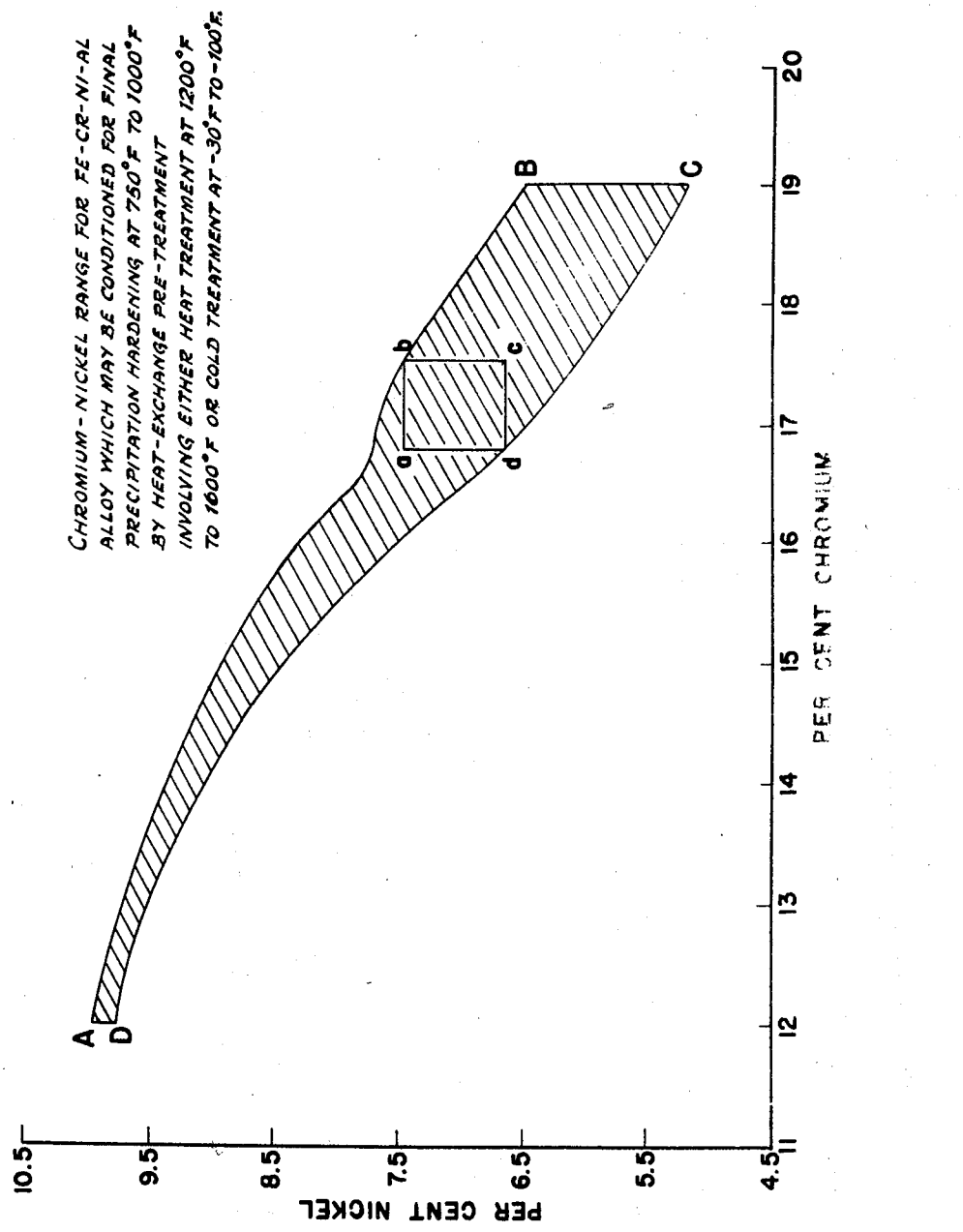
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STAINLESS STEEL AND METHOD

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STAINLESS STEEL AND METHOD

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My application for patent is a continuation-in-part of my copending application, Serial No. 695,216 filed September 6, 1946, and entitled Stainless steel and method and also it is a continuation-in-part of my copending application, Serial No. 695,217 of the same date and title, and the invention relates to chromium-nickel stainless steels of low-carbon content, more particularly to a method for conditioning the steels to the hardenable or hardened state, and to the resulting products and manufactures themselves.

