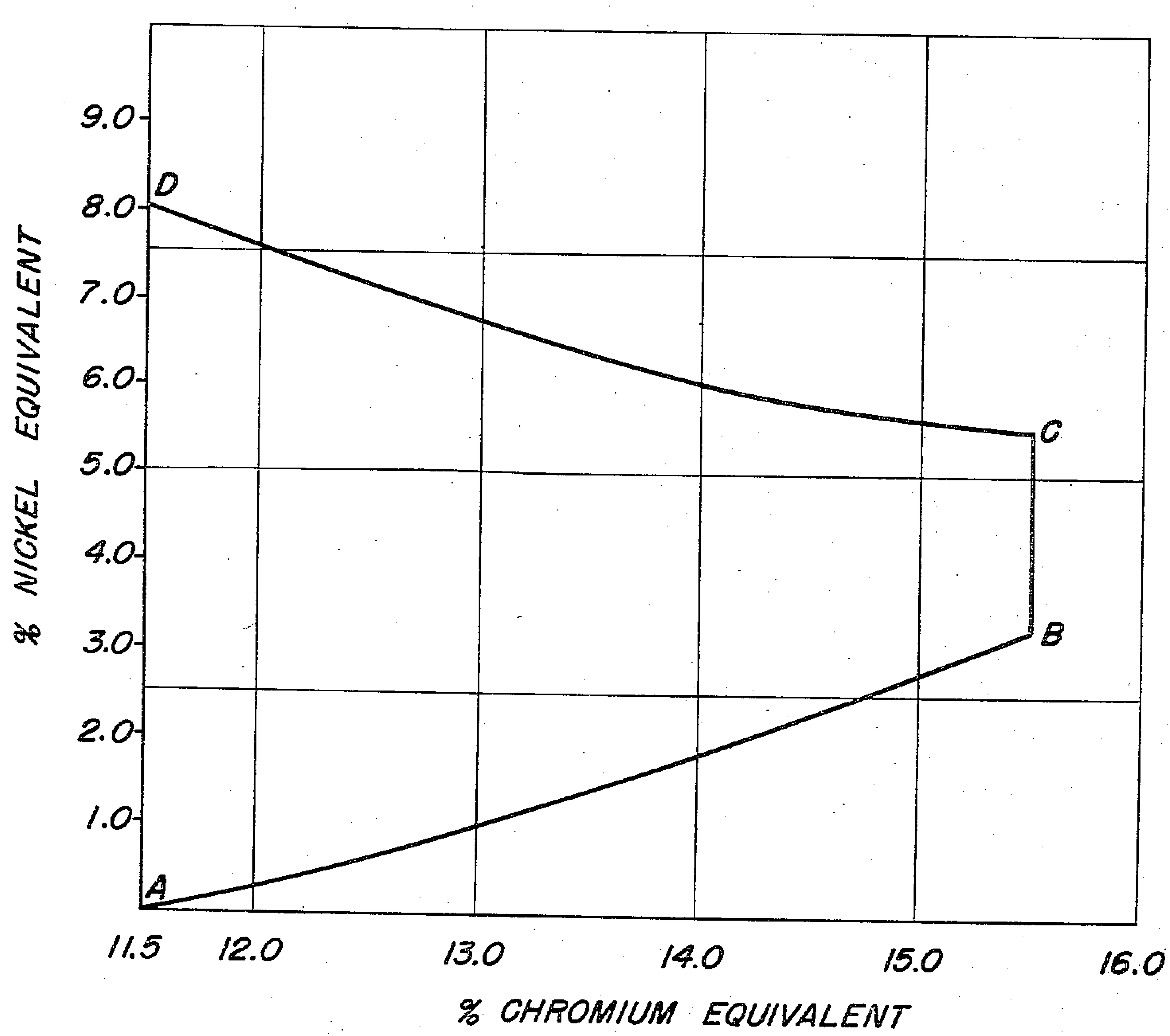
Sept. 2, 1958 W. C. CLARKE, JR 2,850,380

STAINLESS STEEL

Filed March 4, 1957

COMPOSITION RANGE OF PRECIPITATION-HARDENING CHROMIUM-NICKEL-COPPER STAINLESS STEEL.



