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STAINLESS STEEL AND METHOD

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ABSTRACT OF THE DISCLOSURE

Heat-hardenable stainless steel which, in addition to chromium and carbon, essentially contains nitrogen and columbium-tantalum in particular amount, and in which any molybdenum and/or tungsten is maintained in critically low amount. More particularly, the steel essentially consists of about .01% to about .25% carbon, about .01% to 3% manganese, about .01% to about 2% silicon, about 10% to about 16% chromium, any molybdenum not exceeding .3% and any tungsten not exceeding .5% and with molybdenum and tungsten together not exceeding about .5% in total, about .04% to about .2% nitrogen, about .03% to about .75% columbium-tantalum, up to about .75% vanadium, and remainder substantially all iron. The steel is particularly produced in the form of bar stock from which various products are fashioned, especially turbine blading and the like.

My invention relates to the straight chromium grades of stainless steel, more particularly the A.I.S.I. (American Iron & Steel Institute) 400 series of compositions generally indicated below.

One of the objects of the invention is the provision of a high temperature stainless steel which is hardenable by heat-treatment, to give high tensile strength and high yield strength at room temperatures and at high temperature as well, and which, moreover, is tough, ductile and of good impact strength.

A further object is the provision of such a steel which works well in the hot-mill, as in the production of plate, sheet and strip as well as bar, rod and wire and which lends itself to a variety of working and forming operations such as machining, cutting, blanking, threading, and the like, as well as forging, and which in addition readily lends itself to soldering, brazing and welding as in the production of a variety of articles and products of ultimate use suited to high temperature applications, that is, applications where there are reached temperatures up to about 1100° F.

Another object is the provision of a stainless steel and method of heat-treating the same wherein the response to heat-treatment is uniform throughout the metal and which stainless steel exhibits great resistance to tempering and to creep.

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

My invention, in general, is considered to reside in the combination of chemical elements, in the composition of ingredients and in the relation of each of the same with one or more of the others as described herein, and in the sequence of operational steps and interrelation between them as also described, the scope of the application of all of which is set out in the claims made at the end of this specification.

Background of the invention

As an aid to a better understanding of certain features of my invention, it is to be noted at this point that the straight chromium grades of stainless steel which are hardenable by heat-treatment, that is, the A.I.S.I. 400

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series from 403 up to 440, are of a martensitic structure. This embraces Type 403 (11.5% to 13% chromium, 1.00% max. manganese, 0.50% max. silicon, 0.15% max. carbon, and remainder iron), Type 410 (11.5% to 13.5% chromium, 1.00% max. manganese, 1.00% max. silicon, 0.15% max. carbon, and remainder iron), Type 414 (11.5% to 13.5% chromium, 1.25% to 2.50% nickel, 1.00% max. manganese, 1.00% max. silicon, 0.15% max. carbon, and remainder iron), Type 416 (12% to 14% chromium, 1.25% manganese, 1.00% max. silicon, 0.15% min. sulphur, with molybdenum and zirconium each up to 0.60% max., 0.15% max. carbon, and remainder iron), Type 420 (12% to 14% chromium, 1.00% max. manganese, 1.00% max. silicon, over .15% carbon, and remainder iron), Type 431 (15% to 17% chromium, 1.25% to 2.50% nickel, 1.00% max. manganese, 1.00% max. silicon, 0.20% max. carbon, and remainder iron), and Type 440 (16% to 18% chromium, 1.00% max. manganese, 1.00% max. silicon, with molybdenum to 0.75% max., 0.60% to 1.20% carbon for different varieties of the Type 440, and remainder iron).

While, as suggested above, the heat-hardenable stainless steels of the 400 series are possessed of many favorable properties and lend themselves to a variety of applications, I find that they are deficient in a number of respects and are not truly suited to certain applications. Thus these prior art steels are subject to severe segregation effects, rather inadequate toughness, limited machinability and a susceptibility to stress-corrosion cracking. More particularly, these steels are inclined to suffer from non-uniformity in texture and weakness in mechanical strength due to segregation of massive carbides. And the steels are susceptible to quench cracking.

Although the straight chromium grades of stainless steel in recent years have been modified through the addition of one or more further ingredients such as molybdenum, tungsten, vanadium and columbium, still a desired combination of strength, both at room temperatures and at high temperatures, and toughness, is not fully achieved. Reference is made to the modifications introduced over the years to the 12% chromium grade of stainless steel. Initially this steel, identified as Type 410, as noted above, analyzed 11.5% to 13.5% chromium, up to 1.00% max. each of manganese and silicon, 0.15% max. carbon, and remainder substantially all iron. The steel was subsequently modified and identified as Type 422 through the introduction of small amounts of the ingredients nickel, molybdenum, tungsten and vanadium, the steel typically analyzing 13.0% chromium, .75% nickel, 1.0% molybdenum, 1.0% tungsten, .34% vanadium, .22% carbon, and remainder iron. A further modified steel, generally referred to as 12 Cr-Ni-Mo-V typically analyzes 11.5% chromium, .70% nickel, 1.0% molybdenum, .25% vanadium, .17% carbon, and remainder iron. Another, referred to as 12-2W, analyzes 12.0% chromium, 2.0% nickel, 3.0% tungsten, .18% carbon, and remainder iron. But I find that these various modified steels also lack the desired combination of strength and toughness. They lack the combination of room temperature strength along with high temperature strength; when one is satisfactory the other is deficient. And they lack toughness; the impact strength is inadequate and so, too, the resistance to stress-corrosion cracking. They are notch-sensitive. Moreover, with substantial additions of nickel, molybdenum and tungsten, they are expensive.