An object of my invention is the provision of chromium-nickel stainless steels which are amenable to hardening by heat treatment from a soft, formable and machinable condition.

Another object is the provision of chromium-nickel stainless steels so proportioned in composition as to be consistently and reliably produced to analysis specification and of such composition as to be amenable to annealing, and working and fabricating in the annealed condition, and thereafter to hardening treatment without, however, being unduly sensitive to cold weather in the prefabricated condition.

A further object of my invention is the provision of a simple, practical and reliable method for conditioning chromium-nickel stainless steels to a workable state suited for such operations as cold working, forming, stamping, punching, spinning, drawing, bending, heading, and machining, and to the hardened state by heat exchange treatment at temperatures sufficiently low to avoid substantial warping and the formation of heat scale.

A still further object of my invention is the provision of hardened chromium-nickel stainless steels, as for example cold worked and hardened articles and products, which are characterized by excellent physical properties including high yield strength and high ultimate strength.

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 several method steps and the relation of each of the same to one or more of the others as described herein, and in the resulting articles and products had thereby, the scope of the application of which is indicated in the following claims.

The single figure of the accompanying drawing graphically represents proportions of chromium and nickel which are employed in the composition of my stainless alloy steel, as will be pointed out more fully hereinafter.

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As conducive to a clearer understanding of certain features of my invention, it may be noted at this point that the better known chromium-nickel stainless steels, as for example the 18% chromium-8% nickel steels, are stably austenitic at room temperatures and do not appreciably respond to hardening by heat treatment. They do attain hardness by cold working but, in actual practice, there are sharp limitations upon the possible use of this property to achieve desired hardness. The products so hardened are under strain, and the customary annealing treatment to relieve the strain tends to reduce the hardness. There are many valuable properties of the steels, for instance cold workability as by rolling, swaging, cold heading and drawing, machinability, and, as well, many additional features such as excellent resistance to corrosion, which place the steels in very considerable demand.

In accordance with the general definition of stainless steels, the chromium-nickel varieties frequently include additions of such elements as copper, manganese, silicon, cobalt, molybdenum, tungsten, vanadium, titanium, columbium, and sulphur, for special purposes. Some few of the chromium-nickel stainless steels have been known to respond to hardening by heat treatment, this by virtue of the addition of titanium or columbium in well studied proportionment with other elements present coupled with a critical form of heat treatment to effect precipitation hardening. Columbium and titanium, however, are relatively expensive materials. The chromium-nickel-titanium or chromium-nickel-columbium stainless steels, moreover, usually contain stress laden ferrite as an essential to hardenability from the annealed condition. When the steels are produced to such composition as to present a comparatively soft, substantially fully austenitic structure at about room temperatures after annealing, they are more amenable to cold working and forming operations, but hardenability by heat treatment is usually sacrificed.

The production and treatment of certain grades of stainless steels heretofore has involved the introduction of aluminum into the steel melt for serving as a deoxidizing material, and also as an alloying element to develop an aluminum-containing oxide film on the metal which is resistant to heat and corrosion. The alloying of aluminum with suitable quantities of other included elements of the steel is known to impart high temperature properties which, depending upon degree, have justified the production from the metal of such articles as heat engine valves,

turbine blades, and the like. Aluminum, in many of the stainless steels, is said by previous investigators to exert an impairing effect upon the ability of these steels to harden. I find that this by far is not true of all stainless steels; instead, aluminum offers great benefits as a relatively cheap hardening agent when properly correlated with other elements in the steel

Now in my parent copending applications, Serial Nos. 695,216 and 695,217, I describe certain chromium-nickel-aluminum stainless steels and methods of hardening the same, some of which steels unfortunately are inclined to prematurely harden upon encountering intensely cold weather. Thus, where these steels are subjected to sub-zero weather, as in shipment, substantial hardening may be encountered. This hardening, of course, results in subsequent difficulties in machining, forming or other fabricating operations.