INVENTOR
William C. Clarke, Jr.

BY [signature]

HIS ATTORNEY

United States Patent Office

2,850,380

Patented Sept. 2, 1958

1

2,850,380

STAINLESS STEEL

William C. Clarke, Jr., Baltimore, Md., assignor to Armco Steel Corporation, a corporation of Ohio

Application March 4, 1957, Serial No. 643,799

7 Claims. (Cl. 75—125)

My invention relates to stainless steel and more particularly to a heat-hardenable chromium-nickel stainless steel and various heat-hardened products and manufactures of the same.

One of the objects of my invention is the provision of a comparatively inexpensive chromium-nickel stainless steel which is heat-hardenable.

Another object is the provision of heat-hardened chromium-nickel stainless steel which is substantially entirely free of delta ferrite and which possesses high ultimate tensile strength and high yield strength.

A further object is the provision of a comparatively inexpensive heat-hardenable stainless steel which lends itself to working, forming, machining and the like, and then hardened by heat-treating methods with freedom from distortion, dimensional change or surface discoloration.

Other objects of my invention will in part be obvious and in part pointed out in the description which follows.

Accordingly, my invention consists in the combination of various elements, in the composition of the ingredients employed, and in the mixture of materials, the scope of which is set forth in the claims at the end of this specification.

In order to gain a better understanding of certain features of my invention it may be noted at this point that the well known austenitic chromium-nickel stainless steels, for example, the 18–8 steel, may be successfully subjected to a wide variety of fabricating operations, including bending, stamping, pressing, drawing, machining, and the like, in either the hot or cold condition. Moreover, in fabrication, the steels may be riveted, welded or soldered. But in general these steels may not be hardened by heat-treating methods following fabrication; nor, indeed, prior to fabrication. Any hardening ordinarily is through cold-working operations prior to fabrication; that is, cold-rolling, cold-drawing, and the like, in fashioning the metal into plate, sheet, strip, bars, rods, wire, tubes and special shapes.

Within comparatively recent years, however, that is, the past 12 or 15, there have been developed a number of special chromium-nickel stainless steels which are hardenable by heat-treating methods. I refer to the chromium-nickel steels employing one or more of titanium, columbium, aluminum and copper in a substantial amount. The addition ingredient serves as an age-hardening or precipitation-hardening agent. And although there are certain inherent objections to the columbium-bearing steel and titanium-bearing steel, particularly the latter, in matters of precisely controlling the titanium content in the melting operation and certain irregular losses of titanium in welding, success is had with the aluminum-bearing age-hardening chromium-nickel stainless steel and also with the copper-bearing age-hardenable steel. But these steels are rather expensive and the art is receptive to heat-hardenable chromium-nickel stainless steel which possesses the physical properties of the known copper-bearing age-hardening steel with savings of important alloying ingredients and consequently at less expense. And particularly, the art is receptive to a heat-hardenable chromium-nickel stainless steel which is substantially entirely free of delta ferrite.

2

Accordingly, therefore, one of the outstanding objects of my invention is the provision of a chromium-nickel stainless steel of minimum expensive alloying ingredients, a steel which lends itself to ready fabrication by known methods and which, subsequent to fabrication, may be heat-hardened to achieve great tensile strength and great yield strength with substantially complete freedom from the presence of delta ferrite.

In the accompanying drawing there is graphically indicated the composition balance preserved in the steel of my invention as defined in terms of the chromium equivalents versus the nickel equivalents.