Perhaps the most recent modified Type 410 stainless steel which has been made available is that described and claimed in my prior U.S. Letters Patent 3,000,729 of Sept. 19, 1961. That steel, in addition to some 10.0% to 14.0% chromium and .07% to .14% carbon, contains columbium-tantalum in the amount of .05% to

.35% with or without vanadium in amounts up to .20%. The remainder of the composition, of course, is substantially all iron. While this steel possesses many of the characteristics now sought, it is lacking in strength both at room temperatures and at elevated temperatures. And I find that the desired strength is not achieved merely by adding more of the columbium-tantalum and vanadium ingredients.

There is the further steel, this being that described and claimed in the U.S. Letters Patent 3,139,337 issued to Boyle et al. on June 30, 1964. But here again, the tensile strength is inadequate. And moreover, the impact strength is deficient. Additionally, the steel like several of those referred to above is objectionably expensive because of the kind and quantity of alloying ingredients employed.

Accordingly, one of the objects of my invention is the provision of a steel that overcomes the deficiencies of the steels of the prior art, which is a comparatively inexpensive modified grade of heat-hardenable straight chromium stainless steel; which, moreover, lends itself to hardening and tempering to give a steel which is strong, tough and resistant to stress-corrosion cracking both at room temperatures and at high temperatures as well; which readily may be machined and fabricated as by cutting, blanking, threading, and the like and brazed or welded as desired in the production of a variety of articles of ultimate use; and which may be heat-treated in simple and direct fashion with uniform and consistent results.

Summary of the invention

Referring now more particularly to the practice of my invention, I find that in the steels of the prior art strength and hardness are developed by virtue of the substantial carbon content. The steels, when hardened, of course are martensitic. With the prior art steels, massive ledeburitic carbides are formed in the ingot. These carbides remain as segregates which are not readily dispersed in the steel matrix, either by working or by thermal treatment. On the contrary, they remain as clusters or as stringers (extended fibres) following conversion of the ingot to semi-finished sections or in the final product. As a consequence, the metal is weakened, particularly in transverse direction, that is, transverse to the direction of rolling or drawing.

And while in certain steels of the prior art greater strength is had as a result of additions of molybdenum and/or tungsten, I find that the addition of either one or both of these ingredients definitely decreases the solubility for carbon; that it becomes difficult to get the carbon into solution and difficult to achieve a desired quench-hardness which hardness is retained following a tempering treatment. Moreover, as in the case of chromium carbides, the molybdenum carbides and tungsten carbides which form are inclined to coalesce or enlarge, giving massive carbides dispersed throughout the metal. I feel that these massive carbides, while providing a block to the flow of the metal under stress, and in a sense strengthening the metal, necessarily detract from the ductility and toughness. The action is not a true hardening and strengthening effect, but rather is in the nature of an impediment to flow which is purposely introduced. And particularly increases in high temperature hardness and strength are not fully had through further increases of carbon, molybdenum and tungsten because of even greater difficulty in taking the carbon into solution with the larger carbides. In addition, with increases in carbon the metal becomes more difficult to process in the mill.

Regardless of theory, however, I find that the steels of the prior art employing molybdenum and/or tungsten or even chromium with substantial quantities of carbon, do not enjoy a combination of ductility and toughness along with tensile strength.

Now it is my discovery that a secondary hardening

effect is had in the so-called straight chromium steels, this over and beyond the hardening had with carbon, by way of an addition of nitrogen and columbium-tantalum. Apparently there is a reaction between nitrogen and columbium-tantalum which is most beneficial in achieving a fine grain structure, with nitrides finely dispersed throughout the metal which strengthens the matrix. There results an increase in hardness and strength not only at room temperatures but at elevated temperatures, as well. This is had in absence of massive carbides for I find that the presence of columbium-tantalum minimizes the formation of the massive chromium carbides; the chromium carbides which do form are small and well dispersed throughout the steel. And ductility and toughness directly benefit.

For best results, since the carbon reaction seems to take precedence over the nitrogen reaction, a large amount of carbon is not desirable but rather there is employed only just sufficient carbon to achieve desired quench-hardness. Greater amounts of carbon merely tie up or combine with one of the columbium-tantalum, chromium and others of the alloy ingredients present. There directly results a loss in their effectiveness. And the carbides formed serve as undesirable inclusions which lower ductility and toughness.

Nitrogen is used in amount sufficient to achieve the desired final hardness and retain that hardness upon tempering. With the nitrogen addition hardness and strength are had and subsequently retained at elevated temperatures. There seems to be had some molecular locking rather than the interference effect noted with massive carbides found in the steels of the prior art. But here again, irrespective of theory, in my steel there is had ductility and toughness along with hardness and strength. Hardness and strength, without loss in ductility and toughness, are further heightened by an addition of vanadium, this in controlled amount as appears more fully below.