Accordingly, one of the objects of my invention is the provision of a chromium-nickel-aluminum stainless steel and method, which steel is readily fabricated into a host of different products hardenable at temperatures sufficiently low to avoid substantial scaling and distortion due to heat effect, and yet which are sufficiently stable in the prehardened and prefabricated condition that premature hardening is not encountered in cold weather as in shipping for example.

Referring now more particularly to the practice of my invention, I provide an especial quality of chromium-nickel stainless steel which, through the close correlation of amounts of chromium and nickel, with critical amounts of the ingredients aluminum and carbon, in the composition thereof, is highly suitable for fabrication in the relatively soft condition and for subsequent hardening by heat exchange treatment to a corresponding condition of increased tensile strength and yield strength.

In the practice of my invention, I provide stainless steel in which the chromium and nickel contents are in substantial accord with the abscissa and ordinate of any given point of area ABCD in the accompanying diagram, and which further contains anywhere from about 0.02% to 0.12% carbon, aluminum from about 0.50% to 2.50%, from incidental amounts up to about 8.0% manganese, from incidental amounts up to approximately 2.0% silicon, with or without molybdenum ranging up to about 3.0% illustratively to enhance corrosion resistance of the steel, and the remainder substantially all iron. In this, however, should the carbon, aluminum, silicon, or manganese content be somewhat different from the amount upon which the accompanying diagram is based (the basis of the diagram being amounts of actual chromium and nickel as called for, about 0.06% to 0.08% carbon, 0.60% to 1.0% aluminum, incidental amounts of manganese and silicon up to 1.0% each, sulphur and phosphorus up to 0.040% each, and the remainder substantially all iron) or should molybdenum be used, I find it preferable to modify the chromium or nickel content of the steel, or both of the contents as the case may be, so as to achieve chromium-like and nickel-like components in the steel which are substantially equivalent respectively in ferrite and austenite-forming relation to those amounts of chromium and nickel and of the other elements represented in the diagram. For example, I often replace a part of the chromium called for in the diagram with a quantity

of aluminum, silicon or molybdenum, the replacement being approximately on a 1 to 1 ratio with respect to chromium, and for such purpose as maintaining a desired relation between the austenite and ferrite forming components of the steel substantially as would be achieved by rigid adherence to the diagram. Similarly, I occasionally add several or all of the replacement elements in partial substitution for the chromium. The practice of substitution I find is particularly advantageous where either the aluminum or silicon is to exceed about 1.0%, or where molybdenum is a constituent of the steel. Following substitution, the actual chromium content of the steel may at times be somewhat below those amounts prescribed by area ABCD in the diagram and still, in view of the effect of the substituted element or elements, be in substantial accord with the area.

Where the permissible quantity of carbon exceeds about 0.08%, or where more than small amounts of manganese are present (say for example amounts in excess of about 1.0%) I usually employ a proportionally decreased quantity of nickel in the steel as compared with the accompanying diagram. The actual nickel content of the steel, however, is importantly not less than about 3.5% after substitution. Should the permissible quantity of carbon be on the low side, i. e. below about 0.06%, I usually increase the nickel content as compared with the diagram, or even at times instead increase the manganese content. For each part of nickel I add about 2 parts manganese or on the order of about $1/20$ to $1/30$ part carbon as the substantial equivalent. The actual nickel content of the steel, after partial substitution, consequently may on occasions fall even considerably outside those amounts prescribed by area ABCD in the diagram or remain inside and still, in view of the substituted element or elements and the contributed effect thereof, be in substantial accord with the area.

Where desired the steel contains such addition elements as sulphur and/or selenium in amounts sufficient to enhance free-machining properties. The value of such elements is realized especially in machining the steel in the annealed state.

