper. The combined carbon and nitrogen contents of any of the preferred compositions just identified should range between about 0.14% and approximately 0.21% as pointed out hereinbefore in a broader sense.

I employ a special conditioning treatment which includes annealing the herein disclosed chromium-nickel-copper stainless steels within a temperature range of about 1700° F. extending up to around 2100° F., a temperature of approximately 1700° F. to about 2000° F. for the relatively high-nitrogen, low-carbon steels and a temperature of about 1700° F. to 2100° F. for the relatively high-carbon low-nitrogen steels being pref-

erable. These high annealing temperatures serve effectively to put the metal in an austenitic copper-soluble condition which is retainable down to at least about room temperature. The holding time at the annealing temperatures just mentioned is not too critical. I prefer, however, to employ a treatment period of about ½ hour for this purpose. As a matter of convenience, I anneal the metal in a suitable heat-treating furnace by bringing the same to temperature therein and holding at temperature for the necessary period.

Following the annealing heat, I quench the steel as in air, oil or water to around room temperature, as at a quenching rate of about 400° F. per minute, and thus provide an annealed or pre-hardened copper-soluble alloy which retains an austenitic structure much in the manner as do 18% chromium-8% nickel austenitic stainless steels after similar treatment. As quenched, the alloys are reasonably ductile, have good directional qualities and hardness usually below about Rockwell B100. In addition, they are formable, weldable and machinable, one or more of which properties contribute to the ease of fabricating the metal at this point, if desired, into any of a wide variety of pre-hardened products.

Before hardening the quenched or pre-hardened metal in a manner to be described more fully hereinafter, I illustratively provide products of the same in such forms as bars, rounds, wire, sheet, strip or plate. Likewise, I provide shapes which are more intricate, for example, trim, structural members or the like, as for the aircraft industries, cold-headed bolts and screws requiring hard shanks, shafting, surgical instruments, valves and valve seats. In the provision of these, I take advantage of excellent working and forming properties of the pre-hardened metal such as amenability of the same to cold-forming, upsetting, drawing, spinning, machining, stamping, punching, cutting, and the like.

Subsequent to the annealing or pre-hardening treatment and usually after certain fabricating operations on my pre-hardened chromium-nickel-copper stainless steel, I subject the same to either one of two preliminary heat exchange hardening treatments. As a first and preferred alternative, I reheat the metal, illustratively in the same heat-treating furnace employed in the high temperature annealing treatment referred to hereinbefore, so as to enable the achievement of transformation above room temperature. This treatment includes holding the metal within the approximate range of 1250° F. to 1600° F., and preferably around 1400° F., for about five minutes up to six hours or more. A three-quarter hour period or thereabouts usually is quite practical and thoroughly satisfactory, and therefore is preferred as an optimum holding time. Following the reheating stay, I cool the steel as in air or water, with the result that the transformation does occur above room temperature. The transformation produces a chromium-nickel martensitic structure and partial precipitation of a copper-rich phase.

As an alternative, instead of reheating in the manner described, I employ a preliminary hardening treatment which involves cooling the pre-hardened metal to effect transformation below usual room temperatures. In the practice of this alternative, I hold the pre-hardened metal, as in fabricated condition, in a suitable cooling compartment, or the like, at cooling temperatures of about (+)32° F. to (—)100° F. or lower for such periods of time as to effect transformation. Usual

ally at least $\frac{1}{2}$ hour at cooling temperature is preferred, as in Dry Ice and/or acetone for the cooling medium.

After I achieve transformation of the steel either through reheating and quenching or by conditioning below usual room temperature as described, the alloys then are ready for positive precipitation-hardening which as an operation consists in a further step of my hardening treatment. In accomplishing the precipitation-hardening, I heat the transformed alloy steel as, for example, fabricated products thereof, within a temperature range of about 850° F. to approximately 950° F., preferably at about 900° F., and hold the same at temperature for about $\frac{1}{2}$ hour. The time of treatment, however, may vary from approximately fifteen minutes to two hours without excessive under-aging or over-aging. This treatment serves to give substantially complete precipitation of a copper-rich phase throughout the metal grains. The copper-rich precipitate 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.

At the completion of heating at precipitation hardening temperature, I find advantage in quenching the stainless steel to room temperature. In the hardened condition, as after quenching, the alloys display high values both in tension and compression, high yield strength, good directional qualities, a reasonable degree of ductility, and good hardness values, the latter usually falling in or near the range of C37 to C45. The alloy steels and products thereof which I provide also are quite resistant to salt spray and to corrosion in ordinary atmosphere, both before and after hardening.

My stainless steels are weldable by arc, gas, spot, or other welding methods without substantial loss of copper, which is an important advantage remembering that alloys in which full reliance on aluminum, titanium, and like elements for promoting the precipitation hardening effect suffer a loss of the hardening material in welding operations. As a further feature of my invention, therefore, I provide welded joints and welded products from the chromium-nickel-copper steels disclosed herein and treat the weld, and/or the parent metal itself, in accordance with my annealing and hardening treatment. In order to afford a beneficial source of weld addition metal, I also provide weld rods which include the chromium-nickel-copper stainless steel disclosed herein as filler deposit metal.