In accordance with the teachings of my invention, I provide a stainless steel essentially consisting of about .01% to about .25% carbon, about 10% to about 16% chromium, about 0.4% to about .2% nitrogen, about .03% to about .75% columbium-tantalum, and remainder substantially all iron. In the steel of my invention manganese may be present in the amount of about .01% to about 3% and silicon in the amount of about .01% to about 2%. So, too, nickel may be present in amounts up to 2% as a maximum. The ingredients phosphorus and sulphur, commonly present in all stainless steels, are maintained in amounts each not exceeding .050% as a maximum. And any molybdenum which may be present is maintained at a value not exceeding .3% and preferably not exceeding about .2% because of the ferritizing tendency, as more particularly pointed to below. Similarly, any tungsten which may be present is maintained at a value not exceeding about .5% and preferably not exceeding about .2% for best results. The combined molybdenum and tungsten is maintained at a figure not exceeding about .5%, preferably not exceeding about .2% for best ductility and toughness for steel of minimum cost. Actually, molybdenum and tungsten seldom exceed .05% to .08% for the molybdenum and about .10% for the tungsten.

Vanadium, this in amount up to about .75%, preferably is included in the composition as appears more fully hereinafter. Customarily, vanadium amounts to some .03% to about .75%, preferably about .03% to about .35%, or more preferably about .10% to about .35% for the best combination of hardness, strength and toughness.

Now in the steel of my invention the ingredients carbon, chromium, nitrogen and columbium-tantalum are in every sense critical. Thus the chromium content must be at least about 10% for otherwise there is a sharp loss in corrosion resistance and an undesired development of heat-scale in service at elevated temperatures. Moreover,

there is a loss in the solubility for nitrogen, an ingredient essential to my steel. On the other hand, the chromium content should not exceed about 16% because chromium in excess of this figure is inclined to give a steel which is excessively ferritic with attendant loss of mechanical properties. For a steel of minimum cost the preferred chromium content amounts to about 11% to 12%, or even about 10% to about 13%. For a steel of greater strength and toughness as well as greater corrosion resistance, the chromium content amounts to about 13% to about 15%, more especially, about 15%.

The carbon content of my stainless steel is maintained at a value of at least .01% since little purpose and little benefit is achieved by a lesser amount. Carbon, however, must not exceed about .25%, because I find that any further amount of carbon develops an excessive number of segregates which adversely affect the toughness of the metal. A preferred carbon content amounts to about .15% to about .25%, more preferably about .1% to about .2%, for certain applications, for example, turbine blading and blades for compressors. In some applications as for steels of general utility, I prefer a carbon content of about .05% to about .15% for the steels of the higher chromium contents. In still others, as where greater hardness is required, a carbon content of about .10% to about .20% is preferable.

The ingredient nitrogen, as indicated above, is essential, this in the amount of about .04% to about .2%. A nitrogen content less than about .04% I find to be of no particular benefit. And with a nitrogen content exceeding about .2% even with a chromium content as high as about 16%, there is a possibility of gassiness with the result that unsound metal is had. In general, I prefer a nitrogen content of about 0.06% to about .16%, although in some embodiments, as noted below, the nitrogen content amounts to about .04% to about .2%.

Columbium-tantalum, as noted above, is in the amount of about .03% to about .75%. At least .03% columbium-tantalum is required in order to give any benefit either in grain size control or in reaction with the nitrogen present. And columbium-tantalum in excess of .35% merely ties up carbon, thereby lowering the amount which may be taken into solution, with the result that both the quench hardness and the temper hardness suffer. Moreover, an excess quantity of columbium-tantalum gives rise to massive segregates which impair the ductility and toughness of the metal. For most steels, the preferred columbium-tantalum content is on the order of about .1% to about .3%, or even about .1% to about .2% or, more particularly .08% to .15%, depending upon the proportioning of the other ingredients, as more fully noted below.

Vanadium, where employed, is in the amount of at least .03%, any lesser amount offering little or no benefit. The vanadium, however, should not exceed about .75% because, like an excess of columbium-tantalum, the excess merely ties up carbon, thereby decreasing the amount which may be taken into solution and both quench hardness and temper hardness are adversely affected. As well, massive segregates appear causing a loss of yield strength, ductility, toughness and impact resistance. With both columbium-tantalum and vanadium present in the steel, it appears that the columbium-tantalum reacts with the carbon present, leaving the vanadium to act with the nitrogen content to best increase hardness and strength. The presence of both gives the steel its best mechanical properties.

In my steel, as noted above, there are present the ingredients manganese, silicon, phosphorus and sulphur, ingredients which commonly are present in all stainless steels. The manganese and silicon contents are each in the amount of at least .01%, this being a practical lower limit for these ingredients, on up to about 1% or even about 2% for the silicon as noted above and on up to about 1% for the manganese. Actually, as also noted above the

manganese may be employed beneficially in amounts up to about 3%, this serving principally as a means of stabilizing the high temperature austenite of the steel. An excess, however, would be inclined to make the metal sluggish in transforming to martensite in quench hardening. The manganese additionally has the benefit of serving as a convenient vehicle for introducing a substantial part of the nitrogen required; the nitrogen generally being added by way of a nitrided electrolytic manganese. The silicon employed serves to impart a resistance to heat-scale in high temperature applications. But silicon in an amount exceeding 2% induces segregates, in this respect acting very much like an excess of carbon. Moreover, the excess silicon is inclined to make the metal objectionably ferritic.

