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PRECIPITATION HARDENABLE STAINLESS STEEL

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The present invention relates to stainless steels, and, more particularly, to precipitation hardenable stainless steels which afford a level of strength and toughness characteristics of such magnitude that the steels are eminently suitable for structural applications, e.g., pressure vessels, components for aircraft and the like.

As is well known to those skilled in the art, stainless steels have been classified, in the broadest sense, as being austenitic, martensitic or ferritic. Of the three types, the austenitic variety, particularly the AISI 300 series, enjoys the greatest degree of commercial usage. This is readily understandable in view of, inter alia, the outstanding combination of corrosion resistance and ease of fabricability inherently characteristic of these steels. Nonetheless, the yield strengths thereof are relatively low and, as a general proposition, they do not undergo any appreciable hardening upon being subjected to heat treatment whereby a strengthening effect would be induced. High yield strength, e.g., up to 200,000 p.s.i. or above, can be attained with respect to the AISI 300 series of stainless steels via the application of cold rolling processing, but such techniques can give rise to attendant difficulties. For example, cold rolling is commonly applied in one direction and as a result thereof the mechanical characteristics of the steels generally become, as is known, undesirably anisotropic. Too, the increase is strength is normally achieved at the expense of concomitantly reducing the modulus of elasticity and the latter is an important factor to a designer coping with structural engineering problems.

In contrast to the AISI 300 series above mentioned, the AISI 400 series of martensitic stainless steels, e.g., AISI 440, generally manifest hardening capabilities upon heat treatment (quenching followed by tempering) and thus afford strength levels significantly higher than that characteristic of the non-cold rolled austenitic stainless steels. For example, the "Metals Handbook," 8th ed., (1961), indicates at page 414 that AISI 440 (A) exhibits a yield strength (0.2% offset) as high as 240,000 p.s.i. in the tempered (hardened) condition. This particular grade of martensitic stainless is of high carbon content and to achieve the effectiveness of this potent element quenching must be utilized to obtain the hard martensitic structure. As is the case with the carbon and low alloy steels, quenching operations are no little source of difficulty and the literature is well documented with the problems of quench cracking, distortion, dimensional change, etc., associated with the quench operation. Such steels also invite weldability problems and, where welding is necessary to form a structural component, a postweld quenching treatment is also necessary. Here too, the problem is rather well documented. To this should be added the important fact that while high strengths can be achieved with the quenched and tempered martensitic stainless steels of the AISI 400 type, the toughness of such steels is quite low, a factor which is the antithesis of good fabricability. The aforementioned "Metals Handbook" reflects that AISI 440 (A) has a tensile ductility of but 5% and a reduction of area of only 20% at the 240,000 p.s.i. yield strength level. In accordance with the present invention, a reduction in area value of even 30% is considered "brittle."

The above discussion is indicative of the fact that a

hiatus exists between the AISI 300 and AISI 400 series of stainless steels. One type is corrosion resistant and relatively easy to fabricate but is of low strength. The other is characterized by high strength but is afflicted with poor toughness and is thus difficult to fabricate. Neither type provides a high magnitude of both strength and toughness and this fact is undoubtedly responsive in large measure for the increasing technological activity with regard to the precipitation-hardening stainless steels.

The precipitation-hardening stainless steels can, for convenience, be categorized as falling within three major areas (although there are others). In the first category are those stainless steels which are both martensitic upon cooling from the solution anneal temperature and upon cooling after aging, i.e., they undergo a substantial phase transformation from the austenitic face-centered cubic (f.c.c.) structure to the martensitic body-centered cubic (b.c.c.) structure upon cooling to about room temperature from the annealing treatment. The second class includes those stainless steels which are substantially austenitic upon cooling from the annealing temperature (no substantial phase transformation) but which become substantially martensitic after cooling from the aging treatment. Many of such steels can be transformed prior to aging by the utilization of a conditioning treatment (a heat treatment intermediate that of the solution anneal and aging treatments) prior to the final aging step or by the application of a cold treatment, e.g., refrigeration or cold working, or by both conditioning and cold treating. Precipitation-hardening stainless steels which are austenitic in both the annealed and aged conditions comprise the third category and thus do not undergo any substantial martensitic transformation. Common to all three types is an annealing treatment and an aging treatment, although it is to be understood that sundry complex intermediate treatments have been proposed. The present invention is primarily concerned with the first category of precipitation-hardening stainless steels, although the invention also encompasses the second class, as will become clearer herein.