Referring now more particularly to the practice of my invention, I provide a chromium-nickel stainless steel essentially consisting of chromium in the amount of 11.5% to 15.5%, nickel from residual amounts up to 8%, the particular amount employed being correlated with the chromium content and other ingredients as dealt with below, copper in the amount of 1% to 5%, and the remainder substantially all iron. Preferably, the steel contains about 12.5% to 15% chromium, about 1% to 4% nickel, and 2.5% to 4.5% copper, with remainder iron.

Carbon, of course, is present in my steel, this in amounts up to 0.20%, and in the preferred steel, up to 0.07%. Nitrogen also may be present in amounts up to .20%. The silicon content is maintained at 1% maximum. And the phosphorus is in the normal residual amount, say 0.04% maximum.

In my steel molybdenum may be substituted for chromium, this on an equal basis with the chromium replaced, and in an amount up to 3%. So, too, manganese may be substituted for nickel, this, however, on the basis of the manganese addition being twice that of the nickel which it is to replace. Either columbium or titanium may be added to my steel, the former in amounts up to 1.00% and the latter up to 0.50%, with the provision, however, that the columbium addition preferably does not exceed about 8 times the carbon content, and the titanium addition not more than about 5 times the carbon content. And either sulphur or selenium, or both, may be added in amounts up to 0.40%, to improve the machinability of the metal. There may be added beryllium in amounts up to 0.50% to achieve a further heat-hardening effect, that is, some hardening in addition to that had with the copper.

In the heat-hardenable chromium-nickel stainless steel of my invention there is a further limitation on composition, however. I find it essential there be preserved a particular balance between the sum of the chromium and molybdenum contents, on the one hand, and the sum of the nickel, manganese, carbon and nitrogen contents, on the other. This relationship is in every sense critical. The composition of the steel of my invention, as expressed in terms of the chromium equivalents, that is, the chromium content plus the molybdenum content, as compared with the nickel equivalents, that is, the sum of the nickel content plus half the manganese content plus thirty times the total of the carbon and nitrogen contents less 0.06%, is defined by the area ABCD of the accompanying diagram. Where there is employed a lesser chromium content and lesser chromium equivalent, I find that the corrosion-resisting properties of the steel sharply suffer. And where greater amounts of chromium or chromium equivalent are employed there is no assurance of the absence of delta ferrite. And similarly, where there is employed nickel in amounts less than required in the critical steel of my invention for any particular amount of chromium equivalent, I find that there is a loss of solubility for copper. With excessive amounts of nickel or nickel equivalent, that is, amounts over and above those employed in the steel of my invention, the ultimate tensile strength and particularly the yield strength sharply suffer. In short, then, the steel of my invention, as first defined in terms of the various particular ingredients noted above within the percentage ranges there given, and further defined in terms of correlation between the chromium equivalents versus the nickel equivalents as given in the accompanying drawing, is highly critical.

The steel of my invention in either cast or wrought form, for example, plate, sheet, strip, bar, rod, wire or special shapes, is usually supplied the manufacturer or fabricator in annealed condition, that is, in a condition following heating at a temperature of some 1550° F. to 2000° F. and cooling. And in this condition the steel is machined in the case of castings or is bent, stamped, punched, drawn, upset or otherwise formed and then machined, where necessary, in the production of the variety of articles of ultimate use. Typically, the flat products are fashioned into structural members and trim for aircraft. And the rod and wire is fashioned into bolts, screws, nuts, surgical instruments and a host of similar articles.

The great strength and hardness of the comparatively inexpensive steel of my invention is now had by appropriate heat-treatment. The various articles and products of manufacture are brought to a temperature of about 850° to 950° F. for a period of some 15 minutes on up to 2 hours, and then cooled to room temperature. The hardening is had with freedom from distortion and with substantially no noticeable surface discoloration.

Where desired, it will be understood that full hardening of the steel may be had prior to machining, for example, in the production of various cast products. Although even with such products machining prior to heat-hardening is generally preferred because of the lower hardness in that condition.