In accordance with the preferred practice of my invention, I produce a stainless steel containing chromium and nickel in amounts substantially in accord with the abscissa and ordinate respectively of any given point substantially falling within area ABCD in the accompanying diagram, the amounts advantageously being about 16.5% to 17.5% actual chromium and approximately 6.75% to 7.5% actual nickel as represented by the area ABCD. The steel, also preferably contains, on the basis of the diagram, aluminum in amounts between about 0.60% and 1.1%, carbon within the approximate range of 0.06% to 0.08%, and the remainder substantially all iron. There are preferably small amounts of such elements as manganese, silicon, sulphur and phosphorus in the steel, as for example manganese and silicon each not exceeding about 1.0% and sulphur and phosphorus each up to about 0.040%.

To condition the steel, either as wrought or cast, for subsequent forming and fabrication and for hardening of the formed and fabricated products, I heat the metal in a temperature range preferably not lower than about 1800° F. and extending up to about 2000° F., for such time as to achieve an austenitic aluminum-soluble condi-

tion which is retainable down to substantially below ordinary room temperature. This heating is in the nature of an annealing treatment. To achieve the annealing, I usually adjust the metal to temperature and maintain or hold the same at temperature as in a conventional heat-treating furnace for a suitable period of time. The holding time as applied to the steel is not too critical. About one-half hour usually is quite satisfactory from the standpoint of economy and of ensuring adequate solubility of the aluminum. I then quench the annealed metal as in air, oil or water, preferably to around room temperature. As a result of the annealing and quenching, the stainless steel displays a soft, substantially fully austenitic structure, is ductile, has good directional properties, hardnesses usually below about Rockwell B–92, and readily lends itself to forming, machining, and the like.

I find, as briefly noted above, that with the quenching, however, certain internal stresses apparently are set up in the steel which permit the transformation from austenite to martensite upon subsequent severe cooling. Thus, in shipping the steel during unusually cold winter weather, I note that a hardening occurs which in many cases is most objectionable. Under unusual conditions, the hardness had may amount to as much as Rockwell C–30. This hardening notably increases the difficulties of the forming, machining or like operations.

In accordance with my invention, I subject the steel, following the annealing and quenching steps, to a stabilizing treatment, this by heating the steel to a temperature of some 600° F. to 1100° F. for a short period of time. Ordinarily, heating at a temperature of 900° F. for about one hour is found to give good results. Where the lower temperatures are employed, however, a longer period of time is used and conversely where the higher temperature is used less time of treatment is required. This treatment leaves the steel with substantially no change in hardness or other physical properties.

My stainless steel at any time subsequent to the stabilizing treatment and prior to the heat exchange hardening treatments, is machined, formed or worked as desired. My steel in the form of bars, wire, rounds, sheet, strip or plate may be fabricated into various ultimate articles of use. I frequently provide shapes of a more intricate character, illustratively trim and structural members such as parts for aircraft including those components requiring great strength from the standpoints of yield, in tension and compression coupled with toughness and corrosion resistance. I provide cold-headed bolts and screws, as for example those eventually to include hardened shanks; surgical instruments and dental tools; valve and valve seats; die blocks; and the like. In all of these articles of ultimate use, I take advantage of the excellent workability and formability of the soft annealed metal through such operations as cold-forming, upsetting, drawing, spinning, stamping, punching, machining, and other steps consistent with the properties of the metal. Although I prefer to conduct the working and fabricating operations prior to any hardening treatment, I may delay part or all of the forming and fabricating operations until after the achievement of a preliminary hardening pre-treatment now to be described.

To preliminarily harden the annealed and stabilized chromium - nickel - aluminum stainless steel, as after the forming and fabricating steps

illustratively conducted before undertaking the hardening treatment, I subject the steel to a heat exchange treatment consisting either of heating the steel to substantial temperatures or of cooling it to very low temperatures. For the one, I reheat it, illustratively in the same heat-treating furnace employed for the annealing, this time up to within the approximate temperature range of 1200° F. to 1600° F., preferably up to about 1400° F., and there hold the metal to desired temperature or temperatures for approximately ¼ hour or more. During the holding operation, as for example with the steel at around 1400° F., there results a precipitation of carbides, possibly some precipitation of aluminum compounds, and a raising of the transformation point of the austenitic matrix. The steel, upon cooling, consequently transforms to include a "soft" martensite-like constituent. The transformation occurs at quite low temperature such as between about 175° F. and 225° F. Thus, at the completion of the reheating stay, I quench the steel as in air, oil or water with the result that transformation does occur above room temperature to achieve a partial hardening of the metal, or of the articles made thereof as described hereinbefore. Hardnesses after this transformation vary in or near the range of Rockwell C–24 to C–28 depending upon the particular composition and the conditions of treatment within the limits noted.