The phosphorus and sulphur contents each should not exceed .05% as a maximum because they are inclined to introduce hot-working difficulties. And, moreover, with the higher sulphur contents the impact strength of the metal drastically suffers.

The nickel content of my steel should not exceed 2% as indicated above, for nickel is an austenite stabilizer and with the higher nickel content there is difficulty in annealing the metal. Moreover, nickel is an expensive ingredient. In my steel I prefer a nickel content not exceeding 1% as a maximum, and more preferably a maximum of .5%.

As an important feature, the steel of my invention is made virtually free of the ingredients molybdenum and tungsten, ingredients which commonly are present in substantial quantity in the high temperature straight chromium stainless steels of the prior art. For I find that these two ingredients incline toward the development of a hyper-eutectoid steel and the production of massive segregates. While both molybdenum and tungsten long have been recognized as strong carbide forming elements and to lend strength at high temperatures, I find that the carbides of these two ingredients, possibly because of the tendency toward the production of massive carbide segregates, definitely impair ductility, toughness and impact resistance. This impairment I attribute to an impeding of plastic flow. Regardless of theory, however, I find that massive carbides do exist. And in the steel of my invention I purposely limit the amount of any molybdenum to a figure not exceeding about .3%, preferably not exceeding about .2%, and an tungsten present in the metal to a level not exceeding about .5%, and preferably not exceeding about .3%, with the sum of the two not exceeding about .5% and preferably not exceeding about .2% in total.

Description of the preferred embodiments

A preferred steel according to my invention essentially consists of about .01%, or even about .05%, on up to about .25% carbon, about .01% to about 1% manganese, about 10% to about 13% chromium, about .04% to about .16%, or even to about .2% nitrogen, about .03% to about .75% or more preferably about .1% to about .3% columbium-tantalum, up to about .75% and preferably about .03% to about .75% vanadium, with the sum of any molybdenum and tungsten not exceeding about .5%, preferably not exceeding about .2% as a maximum, and remainder substantially all iron. Another essentially consists of about .01% to about .2% carbon, about 11% to about 12% chromium, about .04% to about .16% nitrogen, about .1% to about .75% or more preferably about .1% to about .3% columbium-tantalum, about 0% to about .60% vanadium, the vanadium content preferably amounting to about .2% to about .4%, with any molybdenum and tungsten not exceeding about .5% in total, preferably not exceeding .2% in total, and remainder substantially all iron. A further steel, particularly suited to petroleum and chemical applications where strength, toughness and resistance to softening at high temperature is required, essentially consists of about

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1.1% to about .2% carbon, about 13% to about 15% chromium, about .04% to about .2% nitrogen, about 1% to about .3% columbium-tantalum, 0% to .6% and preferably about .2% to about .6% vanadium, with the sum of any molybdenum and tungsten not exceeding about .5% and preferably not exceeding .2%, with remainder substantially all iron.

The stainless steel of my invention conveniently may be melted in the electric arc furnace. Or, as desired, it may be melted in the induction furnace. Of course, it may also be vacuum-melted, i.e., melted in the electric arc furnace under vacuum conditions. Or there may be

is presented the chemical compositions of some five 12-chromium grades of stainless steel, one according to the present invention containing the ingredients columbium-tantalum and nitrogen in combination, another according to the invention in which vanadium also is present, and three others, these departing from the steels of the present invention in the absence of one or both of the ingredients columbium-tantalum and nitrogen. And in Table II below there are presented the Rockwell hardness values of these various steels, following heating and quenching from different temperatures and also following a tempering treatment of the several hardened steels.

TABLE I.—CHEMICAL COMPOSITION OF FIVE 12-CHROMIUM STAINLESS STEELS

	C	Mn	P	S	Si	Cr	Ni	Mo	N	Cb ²	V
Heat No.:											
R4982-1.....	.049	.74	.015	.017	.33	12.25	.13	.04	.058	.005	.01
R4982-2 ¹	.049	.74	.015	.017	.33	12.25	.13	.04	.058	.11	.01
R4982-3 ¹	.049	.74	.015	.017	.33	12.25	.13	.04	.058	.11	.21
12Cr-Cb.....	.12	.30	.015	.016	.28	12.00	.15	.04	.027	.15	.01
12Cr-Cb-V.....	.13	.43	.011	.019	.20	11.67	.16	.08	.026	.10	.11

¹ Steel of invention.
² Columbium-tantalum, reported as Columbium.

NOTE.—The remainder of the composition is substantially all iron.

employed a double melting process, i.e., melting in the electric arc furnace or induction furnace followed by remelting under vacuum conditions. But, in general, in order to produce a satisfactory steel, this at minimum cost, electric arc furnace melting is found to be entirely satisfactory.

The steels of Table I were variously solution-treated at 1700° F., 1800° F. and 1900° F. and quenched in oil and subsequently tempered at 1200° F. for 4 hours and air-cooled. The Rockwell hardness figures were taken for all samples in quenched and in tempered conditions, the hardness figures being reported in Table II below:

TABLE II.—ROCKWELL HARDNESS FIGURES FOR THE STEELS OF TABLE I IN THE HARDENED AND IN THE HARDENED AND TEMPERED CONDITION

	1,700° F., O.Q.	1,800° F., O.Q.	1,900° F., O.Q.	1,700° F., O.Q. +1,200° F., 4 hrs., A.C.	1,800° F., O.Q. +1,200° F., 4 hrs., A.C.	1,900° F., O.Q. +1,200° F., 4 hrs., A.C.
Heat No.:						
R4982-1.....	C39	C38	C38	B95	B95	B95
R4982-2 ¹	C38	C38	C37	C24	C24	C23
R4982-3 ¹	C37	C38	C36	C26	C27	C29
12Cr-Cb.....	C42	C44	C44	C23	C24	C25
12Cr-Cb-V.....	C43	C44	C44	C23	C25	C25

¹ Steel of invention.