As illustrative of the practice of my invention, I have prepared five specific examples of the steel of my invention as given in Table I below. And following rolling into bars, the steels were annealed and then hardened.

TABLE I

Chemical analysis of five preferred austenitic chromium-nickel-copper stainless steels

Heat No.	C	Mn	P	S	Si	Cr	Ni	Cu	Cb
E1202	.048	-----	-----	-----	-----	15.26	3.92	4.10	-----
E1452	.047	.65	.006	.008	.48	12.73	.88	3.74	.40
E1434	.052	.66	.006	.009	.48	12.52	1.86	3.97	.40
E1451	.053	.59	.006	.009	.41	12.59	2.92	3.74	.28
E1453	.047	.59	.007	.012	.47	12.47	4.85	3.72	-----

The five specific examples of the steel of my invention as given in Table I above were annealed at 1800° F. for ½ hour and water quenched; and tested, with results as given under the designation "Annealed" in Table II below. Other samples were annealed as noted and then hardened by reheating to 900° F. for 1 hour and air-cooling. These were tested with the results given under the notation "Hardened" in Table II below:

TABLE II

Mechanical properties of the steels of Table I in the annealed condition and in the hardened condition

Heat No.	Ult. tens. str., p. s. i.	.2% yld., p. s. i.	Elong. 2″, percent	Red. area, percent	Hardness Rc
E1202 annealed	162,000	118,000	5.5	16.0	32–33
E1202 hardened	210,600	183,500	7.0	35.7	45
E1452 annealed	152,600	135,000	8.5	50.0	35–37
E1452 hardened	200,000	185,000	10.0	51.0	42
E1434 annealed	151,000	131,700	5	35.4	31.5
E1434 hardened	199,500	182,700	10	52.2	41.0
E1451 annealed	154,500	131,000	2.0	3.6	31
E1451 hardened	202,800	186,700	10.0	49.5	42.5
E1453 annealed	171,600	135,100	5.0	15.0	37.5
E1453 hardened	211,800	188,000	6.5	35.8	44.0

It will be noted that the steel of my invention is possessed of excellent mechanical properties, particularly that the ultimate tensile strength is on the order of 200,000 p. s. i. or even more and that the yield strength rather closely approaches the high ultimate tensile figure. Thus, in the examples analyzing about 12.5% chromium, 1% to 5% nickel, about 4% copper and remainder substantially all iron, the yield strength in the heat-hardened condition amounts to about 183,000 to 188,000 p. s. i. (Heats E1452, E1451, E1434 and E1453) while the corresponding ultimate tensile strength ranges from about 200,000 to 212,000 p. s. i. Even in the annealed condition the steel is possessed of substantial yield strength, this ranging for the four examples of the 12.5% chromium steel from about 131,000 to 135,000 p. s. i.

As may be seen from a comparison of the steels of Heats E1202 and E1453 which are free of columbium, with those of Heats E1452, E1434 and E1451 which contain the columbium addition, there is an appreciable difference in ductility. In the one group the reduction in area in the annealed condition amounts to about 15%, while in the other group this is on the order of 35% to 50%. Moreover, this ductility is reflected in the hardened steels, the two examples without columbium having ductility on the order of 35%, whereas the three examples with columbium enjoy ductilities on the order of 50%. It is to be noted, however, that the gain in ductility is enjoyed at some sacrifice to the ultimate tensile strength, although of no appreciable sacrifice to yield strength.

In general, however, the steels of my invention are made free of titanium and/or columbium, since I prefer to rely upon small amounts of carbon and nitrogen, too, as partial substitutes for nickel in amount and value as given above. With the introduction of columbium and/or titanium, a certain amount of the carbon apparently combines with these ingredients and additional nickel or additional carbon is required to compensate for the loss and maintain the balance between the chromium equivalents and the nickel equivalents in the steel of my invention.

