

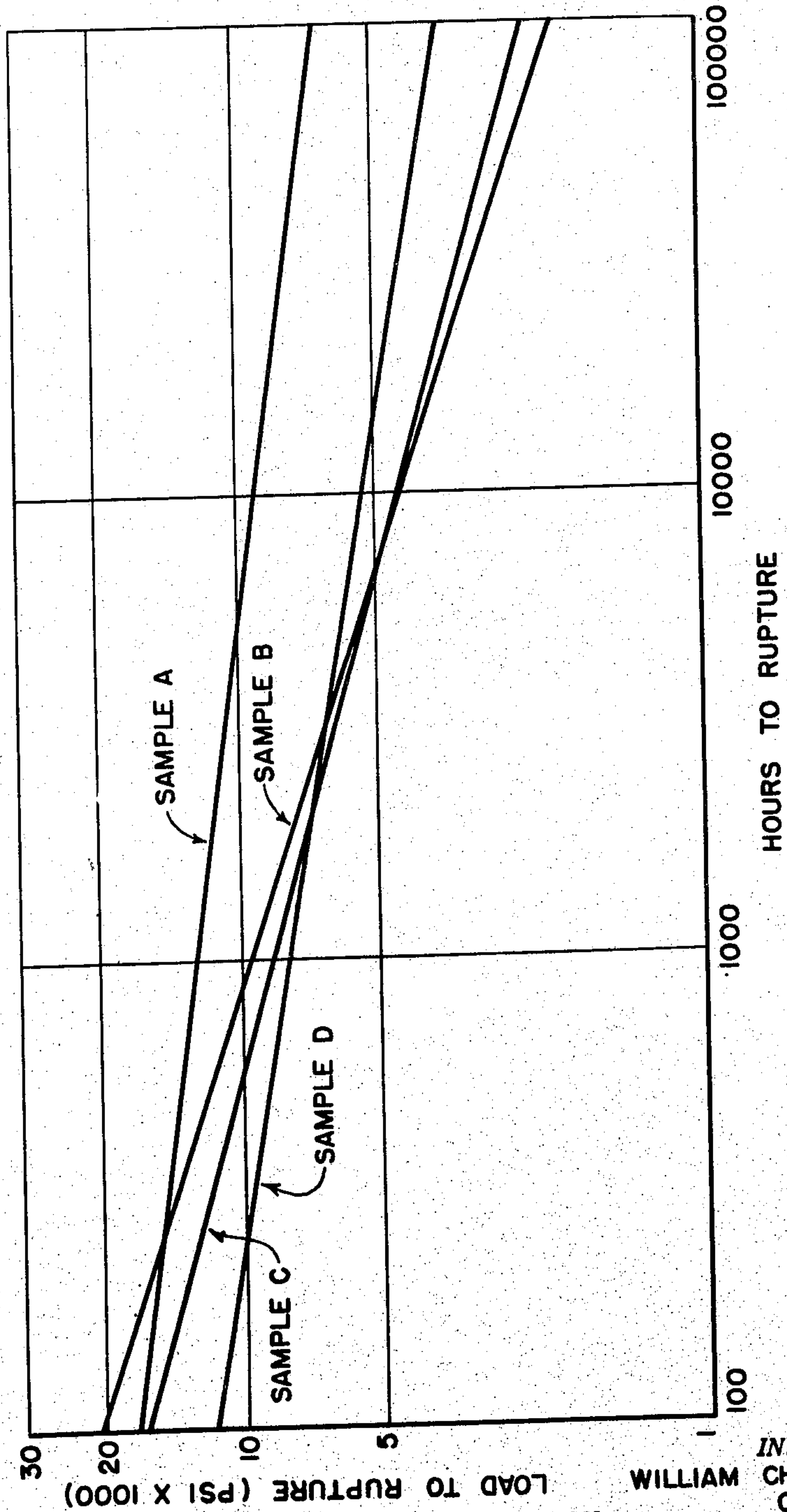
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HIGH-TEMPERATURE STAINLESS STEEL

2,540,509

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STRESS - RUPTURE CHARACTERISTICS
FOR FOUR DIFFERENT
CHROMIUM NICKEL STAINLESS STEELS
AT 1500° F



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HIGH-TEMPERATURE STAINLESS STEEL

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The present application is a continuation-in-part of my copending applications, Serial No. 645,015, filed February 1, 1946, now Patent 2,447,896, and Serial No. 671,905, filed May 23, 1946, now Patent 2,447,897, both of August 24, 1948, and the invention relates to high temperature steel.