With regard to precipitation-hardening stainless steels in general, it can be said that a fair number of those well known in the art do not exhibit yield strengths of the order of over 200,000 p.s.i., e.g., 215,000 p.s.i. and above. There are a few such steels which have been advanced as having such high levels of yield strength, but for the most part and at least insofar as I am aware, the toughness characteristics of such steels have been lacking in one or more respects. This deficiency has been sufficiently severe, so that "overaging" techniques have been employed to achieve a better degree of toughness at the expense of strength. Various prior art data reflect, for example, that to raise the tensile ductility of an alloy about a few per cent, say up to about 10% or 12%, has resulted in a considerable drop in yield strength.

The term "toughness" is rather elusive and defies precise definition. As used herein, toughness connotes and includes more than tensile ductility and reduction of area values. It also includes the ability to manifest high notch tensile strength coupled with the important barometer of a high ratio of notch tensile strength to ultimate tensile strength. Experience has shown that tensile ductility and reduction of area values arrived at from testing smooth specimens are not always an unqualified indicator as to reliability. This stems from the fact that in commercial usage structural components develop cracks which may be internally or externally induced. Too, it is more than possible that the alloy from which the component was formed contained incipient cracks, notches or other flaws.

Notch toughness is a reflection of the ability of a material to yield by plastic flow to localized stress. As is known, a crack, notch or other flaw is an initiating or focal point of self-propagation. It has been established and is generally accepted that stresses tend to concentrate at such points whereby a localized stress concentration is induced. If a material is sufficiently resistant to the propagation of the flaw, i.e., if it is sufficiently "self-yielding," it is considered as being notch-ductile; if not, it is deemed notch-sensitive, i.e., it is prone to the development of deleterious brittle fracture or brittle failure characteristics.

The above-mentioned brittle failure problem occurs in many materials notwithstanding that the yield strength, tensile ductility and reduction of area of smooth specimens of the material are otherwise acceptable. The propagation of the flaw leading to brittle fracture can be induced by a number of factors, including the heat treatment applied to the material. In addition and of considerable importance, is the strength of the material. It is known that with an increasing magnitude of yield and tensile strengths the smaller becomes the minimum size of a flaw which can cause or promote subsequent brittle fracture. Thus, even relatively small flaws must be taken into consideration. Put another way, where dealing with yield strengths of, say, 100,000 or 150,000 p.s.i., the problem is not nearly as severe as is the case where yield strengths of 200,000 p.s.i. and above are involved. The carrying out of the notch-tensile test is well known and is not dwelt upon herein; however, in accordance with the present invention the steels contemplated must manifest a ratio of notch-tensile strength to ultimate tensile strength of at least unity (the notch acuity factor, K_t, being 10 or greater) to be classed as being notch-ductile. Advantageously, the ratio is at least 1.2.

From the foregoing, it is clear that it would be desirable to have at hand a steel which affords the above described combination of corrosion resistance, ease of fabrication and high strength together with good toughness, including notch toughness. In terms of strength and toughness and in accordance with the invention, this requires a yield strength of over 200,000 p.s.i. (0.2% offset), e.g., a yield strength of about 210,000 p.s.i. or 215,000 p.s.i. and above, a tensile ductility of at least 10% (standard gage measurements), a reduction of area of at least 40% and a high-tensile strength and a ratio of notch-tensile strength to ultimate strength of at least unity and advantageously of at least 1.1.

It is noteworthy of mention that in attaining the foregoing objectives processing operations should be simple to minimize cost as well as to obviate processing difficulties. Thus, the optimum would be the utilization of a simple solution annealing treatment and aging treatment without the necessity of recourse to various cold treatments and/or intermediate conditioning treatments as will be discussed hereinafter. Further, a number of recent proposals relating to achieving high strength in precipitation-hardening stainless steels have advanced the necessity of using substantial amounts of elements such as cobalt. Such constituents are not inexpensive and, thus, measurably contribute to the overall cost of the final stainless steel product.