Where I employ a low temperature heat exchange treatment, I cold-treat the metal, as in fabricated condition, at temperatures of about −30° F. to −100° F. or lower, this preferably being in a suitable cooling compartment, or the like. A satisfactory temperature is −60° F. It will be understood that because of the extremely low temperature required, my steel does not preliminarily harden to any substantial extent during shipment even under the most severe cold weather conditions.

In preliminarily hardening the steel by cold treatment, a holding time of about ½ hour or more at cooling temperatures within the cooling range noted is preferred to effect phase transformation and the preliminary hardening. The cooling medium illustratively is dry ice in acetone. Hardnesses of the chromium-nickel stainless steel after this transformation vary in or near the range of Rockwell C–32 to C–36 depending upon the particular composition and conditions of treatment within the limits mentioned.

The chromium-nickel-aluminum stainless steel in the preliminarily hardened condition whether by heat treatment or by cold treatment, retains a reasonable amount of workability and formability, illustratively cold rolling or drawing properties, and the steel is machinable and may be fabricated as by cutting, punching, drilling, and the like. It is for this reason and also the possibility of further hardening the metal without phase transformation and changes in dimensions of the metal accompanying transformation that I frequently put off all or part of certain forming and fabricating operations to be accomplished on the same until after the preliminary hardening treatment, and then produce any of a wide variety of articles and products, as to substantially finished dimensions, of the partially hardened steel.

When transformation has been achieved by the heat exchange treatment as described, and appropriate working and forming operations effected where desired, the alloy steel then is ready for positive precipitation hardening treatment. In performing this operation, representing a further

part of my conditioning treatment, I heat the steel within a temperature range of about 750° F. to approximately 1000° F., preferably at about 900° F., and there hold the same at temperature for about one hour. The time of holding under treatment, however, may vary from approximately one-half hour for the high temperature of 1000° F. to some five hours or more for the low temperature of 750° F., this with satisfactory results. About one hour treatment at 900° F. is preferred, however. The treatment serves to impart a material gain in hardness to the metal. This hardness, I find, upon quenching the metal as in air, oil or water from the hardening temperatures, comes within the approximate range of C–40 to C–46 Rockwell. A precipitated aluminum-rich phase is instrumental to the hardness. This I believe to be an aluminum-nickel compound.

In the precipitation hardened condition which results from the heating at 750° F. to 1000° F., the so-conditioned steel or steel products are very strong both in tension and compression, have high yield strength, good directional qualities, and are quite resistant to corrosion. The steel emerges from the preliminary hardening treatment and precipitation hardening heat treatment substantially free of heat scale and unwarped by heat at the low temperatures employed.

As illustrative of the stainless steel and method of my invention, three samples of stainless steel of composition noted in Table I were subjected to various conditions of heat-treatment with the results as reported below in Tables II and III.

TABLE I

Composition of stainless steels tested

Heat No.	C	Mn	P	S	Si	Cr	Ni	Al
59473	.068	.67	.024	.019	.73	16.55	6.86	.87
19113	.060	.61	.020	.015	.43	16.84	7.01	1.02
29077	.057	.71	.024	.010	.55	16.77	7.06	.85

TABLE II

Hardness of annealed samples and of samples stabilized following annealing

Heat No.	A. Heated 1900° F. ½ hr. and water quenched	B. Samples of A. Stabilized by Heating 900° F. 1 hr. and air cooled
59473	Rockwell B89	B90
19113	Rockwell B79	B79
29077	Rockwell B75	B75

It will be seen that with the stabilizing treatment there is substantially no change in hardness.