An object of my invention is the provision of strong, durable and reliable high temperature stainless steel, and products and articles of the steel, which are capable of resisting the development of sigma phase while under load at high temperatures, which are resistant to stress-rupture and creep at the high temperatures encountered under load, and which are well suited for resisting attack by hot corrosive matter and avoiding the formation of heat scale.

A further object of my invention is the provision of high temperature stainless steel of the character indicated which has good hot working properties.

A still further object is the provision of stainless steel of the character indicated, heat treated for enhanced high temperature properties.

Other objects of the invention 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 articles, products and manufactures thereof, also in the several method steps and 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.

The single figure of the accompanying drawing is a diagram enabling a comparison of the stress-rupture properties of one of my stainless steels (steel A), with those of three steels falling outside the critical composition range.

As conducive to a clearer understanding of certain features of my invention it may be noted at this point that a great variety of steels in the prior art, including a number of the austenitic stainless steels, tend to form a constituent at high temperatures called the sigma phase. This phase although hard and brittle at room temperatures is a non-magnetic intermetallic compound which I find to be weak and ductile at high temperatures. This phase slowly develops while the steel is heated, and when present in appreciable quantities (above about 2%) impairs creep strength and stress-rupture properties of the hot metal. The phase produces a high temperature weakening effect which in extreme instances becomes quite pronounced. It will, therefore, be appre-

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ciated that more than small quantities of the phase are detrimental to the properties of high temperature steels, although these properties perhaps are only impaired and not entirely destroyed.

The austenitic chromium-nickel steels in general may be viewed as high temperature steels. Unfortunately, however, these steels are susceptible to creep and stress-rupture, the susceptibility at times being intensified by the hurtful effects of sigma phase. They nevertheless have a more favorable lattice structure for cohesion under high stress than do ferritic straight-chromium stainless steels. This distinction alone, however, does not necessarily establish good high temperature properties.

As will be more fully understood from my copending applications identified above, I have previously developed certain austenitic stainless steels and articles which have special high temperature utility. These steels, however, while possessing an unusual ability, so far as high temperature steels are concerned, of being readily hot worked, and numerous other characteristics including corrosion resistance and considerable resistance to creep and stress-rupture, are not collectively free of the impairing effects of sigma phase. At temperatures of about 1500° F., the stress-rupture and creep values are found to substantially suffer.

An outstanding object of my invention accordingly is the provision of creep resistant and stress-rupture resistant austenitic chromium-nickel stainless steel having substantial freedom from sigma phase at high temperatures, particularly high temperature austenitic chromium-nickel stainless steel articles such as bolts and fasteners, internal combustion engine valves, gas or steam turbine rotors, buckets, nozzles, and a host of other articles suited for resisting mechanical stress under the high temperature conditions of use.

Referring now more particularly to the practice of my invention, I provide austenitic stainless steels and articles, which in having highly critical composition limits and by containing definite elements such as carbon, chromium, nickel, molybdenum, copper, titanium, columbium, and the remainder substantially iron, are for the intents and purposes free of sigma phase and have excellent high temperature properties including high resistance to creep and rupture. More specifically, I provide stainless steels containing approximately 0.09% to 0.20% carbon, 15.75% to 16.75% chromium, from 13.25% to 14.75% nickel,

1.75% to 2.8% molybdenum, from 2.5% to 3.5% copper, 0.10% to 0.25% titanium, from 0.35% to 0.55% columbium, from 0.20% to 1.5% manganese, up to 0.70% silicon, preferably not more than 0.03% sulphur where hot working properties are desired, and the remainder substantially all iron. Where incidental amounts of phosphorus are present in the steel, these usually range between 0.01% and 0.04%. At times, I employ purposeful additions of phosphorus ranging up to 0.12% or more, with resulting benefits to the high temperature properties. Preferably, the carbon, titanium and columbium contents are in such related amounts as to satisfy the formula:

$$\frac{2(\% \text{Ti}) + \% \text{Cb}}{\% \text{C}} =$$

a numerical value ranging from 5 to 10. By observing this formula ratio more positive assurance is had against sigma formation.