It has now been discovered that by a judicial balance of special chemical constituents including chromium, nickel, aluminum, manganese, silicon, carbon and at least one element selected from the group consisting of columbium and titanium, precipitation-hardening stainless steels possessing the aforementioned combination of characteristics can be attained with a simple, expedient and inexpensive heat treatment.

It is a primary object of the present invention to provide novel precipitation-hardening stainless steels.

Another object of the invention is to provide precipitation-hardening stainless steels which exhibit an improved combination of corrosion resistance, fabrication quality, high yield strength and good toughness.

Other objects and advantages will become apparent from the following description.

Generally speaking, and in accordance with the invention, precipitation-hardening stainless steels contemplated herein consist essentially (by weight) of from 11% to 13% chromium, about 9% to about 11% nickel, about 1.5% to 3% molybdenum with the proviso that the sum of 0.8 times the chromium content plus the nickel and molybdenum contents is at least about 20%, e.g., 20.5% and does not exceed about 23%, e.g., 22.75%, at least one metal selected from the group consisting of titanium and columbium, the titanium being from about 0.1% to not more than 0.5% and the columbium being from 0.05% to 1% and preferably from 0.1% to 0.5%, about 1% to 1.6% aluminum with the proviso that the sum of the aluminum plus any titanium does not exceed about 1.9% and with the further proviso that the ratio of nickel to the sum of the aluminum plus any titanium is at least 5 to 1, carbon in an amount up to about 0.03%, e.g., about 0.005% to 0.02% carbon, up to about 0.2% manganese, up to about 0.2% silicon, and the balance essentially iron. In referring to the iron content as constituting the balance or essentially the balance of the stainless steels, it is to be understood, as will be readily appreciated by those skilled in the art, that the presence of other elements is not excluded, such as those commonly present as incidental elements, e.g., deoxidizing and cleansing elements, and impurities ordinarily associated therewith in small amounts which do not adversely affect the basic characteristics of the steels. In this connection, elements such as sulfur, phosphorus, hydrogen, oxygen, nitrogen and the like should be kept at levels as low as is consistent with commercial steelmaking practice. Other elements which can be present in the steels include the following: up to 0.5% vanadium, up to 1% tantalum, up to 0.5% copper, up to 0.1% beryllium, up to 0.01% boron and up to 0.05% zirconium. As mentioned hereinbefore, cobalt is not essential and can be kept to impurity levels. For purposes of malleabilization, desulfurization, etc., up to 0.1% of elements, such as calcium, cerium, etc., can be present, e.g., 0.02% or 0.03% calcium or 0.05% or 0.06% cerium.

In achieving an optimum combination of strength and toughness, e.g., a yield strength of above about 215,000 p.s.i., a ductility of at least 10%, a reduction of area of over 45%, a notch tensile to ultimate tensile ratio of 1.1 and above, it is most advantageous that the steels be of a composition falling within the following ranges: about 11.5% to 12.75% or 12.5% chromium, from 9% to 10.75% nickel, e.g., 9.75% to 10.5%, about 1.75% to 2.5% molybdenum, with the proviso that the sum of 0.8 times the chromium content plus the nickel and molybdenum contents be from 20.5% to 22%, at least one element selected from the group consisting of about 0.2% to about 0.35% titanium and about 0.2% to about 0.5% columbium, about 1.1% to about 1.5% aluminum with the proviso that the sum of the aluminum plus any titanium does not exceed about 1.8%, up to 0.03% carbon, up to 0.15% manganese, up to 0.15% silicon, the sum of the manganese and silicon not exceeding 0.25%, and the balance essentially iron.