It will be seen, therefore, that I provide in my invention a chromium-nickel stainless steel which accomplishes the various objects hereinbefore set forth together with many practical advantages. My steel employs a minimum of the expensive ingredients chromium and nickel. It readily lends itself to production in cast form as well as in a wide variety of wrought forms such as plate, sheet, strip, bars, rods, wire and special shapes. The steel may be machined or fabricated as by known fabricating methods, including welding and brazing, into a host of articles of ultimate use. And it readily lends itself to hardening by heat-treating methods to achieve great yield strength and great ultimate strength without discoloration. Of particular significance the steel is free of delta ferrite, the delta ferrite in the steel of my invention being substantially less than 5% by volume.

Inasmuch as many possible embodiments may be made of the steel of my invention and as many variations may be made in the particular embodiments hereinbefore set forth, it will be understood that all matter described in this specification or shown in the accompanying drawing is to be interpreted as illustrative and not as a limitation.

I claim as my invention:

1. A stainless steel free of delta ferrite and having precipitation-hardenable properties, said steel essentially consisting of chromium 11.5% to 15.5%, nickel from incidental amounts up to 8%, copper 1% to 5%, carbon up to 0.20%, nitrogen up to 0.20%, manganese up to 16%, molybdenum up to 3%, silicon 1% maximum, phosphorus 0.04% maximum, material of the group columbium up to 1.00% and titanium up to 0.50%, material of the group sulphur and selenium up to 0.40%, beryllium up to 0.50%, and remainder substantially all iron, with the sum of the chromium equivalents and the sum of the nickel equivalents falling within the area ABCD of the accompanying diagram.

2. A stainless steel free of delta ferrite and having precipitation-hardenable properties, said steel essentially consisting of 11.5% to 15.5% chromium, incidental amounts up to 8% nickel, 1% to 5% copper, and remainder substantially all iron, with the particular amounts of chromium and nickel falling within the area ABCD of the accompanying diagram.

3. A stainless steel free of delta ferrite and having precipitation-hardenable properties, said steel essentially consisting of 12.5% to 15% chromium, 1% to 4% nickel, 2.5% to 4.5% copper, and remainder substantially all iron, with the particular amounts of chromium and nickel falling within the area ABCD of the accompanying diagram.

4. A precipitation-hardened stainless steel free of delta ferrite and of high yield strength, said steel essentially consisting of chromium 11.5% to 15.5%, nickel from incidental amounts up to 8%, copper 1% to 5%, carbon up to 0.20%, nitrogen up to 0.20%, manganese up to 16%, molybdenum up to 3%, silicon 1% maximum, phosphorus 0.04% maximum, material of the group columbium up to 1.00% and titanium up to 0.50%, material of the group sulphur and selenium up to 0.40%, beryllium up to 0.50% and remainder substantially all iron, with the sum of the chromium equivalents and the

sum of the nickel equivalents falling within the area ABCD of the accompanying diagram.

5. A precipitation-hardened stainless steel free of delta ferrite and of high yield strength, said steel essentially consisting of 11.5% to 15.5% chromium, incidental amounts up to 8% nickel, 1% to 5% copper, and remainder substantially all iron, with the particular amounts of chromium and nickel falling within the area ABCD of the accompanying diagram.

6. A precipitation-hardened stainless steel casting free of delta ferrite and essentially consisting of 12.5% to 15% chromium, 1% to 4% nickel, 2.5% to 4.5% copper, and remainder substantially all iron, with the particular amounts of chromium and nickel falling within the area ABCD of the accompanying diagram.

7. A wrought stainless steel manufacture free of delta ferrite and essentially consisting of 11.5% to 15.5% chromium, incidental amounts up to 8% nickel, 1% to 5% copper, and remainder substantially all iron, with the particular amounts of chromium and nickel falling within the area ABCD of the accompanying drawing.

References Cited in the file of this patent

FOREIGN PATENTS

437,592 Great Britain ------------ Oct. 23, 1935