My stainless steels are wholly austenitic in structure. Ferrite, if present at all, is only in traces. This I find is essential to the required stress-rupture properties. Where appreciable amounts of ferrite are present, the stress-rupture values fall off; also the working qualities of the metal suffer.

The composition limits given in fact are considered to be in every sense critical since I find that where they are departed from one or more of the desired qualities suffer. For example, with a lower carbon content the creep and stress-rupture properties suffer even at temperatures as low as 1200° F., and because sigma formation is promoted. Carbon in amount exceeding the high side of the range indicated adversely affects hot working properties and high temperature rupture properties. To like effect, with a manganese content exceeding 1.50%, there is a loss in hot working properties. With any appreciable lowering of the chromium content below 15.75%, impaired scaling resistance in oxidizing atmospheres becomes noticeable at high temperatures. Chromium contents exceeding 16.75% markedly promote sigma phase formation. A nickel content below 13.25%, at the chromium level which I employ, encourages the development of sigma phase. Where the nickel content is above 14.75%, this causes the steel to be sluggish in response to heat treatment, and decreases the stress-rupture properties and creep strength of the metal. The element molybdenum, if less in quantity than hereinbefore indicated, produces a decrease in elevated temperature properties, while amounts in excess promote impairment by sigma phase. Any amounts of copper appreciably below the set limit of 2.5% also are detrimental to elevated temperature properties; amounts appreciably exceeding the upper limit of 3.5% adversely affect the hot working properties. The elements columbium and titanium in the quantities indicated hereinbefore given maximum high temperature strength and freedom from sigma phase.

In a preferred embodiment of my invention, the austenitic stainless steels which I provide more specifically contain about 0.09% to 0.20% carbon, 15.75% to 16.50% chromium, from 13.40% to 14.40% nickel, 2.25% to 2.75% molybdenum, from 2.5% to 3.5% copper, 0.10% to 0.25% titanium, 0.35% to 0.55% columbium, from 0.20% to 1.5% manganese, up to 0.70% silicon, up to about 0.03% sulphur, and the remainder substantially all iron. Incidental or purposeful amounts of phosphorus are present as already in-

indicated in connection with the broader composition range of the alloy steel. The amounts of carbon, titanium and columbium advantageously are consistent with the formula ratio previously noted.

I sometimes employ a certain form of heat treatment for enhancing the high temperature load carrying capacity of my stainless alloy steels. In this treatment, I heat the steel to within a solution temperature range of about 2050° F. to 2300° F., at which temperatures substantially all of the titanium and part of the columbium go into solution. The solubility of columbium increases in the higher side of the heating range. For reasons which will appear more fully hereinafter, I prefer to employ annealing temperatures of about 2200° F. to 2300° F.

With the titanium and part of the columbium in solution, I quench the steel as in air, oil, or water, conveniently to a temperature approaching that of the quenching medium. Then, for precipitation treatment, I heat the metal up to anywhere from 1200° to 1500° F., at which time columbium, titanium and copper too it is thought, precipitate in the matrix, the optimum temperature being about 1350° F. In this general treatment, a finely divided precipitate is critically dispersed in the metal lattice along the slip planes. A portion of the precipitated titanium and columbium appears in intermetallic compounds. The titanium and columbium to some extent precipitate as carbides which increase in amount on the higher side of the precipitation treatment temperature range just noted. The copper comes out in fine form it is believed, or possibly as an intermetallic compound including titanium, columbium and nickel. No particular advantage seems to accrue in extending the time of precipitation treatment beyond five hours, although up to fifty or one hundred hours may be used without detriment. The treating time accordingly is not highly critical.

I quench the steel from the precipitation treated condition. The quenched metal has a fine grain structure, and is further characterized by enhanced load-carrying capacity in view of atomic slip interference developed by the precipitates. These precipitates remain uncoalesced and effective against creep and stress-rupture of the steels for extremely long periods of time in high temperature use of the steel. By the annealing, especially within the preferred temperature range of 2200° F. to 2300° F., followed by the precipitation treatment, I substantially arrest any remaining tendency which the untreated steel may have toward sigma phase development.