The chromium content of the steels should not fall below about 11% and preferably should be at least 11.5%; otherwise, the basic purpose of maintaining a high degree of corrosion resistance for which the stainless steels are noted would be seriously impaired, notwithstanding the benefits conferred by molybdenum in certain specific corrosive environments. On the other hand, with chromium contents much above the maximum specified herein, the property characteristics of the steels are adversely affected and/or unnecessary heat treatments might be otherwise necessary, e.g., intermediate conditioning treatments. For example, should the total nickel and molybdenum contents plus 0.8 times the chromium content exceed about 23%, conditioning treatments (heat treating in the austenitic condition) might well be necessary prior to the final aging treatment and subsequent to the solution annealing treatment in order to effect a full transformation from the face-centered cubic structure to a body-centered cubic structure. That is to say, after solution annealing at a temperature of about 1600° F. to 1800° F., it would be necessary to heat treat the steels at some temperature below that of the initial solution anneal temperature, e.g., at about 1100° F. to 1350° F., to precondition the steels such that a transformation to martensite will eventually take place. Even then a cold treatment as by refrigeration at a low temperature or cold working may be necessary to effect a maximum degree of transformation prior to aging. Such additional heat treatments, insofar as the present invention is concerned, are unnecessary and add to the overall cost of the steels without conferring any benefit in comparison with steels within the invention. Such heat treatments can also promote the formation of precipitates in the austenite grain boundaries and this detracts from the ductility and corrosion resistance characteristics of the steels.

The amount of nickel should be at least 9% in order to obtain a combination of good strength and toughness. Excessive amounts of nickel promote the retention of austenite on aging and also undesirably narrow the range of aging temperature both from the view of retained austenite and overaging. Thus, it is advantageous that the nickel content not exceed 11%. Further, as indicated above herein, the ratio of nickel to the sum of aluminum plus titanium must be at least 5 to 1 to insure good toughness characteristics.

Aluminum is particularly responsible for the precipitation-hardening effect. If excessive amounts of aluminum are present, e.g., 2% to 3%, notch toughness is adversely affected and other toughness characteristics can be detrimentally impaired. On the other hand, with aluminum contents below about 1% the highest yield strengths are not obtained. Of course, yield strength levels of 150,000 p.s.i. to 200,000 p.s.i. are quite acceptable for sundry application. Where such yield strengths would be satisfactory, aluminum contents of 0.5% to 1%, e.g., 0.6% to 0.9%, could be utilized.

Carbon should be maintained at the lowest possible levels. High amounts thereof, apart from promoting intergranular corrosion, drastically reduce the M_s–M_f transformation range and impair toughness characteristics. The formation of chromium carbides might effect an increase in the M_s temperature but it is the undesirable precipitation of chromium carbides during heat treatment which can impair toughness. Further, upon aging, opposed reactions would be involved. That is to say, with relatively high carbon contents the carbon would react in both a tempering and hardening manner. Unstabilized carbon would, per se, confer a hardening reaction upon cooling from the solution anneal treatment and this hardening reaction would be tempered (lower strength and softer material) upon aging during the precipitation hardening treatment. Thus, the carbon content should be kept at a low order of magnitude and preferably not above 0.02%. It should be mentioned that carbon essentially has no substantive relation with regard to such elements as nickel and manganese of the steels contemplated herein. Carbon cannot (nor, for that matter, can manganese) be used to replace nickel; carbon simply must be maintained at a low level.

The amounts of silicon and manganese should also be kept to a minimum; otherwise, toughness can be adversely affected. For example, silicon and manganese levels of, say, 0.5% or above, detrimentally affect the notch ductility of the steels. It is most advantageous that the total amount of these elements does not exceed 0.25%. It is most preferred to keep these elements at a level of not more than about 0.1%, respectively; however, this is difficult to consistently achieve commercially because of pickup of these elements from raw materials, slags, refractories, etc.

Molybdenum confers additional corrosion resistance in certain specific environments, particularly chloride-containing environments, e.g., sea water, hydrochloric acid, etc. Molybdenum also affords improved resistance to such acids as sulfuric and phosphoric. With amounts of molybdenum below about 1.5% the resistance to such corrosive environments is lessened. On the other hand, amounts of molybdenum much above 3% promote the retention of austenite. In this connection, the amount of molybdenum must be specially controlled in correlation with the other constituents of the alloys to thereby obviate the necessity of employing conditioning treatments prior to the final aging treatment. Accordingly, it is advantageous that the molybdenum content not exceed about 2.5%.