The steel, however melted, conveniently is cast in the form of ingots from which it is converted into slabs, blooms or billets, from which it is further converted into plate, sheet, strip, bars and wire through conventional hot-rolling operation. The metal readily may be forged as in the production of a variety of rough-fashioned articles and then machined to specification.

My steel is particularly suited to the production of steam turbine blades as well as the compressor blades for jet propulsion engines. Because of its greater yield strength my steel permits the construction and use of larger blades, and thereby increased efficiency in turbine and compressor operation.

The stainless steel and articles of my invention are quench-hardened as by heating at a temperature of about 1700° to about 2100° F. for a time up to about 4 hours or more and then quenched in air, oil, water or the like. Following the quench-hardening the metal may then be subjected to a tempering treatment, this to relieve stresses and impart a desired temper. Here the metal is reheated to a temperature of about 900° to 1300° F. and cooled, as desired. With this treatment, as more fully indicated below, there is had an excellent combination of yield strength, ductility and toughness. There are achieved in the hardened and tempered steel of my invention yield strengths of 125,000 p.s.i. and more, along with a Charpy V-notch impact strength of at least 18 to 20 ft. lbs.

In the stainless steel of my invention the surprising properties had with the combination of columbium-tantalum and nitrogen, with and without vanadium, is perhaps best illustrated by comparison with steels in which one or more of these ingredients is absent. In Table I below there

Of the several steels whose chemical compositions are set out in Table I, it will be noted that the steels designated 12Cr-Cb and 12Cr-Cb-V, while deficient in nitrogen, respectively contain columbium, tantalum and columbium-tantalum+vanadium. And the steel designated R4982-1, while containing the ingredient nitrogen, is deficient in both columbium and vanadium. It is the steels R4982-2 and R4982-3, steels of the present invention, which contain the ingredients nitrogen and columbium-tantalum, with the steel R4982-3 containing the further ingredient vanadium.

In the quench-hardened condition, as may be seen from the data presented in Table II, all five steels exhibited substantial hardness, the hardness figures ranging between Rockwell C36 and Rockwell C44. It is the steels 12Cr-Cb and 12Cr-Cb-V which exhibit maximum hardness, both amounting to about Rockwell C44, quenched from 1800° to 1900° F., this hardness being attributed to the significant carbon content, that is, a carbon content of about .12% to about .13%. The three steels R4982-1, R4982-2 and R4982-3, in quench-hardened condition, display hardnesses amounting to about Rockwell C36-38 when quenched from 1800° to 1900° F., this being attributed to the substantially lower carbon content, a carbon content of .049%, although there is a nitrogen content of .058%, with the sum of the carbon and nitrogen contents in these three steels amounting to .107%.

When tempered, the two steels 12Cr-Cb and 12Cr-Cb-V suffer a substantial loss of hardness, the hardness falling to Rockwell C23-25, a loss of some 20 points for each of these steels for the several different hardening temperatures. The steel R4982-1, a steel free of both

columbium-tantalum and vanadium but containing nitrogen, suffers an even greater loss in tempering, the hardness there dropping to Rockwell B95.

While substantial hardness is retained in the steel bearing both nitrogen and columbium-tantalum, the steel R4982-2, the final hardness had varies substantially, depending upon the temperature of hardening, this ranging from Rockwell C22 for the 1700° F. treatment to C28 for the hardening from 1900° F. It is only in the steel R4982-3 containing all three of nitrogen, columbium-tantalum and vanadium in which best retained hardness is had, this irrespective of variations in the temperature of heat hardening. Note that while the steel hardened from 1800° F. and oil quenched and then tempered has a hardness of Rockwell C27, that heat-hardened at 1900° F. and tempered has a hardness of Rockwell C29.

As further illustrative of the steel of my invention, this as compared to certain of the better steels of the prior art, I give below in Table III the chemical composition of five steels and in Table IV their comparative mechanical properties.

TABLE III.—CHEMICAL COMPOSITION OF FIVE 12-CHROMIUM STAINLESS STEELS

Heat No.	C	Mn	P	S	Si	Cr	Ni	Mo	N	Cb ²	V	W
033089 ¹	.12	.85	.014	.019	.23	11.58	.14	.03	.072	.16	.25	-----
12Cr=Ni=Mo=V	.17	.69	.016	.014	.43	11.71	.46	1.03	.032	-----	.19	-----
12Cr=Cb	.12	.25	.014	.015	.28	12.0	.15	.06	.019	.15	<.01	-----
12Cr=Cb=V	.13	.43	.011	.019	.20	11.67	.16	.08	.020	.10	.11	-----
12Cr=Ni=Mo=W=V	.23	.81	-----	-----	.28	13.19	.73	1.03	<.04	-----	.34	1.11

¹ Steel of invention.

² Columbium-tantalum, reported as columbium.

NOTE.—The remainder of the composition is substantially all iron.