Quite frequently, I use my stainless steels without first subjecting them to the combined annealing and precipitation treatment. The untreated steels are useful at temperatures mounting up to 1500° F. or more and have outstanding resistance to stress-rupture, creep, and are substantially free of the impairing effects of sigma phase. The combined heat treatment, however, I find aids as a supplemental protective measure against sigma formation particularly at extremely high temperatures of use.

As illustrative of the practice of my invention, I produce austenitic chromium-nickel stainless steel following the composition limits hereinbefore noted, the production conveniently being achieved in accordance with general stainless steel practices described in Patent 1,925,182 of Alexander L. Felld. By hot rolling or forging ingots of the steel, for example from a temperature of

2250° F., I produce billets. These are then forged into roughly formed high temperature gas turbine parts or other articles intended for high temperature duty. Machining to final size is achieved as desired. Fabrication of certain parts as from sheet, strip, wire or the like, and by welding with the oxy-acetylene torch, or electric arc means, employing welding rods preferably of approximately the same analysis as the metal being welded, is undertaken where desired. The finished articles are capable of withstanding temperatures up to 1500° F. or more. They are strong in tension, compression and torsion at the high temperatures encountered as distinguished from excessive elongation, weakness and premature failure where sigma phase develops. Also, while hot, they resist warping and are resistant to harmful scaling and corrosive or scouring attack by oxidizing gases.

Either before or preferably after finishing the high temperature articles as by machining, welding, or the like, I sometimes introduce my combined annealing and precipitation treatment for better developing the high temperature properties such as creep strength and stress rupture resistance and for further assurance against sigma phase development over and above the excellent resistance to this difficulty offered by the untreated metal itself.

The following tables are provided to illustrate stress-rupture properties of one of my austenitic stainless steels, this being identified as steel A in Table I. Steels B, C and D, also identified, are outside the critical composition range of my steels, and are introduced to enable a comparison of stress-rupture properties. All of the steels under intermediate consideration were subjected at like temperatures to my annealing and precipitation treatment, and thereafter were given stress-rupture tests at 1500° F.

Table I.—Composition

Steel	C	Cr	Ni	Mo	Cu	Ti	Cb	Mn	Si	S	P	Fe
A	0.130	16.39	14.38	1.78	3.03	0.16	0.39	0.78	0.53	0.015	0.018	Bal.
B	0.085	14.26	16.71	4.31	4.59	0.41	0.36	0.49	0.53	0.012	0.008	Bal.
C	0.076	17.25	14.00	2.83	3.14	0.22	0.36	1.45	0.49	0.009	0.026	Bal.
D	0.091	16.85	24.80	2.95	3.09	0.31	0.45	1.32	0.62	0.011	0.015	Bal.

¹ Steels outside the present critical range.

The results of the stress-rupture tests just mentioned are indicated with respect to several periods of loading time in Table II. Curves showing these and other stress-rupture values which may be expected with relation to time under stress, are to be found in the accompanying drawing. It will be seen that the steel A, representing my steels, is considerably superior.

Table II.—Stress rupture test at 1500° F.

[Stress (p. s. i.) required to rupture steel in time indicated.]

Sample	100 hrs.	1,000 hrs.	10,000 hrs.	100,000 hrs.
A	17,000	12,200	8,900	6,500
B	20,000	9,500	4,300	2,000
C	16,500	8,500	4,300	2,500
D	11,500	8,500	5,200	3,500

My austenitic chromium-nickel stainless steels especially where the sulphur content is low are capable of fabrication much on the order of the more commonly known austenitic steels, as by hot forming, yet have outstanding high temperature properties, this by virtue of the particular and highly critical combination of elements there-

in employed. The steels which I provide are especially reliable by reason of the substantial absence of sigma phase development, and accordingly are well suited for carrying load or resisting stress at high temperature. The steels in being amenable to annealing and precipitation heat treatment, thus within themselves offer a factor of safety against sigma formation over and above the excellent resistance in this respect afforded by the untreated metal.

Thus it will be seen that there is provided in this invention austenitic chromium-nickel stainless steel and products thereof in which the various objects noted, together with many thoroughly practical advantages are successfully achieved. It will be seen that the products are tough, strong and durable, corrosion-resistant and heat-resistant and are well adapted to withstand continuous high temperature duty over long periods of time and under the many variable conditions of actual practical use.