The use of columbium is beneficial, partciularly where optimum corrosion resistance and strength combined with optimum toughness characteristics are necessary. While the columbium can be present up to 1%, it is preferred that not more than 0.5% columbium be present. This constituent will preferentially combine with carbon and preclude the precipitation of detrimental chromium carbides in the grain boundaries during aging, thereby enhancing toughness and corrosion characteristics.

The amount of titanium should not exceed 0.5% and advantageously does not exceed 0.35%; otherwise, segregation and other problems arise in processing the steels.

In carrying the invention into practice, air melting may be utilized, preferably followed by vacuum, consumable electrode melting for optimum effects. Use of materials of good purity is advantageous. In processing, the initially formed cast ingots should be thoroughly homogenized as by soaking at temperatures of about 2200° F. to about 2250° F. for about 1 hour per inch of cross section followed by hot working (forging, pressing, rolling, etc.) and, if desired, cold working to desired shape. A plurality of heating and hot working operations are desirable for purposes of assuring thorough homogenization of the cast structure through diffusion. Satisfactory hot working temperatures include 1800° F. to 2000° F. with suitable finishing temperatures being about 1600° F. to 1500° F. Subsequently, the steels are solution annealed at temperatures of about 160° F. to about 1800° F. for about ¼ hour to several hours, depending upon section size. In the production of sheet or strip, short annealing periods, e.g., 10 minutes, can be employed.

Following the solution annealing treatment the steels are cooled, e.g., air cooled. No liquid quench is necessary and thus the attendant difficulties associated therewith are obviated. As a result of solution annealing treatment followed by cooling, the steels transform to the martensitic or substantially martensitic condition or can be readily transformed thereto by subjecting the steels to a cold treatment as by refrigerating the steels at a low temperature, e.g., −100° F. or below, or by cold working the steels. Both refrigerating and cold working can be utilized if desired. However, an attribute of the steels of the invention having a combined chromium plus nickel plus molybdenum content of not more than about 23.5%, and particularly not more than about 23%, is that refrigeration and/or cold working is unnecessary. This aspect minimizes cost and processing difficulties. In the solution annealed condition, the steels are quite ductile and are characterized by a Rockwell "C" hardness of above about R_c 25 and up to about R_c 35. Thus, the steels can be fabricated to shape before aging.

Subsequent to the solution anneal and cooling treatment, the steels are then aged in the martensitic condition to effect the high levels of strength. The aging treatment comprises heating the steels to a temperature of about 800° F. to 1000° F. for about ¼ to 4 hours, the longer aging periods being used in conjunction with the lower aging temperatures. Aging at 900° F. to 950° F. for about 1 to 4 hours has been found very satisfactory. Temperatures on the order of above about 1050° F. or 1100° F. or higher should not be utilized since reversion to austenite and/or overaging can occur with adverse consequential effects, e.g., loss of strength. Further, in accordance with the invention the Rockwell "C" hardness levels of the steels preferably should not be more than about R_c 51; otherwise, the toughness characteristics thereof are impaired.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages thereof, the following illustrative description and data are given:

A substantial number of steels were prepared and are identified in Table I, Alloys A through G being outside the invention and Alloys 1 through 4 being within the scope thereof. The steels were melted in a vacuum induction furnace and the usual and standard deoxidants were employed.

TABLE I.—COMPOSITION*

Alloy No.	Percent						
	Cr	Ni	Mo	Al	Ti	Cb	Fe
A	15	10	2	1.3	0.3	N.A.	Bal.
B	14	10	2	1.3	0.3	N.A.	Bal.
C	14	10	2	1.5	0.3	N.A.	Bal.
D	14	8	2	1.3	0.3	N.A.	Bal.
E	14	8	2	1.5	0.3	N.A.	Bal.
F	11	12	2	1.3	0.3	N.A.	Bal.
G	11	12	2	1.5	0.3	N.A.	Bal.
1	12	11	2	1.3	0.3	N.A.	Bal.
2	12	10	2	1.3	0.3	N.A.	Bal.
3	12	9	2	1.3	N.A.	0.5	Bal.
4	12	9	2	1.3	0.3	--------	Bal.