In Table I below there are noted several chromium-nickel-copper alloy stainless steels which I produce and treat in accordance with my invention. It will be observed that alloys 1 and 2 comprise less than 0.10% carbon and more than about 0.05% nitrogen while alloys 3 and 4 contain at least 0.10% carbon and less than 0.05% nitrogen.

Table I

Alloy	C	Mn	P	S	Si	Cr	Ni	Cu	N
1.....	0.06	0.72	0.010	0.017	0.48	16.91	4.05	4.02	0.085
2.....	0.10	0.68	0.010	0.015	0.58	16.50	4.00	3.50	0.04
3.....	0.14	0.53	0.009	0.012	0.48	17.50	4.60	4.25	0.04

The approximate hardness values to be expected after annealing, and after transforming and precipitation hardening the alloys identified in Table I, are presented in Table II which fol-

lows. The hardness values are obtainable by heating and quenching the alloys in the manner tabulated.

Table II

Alloy	Treatment	Hardness
1.....	1800° F. $\frac{1}{2}$ hour—air cooled..... 1400° F. $\frac{1}{4}$ hour—water quench plus 900° F. $\frac{1}{2}$ hour—water quench.....	Rockwell B-86 Rockwell C-43
2.....	2000° F. $\frac{1}{2}$ hour—air cooled..... 1400° F. $\frac{1}{4}$ hour—water quench plus 900° F. $\frac{1}{2}$ hour—water quench.....	Rockwell B-80 Rockwell C-42
3.....	2000° F. $\frac{1}{2}$ hour—air cooled..... 1400° F. $\frac{1}{4}$ hour—water quench plus 900° F. $\frac{1}{2}$ hour—water quench.....	Rockwell B-81 Rockwell C-40

Thus it will be seen that there is provided in this invention chromium-nickel-copper stainless steels made through the regulation of contents of such elements as carbon and nitrogen to have a relatively low-alloy content, and a method of precipitation-hardening the same, in which the various objects hereinbefore noted together with many thoroughly practical advantages are successfully achieved. It will be seen that the method enables the provision from steels which can be cast, welded, or wrought, or subjected to a number of forming, machining or fabricating operations, products which are hard yet are substantially free of directionality and possess a reasonable amount of ductility. In addition, the hardened steels, articles and products possess ultimate tensile strength, compressive strength and yield strength, all of which are high.

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-hardening properties, said steel comprising about 16.5% to 18.5% chromium, approximately 2.85% to 4.85% nickel, copper between about 3% and 5%, about 0.14% to about 0.21% nitrogen and carbon in sum total, at least one of the latter elements further being in the respective approximate ranges of 0.05% to 0.13% nitrogen and 0.10% to 0.16% carbon, and the remainder substantially all iron.

2. A chromium-nickel stainless steel having precipitation-hardening properties, said steel comprising about 16.5% to 18.5% chromium, approximately 2.85% to 4.85% nickel, copper between about 3% and 5%, carbon and about 0.05% to 0.13% nitrogen constituting approximately 0.14% to 0.21% in sum total, and the remainder substantially all iron.

3. A chromium-nickel stainless steel having precipitation-hardening properties, said steel comprising about 16.5% to 18.5% chromium, approximately 3.25% to 4.85% nickel, copper between about 3% and 5%, carbon and about 0.08% to 0.10% nitrogen constituting approximately 0.14% to 0.21% in sum total and the remainder substantially all iron.

4. A chromium-nickel stainless steel having precipitation-hardening properties, said steel comprising about 16.5% to 18.5% chromium, approximately 2.85% to 4.85% nickel, copper between about 3% and 5%, nitrogen and about 0.10% to 0.16% carbon constituting approximately 0.14% to 0.21% in sum total, and the remainder substantially all iron.

5. Precipitation-hardened wrought or cast austenitic stainless steel articles comprising 16.5% to 18.5% chromium, 2.85% to 4.85% nickel, 3% to 5% copper, about 0.14% to about 0.21% carbon and nitrogen in sum total, at least one of the latter elements being in the respective approximate ranges of 0.10% to 0.16% carbon and 0.05% to 0.13% nitrogen, with remainder iron, transformed by heat-exchange treatment and with copper precipitated in finely dispersed form and in substantial amount giving an increase in the metal hardness.

6. Chromium-nickel stainless steel sheet, strip, bars, wire, and the like products, suited to subsequent fabrication and precipitation-hardening, comprising, about 16.5% to 18.5% chromium, approximately 3.25% to 4.85% nickel, about 3% to 5% copper, about 0.14% to about 0.21% carbon

and nitrogen in sum total, at least one of the latter elements further being in the respective approximate ranges of 0.10% to 0.12% carbon and 0.08% to 0.10% nitrogen and the remainder substantially all iron, said products being characterized by an austenitic copper-soluble condition.

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