TABLE III

Hardness of annealed and stabilized samples of B given heat exchange treatment and then precipitation hardened

1. By combined double heat-treatment:

Heat No.	C. Samples of B. pretreated 1400° F. 3 hrs. water quenched	D. Samples of C Then precipitation hardened 900° F. 1 hr. air cooled
59473	C29	C43
19113	C28	C42
29077	C28	C43

2. By combined cold treatment and heat treatment:

Heat No.	E. Samples of B. cold-treated −30° F. 20 min.	F. Samples of E Then precipitation hardened 900° F. 1 hr. air cooled
59473	C35	C43
19113	C34	C42
29077	C34	C41

Although the hardness values for the samples in the pre-treated condition differ somewhat, being softer for those treated at 1400° F., for one hour than those treated at −35° F. for twenty minutes, the final hardness values following final precipitation hardening are the same.

As a matter of interest the hardness had where the stabilizing treatment is omitted is given in Table IV below.

TABLE IV

Hardness of unstabilized steels as compared to stabilized steels

Heat No.	G. Samples of A (unstabilized) subjected 32° F. 20 mins.	H. Samples of B (Stabilized) subjected 32° F. 20 mins.
59473	C35	B90
19113	C33	B79
29077	C30	B75

The superior working and forming characteristics of the stabilized steels are evident.

The close correlation of aluminum, a comparatively cheap material, with other elements in the steel accordingly enables a commercially valuable hardening effect, which becomes active with proper treatment of the metal from a soft workable or worked condition. It will further be appreciated that the aluminum contributes to heat resistance and to the prevention of heat scale formation as during the low temperature precipitation hardening heat in the vicinity of 750° F. to 1000° F. and in the resulting precipitation hardened, corrosion resistant products.

Thus, it will be seen that in this invention there is provided an improved precipitation hardening stainless steel and method of treating 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 makes possible the provision of wrought or cast chromium-nickel-aluminum stainless steel subjected to any of a number of forming, machining or fabricating operations and effectively and reliably hardened by heat exchange either at substantial temperatures or at low temperatures. Likewise, it will be seen that my method is readily practiced, and enables the production of chromium-nickel grade stainless steel of hardened quality with a minimum of any such treatment as pickling, and otherwise is quite suitable for commercial use. It will further be noted that the steels provided have good directional properties, are quite soft and ductile in the annealed condition and in the annealed and stabilized condition, and are hardenable to a condition of reasonable ductility and high yield and ultimate strengths.

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. In a method of hardening chromium-nickel alloy stainless steel, the art which includes providing a steel containing chromium and nickel in substantial accord with area ABCD of the accompanying diagram, aluminum in amounts between about 0.50% to 2.50%, and from incidental amounts up to approximately 2.0% silicon, manganese from incidental amounts up to approximately 8.0%, and carbon between about 0.02% and 0.12%, and the remainder substantially all iron; then annealing and quenching the steel to provide an austenitic aluminum-soluble structure transformable below usual room temperature; heating the steel to a temperature of about 600° F. to 1100° F. to stabilize the same; subjecting said steel to heat exchange pre-treatment at such temperatures and for long enough time to achieve transformation; and heating the transformed alloy at a sufficiently high temperature and for a sufficient period of time to precipitate an aluminum compound and obtain a substantial increase in the hardness of the steel.

2. In a method of hardening chromium-nickel alloy stainless steel, the art which includes providing a steel containing about 16.5% to 17.5% chromium, with about 6.75% to 7.5% nickel, aluminum in amounts between about 0.60% to 1.1%, and about 0.06% to 0.08% carbon, and the remainder substantially all iron; then annealing and quenching the steel to provide an austenitic aluminum-soluble structure transformable below usual room temperature; heating the steel to a temperature of 600° F. to 1100° F. to stabilize the same; subjecting said steel to heat exchange pre-treatment consisting of cold treatment below about −30° F. for sufficient time to achieve transformation; and finally heating the transformed alloy at a sufficiently high temperature for a sufficient period of time to precipitate an aluminum compound and obtain a substantial increase in hardness of the steel.