The several steels of Table III were forged into test bars, machined to specification and suitably heat-treated, i.e., solution-treated and quenched, followed by tempering. Samples of all five of the steels were solution-treated at 1900° F. for 30 minutes and oil-quenched, following which they were given a tempering treatment at 1150° F. for 4 hours, and brought to room temperature. Further samples of my steel (Heat 033089) and the best of the prior art steels (Heat 12Cr-Ni-Mo-W-V) were solution-treated at 2000° F. for 30 minutes and oil-quenched, followed by tempering at 1150° F. for 4 hours and brought to room temperature. The mechanical properties of the various steels, i.e., the ultimate tensile strength, the 0.2% yield strength, the percent elongation, the percent reduction in area, and the Charpy V-notch impact strength, were run and reported, these results being given in Table IV below:

TABLE IV.—MECHANICAL PROPERTIES OF THE STEELS OF TABLE III IN HARDENED AND TEMPERED CONDITION

Heat No.	Condition	U.T.S., p.s.i.	0.2% Y.S., p.s.i.	In 2" Area		Charpy V-Notch Impact, ft./lbs.
				Percent El.	Percent Red.	
033089 ¹	1,900° F., O.Q. plus 1,150° F., Temp.	151,000	133,000	16	60	25
12Cr=Ni=Mo=V	1,900° F., O.Q. plus 1,150° F., Temp.	140,000	119,000	15	45	20
12Cr=Cb	1,900° F., O.Q. plus 1,150° F., Temp.	132,000	116,000	19	64	-----
12Cr=Cb=V	1,900° F., O.Q. plus 1,150° F., Temp.	133,000	117,000	19	62	-----
12Cr=Ni=Mo=W=V	1,900° F., O.Q. plus 1,150° F., Temp.	154,000	130,000	17	50	12
033089 ¹	2,000° F., O.Q. plus 1,150° F., Temp.	155,000	138,000	16	58	18
12Cr=Ni=Mo=W=V	2,000° F., O.Q. plus 1,150° F., Temp.	153,500	130,000	14	32	9

¹ Steel of invention.

It will be seen from the chemical analyses presented in Table III above that of the four steels of the prior art, one (steel designated 12Cr-Cb) in addition to chromium and carbon, essentially contains columbium but is virtually free of vanadium and nitrogen, while another of virtually the same composition (the steel designated 12Cr-Cb-V) does contain the further ingredient vanadium but not nitrogen. Two others of the prior art steels, notably the one designated 12Cr-Ni-Mo-V, although free of columbium and nitrogen, does contain vanadium but of even greater consequence, it contains a large quantity

of molybdenum, while the other, 12Cr-Ni-Mo-W-V, in addition to the vanadium and molybdenum, also contains a large amount of tungsten. As distinguished from these steels of the prior art, the preferred steel of the present invention, while free of the ingredients molybdenum and tungsten, essentially contains columbium, tantalum and nitrogen, as well as vanadium.

Now the hardened and tempered steel of my invention (Heat 033089), as shown in Table IV above, has a tensile strength of 151,000 p.s.i. with a yield strength of 133,000 p.s.i., while the 12Cr-Cb and 12Cr-Cb-V steels of the prior art, respectively have tensile strengths of 132,000 and 133,000 p.s.i., and 0.2% yield strengths of only 116,000 and 117,000 p.s.i. The prior art steel 12Cr-Ni-Mo-V is but little better than the other two prior art steels noted, this steel having a tensile strength of 140,000 p.s.i. and a yield strength of 119,000 p.s.i. Thus, the superior strength of my preferred steel as compared to that of three of the prior art steels is at once apparent.

While the further prior art steel 12Cr-Ni-Mo-W-V is

possessed of about the same tensile strength and yield strength of my preferred steel, a tensile strength of 154,000 p.s.i. and a yield strength of 130,000 p.s.i. as compared to the 151,000 p.s.i. and 133,000 p.s.i. of the present steel, it is noted that that prior art steel falls far short of the ductility and toughness had in the steel of interest. While the present steel has an elongation of 16% with reduction in area of 60% and a Charpy V-notch impact strength of 25 ft. lbs., the prior art steel has an elongation of 17% with a reduction in area of only 50% and a Charpy V-notch impact strength of 12 ft. lbs. And this difference in ductility and strength becomes even more pronounced where there is employed a higher temperature for solution-treatment. Thus, as seen from Table IV above, while the best steel of the prior art (the 12Cr-Ni-Mo-W-V steel) has an elongation of 14% with a reduction in area of only 32% and a Charpy V-notch impact strength of only

9 ft. lbs. when oil-quenched from 2000° F. and then tempered at 1150° F., the steel of the present invention when identically treated has an elongation of 16% with a reduction in area of 58% and a Charpy V-notch impact strength of 18 ft. lbs. And with the higher solution-treatment the steel of the present invention is superior in tensile strength and yield strength as well. In short, then, the steel of the present invention is at least equal in tensile strength and superior in yield strength, ductility and impact strength, this latter by a great margin, to the best steels of the prior art.