While there are many advantages attendant upon the inclusion of both of the elements titanium and columbium in my high temperature steels and products, and while the use of both elements is preferred, there are occasions where I modify the steels to the extent of using either titanium or columbium to the exclusion of the other, all further ingredients of the steel remaining substantially the same in character and amount as hereinbefore described. Upon employing the ingredient titanium under these circumstances, I usually resort to amounts within the range of 0.20% to 0.50% so as to compensate to some extent for the absence of columbium. These amounts are advantageously further restricted to consistency with the formula ratio:

$$\frac{2(\% \text{ Ti})}{\% \text{ C}} =$$

a numerical value ranging from 5 to 10. Con-

versely, in using columbium to the exclusion of titanium, the amounts of columbium preferably range from about 0.60% to 0.90% and further are advantageously held consistent with the formula ratio:

$$\frac{\% \text{ Cb}}{\% \text{ C}} =$$

a numerical value ranging from 5 to 10. The steels so provided, whether of titanium or columbium grade, are amenable to the annealing and precipitation heat treatments hereinbefore described.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiment hereinbefore set forth, it is to be understood that all matter described herein is to be interpreted as illustrative and not as a limitation.

I claim:

1. Austenitic stainless steel substantially free of sigma phase at elevated temperatures, said steel containing approximately 0.09% to 0.20% carbon, 15.75% to 16.75% chromium, from 13.25% to 14.75% nickel, 1.75% to 2.8% molybdenum,

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from 2.5% to 3.5% copper, 0.10% to 0.25% titanium, 0.35% to 0.55% columbium, from 0.20% to 1.5% manganese, up to 0.70 silicon, and the remainder substantially all iron.

2. Hot workable austenitic stainless steel substantially free of sigma phase at elevated temperatures, said steel containing approximately 0.09% to 0.20% carbon, 15.75% to 16.75% chromium, from 13.25% to 14.75% nickel, 1.75% to 2.8% molybdenum, from 2.5% to 3.5% copper, 0.60% to 0.90% columbium, from 0.20% to 1.5% manganese, up to 0.70% silicon, up to 0.03% sulphur, and the remainder substantially all iron, and said carbon and columbium further being restricted to amounts consistent with the formula

$$\frac{\% \text{Cb}}{\% \text{C}} =$$

a numerical value ranging from 5 to 10.

3. Hot workable austenitic stainless steel substantially free of sigma phase at elevated temperatures, said steel containing approximately 0.09% to 0.20% carbon, 15.75% to 16.75% chromium, from 13.25% to 14.75% nickel, 1.75% to 2.8% molybdenum, from 2.5% to 3.5% copper, 0.20% to 0.50% titanium, from 0.20% to 1.5% manganese, up to 0.70 silicon, up to 0.03% sulphur, and the remainder substantially all iron, and said carbon and titanium further being restricted to amounts consistent with the formula:

$$\frac{2(\% \text{Ti})}{\% \text{C}} =$$

a numerical value ranging from 5 to 10.

4. Heat treated austenitic stainless steel substantially free of sigma phase at elevated temperatures, containing approximately 0.09% to 0.20% carbon, 15.75% to 16.75% chromium, from 13.25% to 14.75% nickel, 1.75% to 2.8% molybdenum, from 2.5% to 3.5% copper, 0.10% to

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0.25% titanium, 0.35% to 0.55% columbium, from 0.20% to 1.5% manganese, up to 0.70% silicon and the remainder substantially all iron; said steel being characterized by heating within solid solution temperature range of said copper, titanium and columbium, and by re-heating to within temperatures giving precipitation and critical dispersion of a finely divided precipitate including titanium and columbium from solution.

5. Heat treated austenitic stainless steel substantially free of sigma phase at elevated temperatures, containing approximately 0.09% to 0.20% carbon, 15.75% to 16.75% chromium, from 13.25% to 14.75% nickel, 1.75% to 2.8% molybdenum, from 2.5% to 3.5% copper, one of the elements 0.20% to 0.50% titanium and 0.60% to 0.90% columbium, from 0.20% to 1.5% manganese, up to 0.70% silicon and the remainder substantially all iron; said steel being characterized by heating within solution temperature range; and by re-heating to achieve precipitation from solution.

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