3. In the production of hardened chromium-nickel alloy stainless steel articles and products, the art which includes providing a steel containing about 16.5% to 17.5% chromium, with about 6.75% to 7.5% nickel, aluminum in amounts between about 0.60% and 1.1%, and about 0.06% to 0.08% carbon, and the remainder substantially all iron; annealing said steel at approximately 1800° F. to 2000° F. and quenching the same to provide an austenitic aluminum-soluble structure transformable below usual room-temperature; stabilizing the steel by treatment at 600° F. to 1100° F.; fabricating articles and products of the austenitic stabilized steel; subjecting said fabricated articles and products to heat exchange pre-treatment at 1200° F. to 1600° F. for sufficient time to achieve transformation; and heating the transformed articles or products within the approximate temperature range of 750° F. to 1000° F. for a sufficient period of time to precipitate an aluminum compound and obtain a substantial increase in hardness of the articles and products.

4. An annealed and stabilized chromium-nickel stainless steel susceptible to aluminum-precipitation-hardening by heat exchange treatment from the annealed and stabilized condition involving a preliminary heat-exchange treatment followed by final precipitation hardening heat treatment, said steel containing the chromium-like components aluminum in the amount of about 0.50% to 2.50%, silicon from incidental amounts up to about 2.0% based on total content of the steel, and the remainder substantially all chromium, said components in total meeting the terms for chromium of area ABCD of the accompanying diagram, said chromium and silicon serving as a substitute for chromium on about a 1 to 1 ratio; the nickel-like components carbon in the amount of about 0.02% to 0.12%, manganese from incidental amounts up to 8.0%, and the remainder substantially all nickel in actual amount not less than about 3.5%, said nickel-like components in total meeting the terms for nickel of area ABCD of the accompanying diagram, and said carbon and manganese serving as a substitute for nickel on the ratios of about $1/20$ to $1/30$ part carbon to 1, and approximately 2 parts manganese to 1; and the remainder substantially all iron.

5. An annealed and stabilized chromium-nickel stainless steel of substantially fully austenitic structure at usual room temperatures, said steel containing about 16.5% to 17.5% chromium, about 6.75% to 7.5% nickel, aluminum between about 0.60% and 1.1%, about 0.06% to 0.08% carbon, and the remainder substantially all iron, and the steel being susceptible to hardening by heat exchange treatment involving pre-treatment at 1200° F. to 1600° F., after the annealing and stabilizing followed by final precipitation hardening.

6. A chromium-nickel stainless steel aluminum-precipitation-hardened by heat exchange treatment involving preliminary treatment below about −30° F. from the annealed and stabilized condition followed by precipitation-hardening final heat treatment, said steel containing chromium and nickel in amounts substantially in accordance with area ABCD in the accompanying diagram, carbon between about 0.02% to 0.12%, about 0.50% to 2.50% aluminum, from incidental amounts up to approximately 8.0% manganese, from incidental amounts up to about 2.0% silicon, and the remainder substantially all iron, said aluminum being precipitated as aluminum compound within the matrix of the steel to give substantial hardness.

7. In the production of a stabilized precipitation-hardenable chromium-nickel alloy stainless steel, the art which includes providing a steel containing the chromium-like components aluminum in the amount of about 0.05% to 2.50%, silicon from incidental amounts up to about 2.0% based on total content of the steel, and the remainder substantially all chromium, said components in total meeting the terms for chromium of area ABCD of the accompanying diagram, said chromium and silicon serving as a substitute for chromium on about a 1 to 1 ratio; the nickel-like components carbon in the amount of about 0.02% to 0.12%, manganese from incidental amounts up to 8.0%, and the remainder substantially all nickel in actual amount not less than about 3.5%, said nickel-like components in total meeting the terms for nickel of area ABCD of the accompanying diagram, and said carbon and manganese serving as a substitute for nickel on the ratios of about $1/20$ to $1/30$ part carbon to 1, and approximately 2 parts manganese to 1; and the remainder substantially all iron; annealing and quenching the steel to provide an austenitic aluminum-soluble structure transformable below usual room temperature; and heating the steel to a temperature of 600° F. to 1100° F. to stabilize the same.

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No references cited.