A further specific example of the preferred steel according to my invention, Heat 3809-2, analyzes as follows: Carbon .16%, manganese .02%, phosphorus .017%, sulphur .016%, silicon .10%, chromium 11.18%, nickel .19%, molybdenum .03%, nitrogen .12%, columbium-tantalum .09%, vanadium .39%, and remainder iron. This steel, hardened by heating at 1800° F. for 30 minutes and oil-quenching, followed by tempering at 1200° F. for 4 hours and air-cooling, has an ultimate tensile strength of 129,800 p.s.i., a 0.2% yield strength of 95,500 p.s.i., an elongation in 2" of 16.7%, a reduction in area

mium content, is of the following composition: about .1% to .2% carbon, about 15% chromium, about .1% to about .2% nitrogen, about .1% to about .3%, or more preferably about .2% columbium-tantalum, about .2% to .6%, more preferably about .3% to .4% vanadium, and remainder substantially all iron. The phosphorus, sulphur, silicon and molybdenum-tungsten contents are low. Four specific examples of this steel, with differing carbon and chromium contents, are set out below. The chemical analyses of the steels are given in Table VI and their corresponding mechanical properties in Table VII.

TABLE VI.—FOUR 15Cr STAINLESS STEELS CONTAINING Cb, V AND N

Heat No.	C	Mn	P	S	Si	Cr	Ni	N	Cb	V
R5304-1---	.098	.89	.008	.018	.21	14.96	.22	.13	.21	.44
R5304-2---	.13	.89	.008	.018	.21	14.96	.22	.13	.21	.44
R5305-1---	.10	.92	.011	.015	.26	14.77	.16	.13	.19	.33
R5305-2---	.14	.92	.011	.015	.26	14.77	.16	.13	.19	.33

of 53.6%, and a Rockwell hardness of C27. Improvement is had in all of these mechanical properties where the steel is hardened by heating at the higher temperature of 1900° F. for 30 minutes and oil-quenching, followed by tempering at 1200° F. for 4 hours and air-cooling. The steel, so treated, has an ultimate tensile strength of 141,900 p.s.i., a yield strength of 102,700 p.s.i., an elongation in 2" of 17.3%, a reduction in area of 56.2%, and a hardness of Rockwell C30.5.

A still further specific preferred steel of my invention, this in the form of 3" square billets and in the form of 1" square bars, was subjected to mechanical test. The chemical composition of the steel is as follows: Carbon, .12%, chromium 12.0%, nickel .15%, molybdenum .06%, columbium-tantalum .15%, vanadium .25%, nitrogen .070%, and remainder substantially all iron. The mechanical properties of this steel, made into standard test bars from a 3" square billet and other test bars from a 1" square bar under differing conditions of hardening, quenching from 1800° F., 1900° F. and 2000° F. with tempering treatments at 1150° and 1200° F., are reported in Table V below:

The mechanical properties of the steels of Table VI in hardened and tempered condition (2000° F. 30 mins., and oil quench, followed by 1150° F. 4 hrs. and air cool, also like hardening but subsequent tempering at 1200° F. for 4 hrs. and air cool) are given below in Table VII.

TABLE VII.—MECHANICAL PROPERTIES OF HARDENED AND TEMPERED 15 Cr STAINLESS STEELS OF TABLE IV

Heat No.	Condition	U.T.S., p.s.i.	0.2% Y.S., p.s.i.	Percent El. in 2"	Percent Red. of Area
R5304-1-----	(1)	153,800	125,500	13	33
R5304-2-----	(1)	168,800	140,000	13	36
R5305-1-----	(1)	161,200	133,600	15	51
R5305-2-----	(1)	171,200	140,900	9	18
R5304-1-----	(2)	149,600	123,600	15	47
R5304-2-----	(2)	157,500	130,000	14	48
R5305-1-----	(2)	152,700	127,300	13	41
R5305-2-----	(2)	157,600	132,100	15	49

¹ 2,000° F., 30 mins. oil quench plus 1,150° F., 4 hrs. air cool.

² 2,000° F., 30 mins. oil quench plus 1,200° F., 4 hrs. air cool.

Comparison of the mechanical properties of the 15% chromium steel as given in Table VII (Heats R5304-2 and R5305-2) with those of the 12% chromium steel of like carbon content as given in Table V reveals the signifi-

TABLE V.—MECHANICAL PROPERTIES OF HARDENED AND TEMPERED 12Cr STAINLESS STEELS CONTAINING Cb, V AND N

Section	Conditions, Degrees F.	U.T.S., p.s.i.	0.2% Y.S., p.s.i.	Percent El. in 2"	Percent R/A	Charpy V-Notch ft./lbs.
3" sq. billet-----	H, 1,800, T, 1,150-----	147,000	131,000	17	58	20/22
Do-----	H, 1,800, T, 1,200-----	139,000	123,000	16	59	34/41
Do-----	H, 1,900, T, 1,150-----	151,000	133,000	16	59	22/22
Do-----	H, 1,900, T, 1,200-----	145,000	128,000	16	60	25/30
Do-----	H, 2,000, T, 1,150-----	156,000	138,000	16	58	18/18
Do-----	H, 2,000, T, 1,200-----	150,000	133,000	15	58	21/25
1" sq. bar-----	H, 1,800, T, 1,100-----	160,000	140,000	16	58	22/29
Do-----	H, 1,800, T, 1,150-----	153,000	135,000	16	55	18/22
Do-----	H, 1,900, T, 1,100-----	163,000	141,000	16	58	17/17
Do-----	H, 1,900, T, 1,150-----	151,000	132,000	17	58	18/18

NOTE.—H=Quench hardened from temperature indicated in ° F.; T=Tempered from temperature indicated in ° F.

In comparing the mechanical properties of the sample prepared from a 3" square billet and those from a 1" square bar, it seems that there is very little difference. Thus, the sample from a 3" square billet quench-hardened from 1800° F. and tempered at 1150° F., while somewhat lower in strength than the sample prepared from a 1" square bar and similarly quench-hardened and tempered, has somewhat better ductility and impact strength, a matter of some 20/22 ft. lbs., as compared to 18/22. At the somewhat higher quench-hardening temperature of 1900° F. with tempering at 1150° F., the mechanical properties are virtually identical, except for the impact strength, this being in favor of the sample taken from the 3" square billet, an impact strength of about 22 ft. lbs. as compared to 18 ft. lbs. for the sample taken from the 1" square bar.

Another preferred steel, this of somewhat higher chro-

cant improvement in tensile and yield strength had with the 15% chromium steel, this, however, at some sacrifice in ductility. The main advantage had with the higher chromium steel, however, is an improved corrosion resistance.

Conclusion

It will be seen that I provide in my invention a quench-hardenable stainless steel in which the various objects hereinbefore set forth together with many practical advantages are successfully achieved. The steel is comparatively inexpensive in that it employs a minimum of costly alloying ingredients, but nevertheless enjoys a combination of good tensile strength, yield strength and toughness. The steel works well in the mill and readily lends itself to fabrication into a variety of articles of ultimate use in various forming, machining, brazing and welding

techniques. The steel and articles fashioned of the same are suited to useful application in the quench-hardened or quench-hardened and tempered condition.

Since many embodiments may be made of my invention and since various changes or modifications may be made in the embodiments set forth above, it will be understood that all matter described herein is intended by way of illustration and not by way of limitation.

I claim as my invention:

1. A heat-hardenable stainless steel essentially consisting of about .01% to about .25% carbon, about .01% to 3% manganese, about .01% to about 2% silicon, about 10% to about 16% chromium, any molybdenum not exceeding .3% and any tungsten not exceeding .5% and with molybdenum and tungsten together not exceeding about .5% in total, about .04% to about .2% nitrogen, about .03% to about .75% columbium-tantalum, up to about .75% vanadium, and remainder substantially all iron.

2. A heat-hardenable stainless steel essentially consisting of about .01% to about .25% carbon, about .01% to about 1% manganese, about .01% to about 1% silicon, about 10% to about 16% chromium, any molybdenum and tungsten together not exceeding about .2% in total, about .06% to about .16% nitrogen, about .03% to about .75% columbium-tantalum, up to about .75% vanadium, and remainder substantially all iron.

3. A heat-hardenable stainless steel essentially consisting of about .01% to about .25% carbon, about 10% to about 16% chromium, any molybdenum not exceeding .3% and any tungsten not exceeding .5% and with molybdenum and tungsten together not exceeding about .5% in total, about .04% to about .16% nitrogen, about .03% to about .75% columbium-tantalum, about .03% to about .35% vanadium, and remainder substantially all iron.

4. A heat-hardenable stainless steel essentially consisting of about .05% to about .25% carbon, about 10% to about 13% chromium, any molybdenum not exceeding .3% and any tungsten not exceeding .5% and with molybdenum and tungsten together not exceeding about .5% in total, about .04% to about .16% nitrogen, about .1% to about .75% columbium-tantalum, about .2% to about .4% vanadium, and remainder substantially all iron.

5. A heat-hardenable stainless steel essentially consisting of about .1% to about .2% carbon, about 11% to about 12% chromium, any molybdenum and tungsten together not exceeding about .2% in total, about .1% to

about .16% nitrogen, about .1% to about .3% columbium-tantalum, about .1% to about .4% vanadium, and remainder substantially all iron.

6. A heat-hardenable stainless steel essentially consisting of about .1% to about .2% carbon, about 13% to about 15% chromium, any molybdenum not exceeding .3% and any tungsten not exceeding .5% and with molybdenum and tungsten together not exceeding about .5% in total, about .04% to about .2% nitrogen, about .1% to about .3% columbium-tantalum, 0% to about .6% vanadium, and remainder substantially all iron.

7. A heat-hardenable stainless steel essentially consisting of about .1% to about .2% carbon, about 15% chromium, molybdenum and tungsten together not exceeding about .5% in total, about .1% to about .2% nitrogen, about .1% to about .3% columbium-tantalum, about .2% to .6% vanadium, and remainder substantially all iron.

8. Stainless steel bar stock essentially consisting of about .01% to about .25% carbon, about 10% to about 16% chromium, any molybdenum and tungsten together not exceeding about .15% in total, about .04% to about .2% nitrogen, about .03% to about .75% columbium-tantalum, about .03% to about .75% vanadium, and remainder substantially all iron.

9. Blading for turbines, compressors and the like essentially consisting of about .01% to about .25% carbon, about .01% to about 3% manganese, about .01% to about 2% silicon, about 10% to about 13% chromium, any molybdenum not exceeding .3% and any tungsten together not exceeding about .5% and with molybdenum and tungsten together not exceeding about .5% in total, about .04% to about .16% nitrogen, about .03% to about .75% columbium-tantalum, up to about .75% vanadium, and remainder substantially all iron.

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