* Not more than 0.03% carbon was added to the steels and all contained less than about 0.15% manganese and less than about 0.15% silicon.

N.A.—Not added.

Upon solidification, the cast ingots, 4 by 4 inches, were soaked at about 2250° F. to effect good homogenization, forged to billets 2 by 2 inches square and thereafter reheated to 1800° F. and hot rolled to rods about ⅞ inch in diameter and about 12 to 15 feet long. The alloys were then machined to tensile specimens having a reduced section of about 0.25 inch diameter. The notch specimens had a V-notch of about 60°. The radius of the notch was 0.0005 inch or less and the notch acuity factor, K_t, was 10 or greater. Notch acuity factors of less than 10 are not considered adequate to provide sufficiently severe test conditions.

Subsequent to cooling from the hot working temperature the steels were heat treated prior to being subjected to test. Different heat treatments were used and are set forth below.

Heat treatment "A":

(1) Solution treated (annealed) at about 1600° F. for about 1 hour and air cooled.
(2) Refrigerated at about minus 100° F. (Dry Ice) for about 16 hours.
(3) Aged at about 900° F. for about 1 hour.

Heat treatment "B":

(1) Solution treated at about 1800° F. for about 1 hour and air cooled.
(2) Aged at about 900° F. for about 4 hours.

Heat treatment "C":

(1) Solution treated at 1800° F. for about 1 hour and air cooled.
(2) Refrigerated at about minus 100° F. (Dry Ice) for about 16 hours.
(3) Aged at about 900° F. for 4 hours.

The determined Rockwell "C" hardness values are given in Table II, as ascertained from cooling after the solution treatment, the refrigerated condition where used and after cooling from the aging treatment.

TABLE II

Alloy No.	Heat Treatment	Rockwell Hardness, R_c			
		Solution 1,600° F.	Treatment 1,800° F.	Refrigeration Treatment	Aging Treatment
A	C	----------	6	32	43
B	C	----------	30	32	47
C	C	----------	32	31	48
D	A	30	----------	31	45
E	A	32	----------	31	47
F	C	----------	21	30	47
G	C	----------	21	29	47
1	C	----------	28	32	50
2	C	----------	34	35	50
3	B	----------	30	----------	48
4	B	----------	29	----------	48

After completion of the heat treating cycle the steels were subjected to standard testing procedures and the results are set forth in Table III. The yield strength (Y.S., 0.2% offset) is given in thousands of pounds per square inch (K.S.I.) as are the ultimate tensile (U.T.S.) and notch tensile strengths (N.T.S.). Tensile elongation (El.) is given in percent (%) using a standard gage length of 4 times the diameter of the specimen and the reduction in area (R.A.) is also given in percent (%). The designation N.T.S./U.T.S. is the ratio of the notch tensile to ultimate tensile strength. None of the steels was cold worked prior to or after aging. Cold working would enhance the property characteristics of the steels, but would interfere with the attaining of a good analysis of results as a reflection of composition and heat treatment.

TABLE III

Alloy No.	Y.S., K.S.I.	U.T.S., K.S.I.	El., Percent	R.A. Percent	N.T.S., K.S.I.	N.T.S., U.T.S.
A	76.2	146.3	33	71	206.8	1.42
B	176.4	197.6	18	61.5	284.6	1.44
C	181.8	207.1	18	57	280.5	1.40
D	220	226	11	56	216	0.957
E	221	228	10	42	141	0.612
F	187.9	211.7	16	60.5	315.8	1.49
G	190.9	221.7	15.5	55.5	310.2	1.40
1	205.4	223.4	13	50	328.1	1.51
2	230.8	244.3	12	58.5	340.5	1.39
3	225.6	240.6	12	51	253	1.12
4	235.5	246.5	13	56.5	311.3	1.25

The data in Tables I, II and III illustrate the adverse effects to be expected with alloys outside the invention. Alloys A through G, with the exception of Alloys D and E, manifested yield strengths of less than the minimum "high yield strength" of 200,000 p.s.i. and substantially less than the preferred minimum of 215,000 p.s.i. required in accordance with the "high yield strength" alloys of the invention. With regard to Alloys A, B and C, the chromium content for these alloys was too high and the factor determined by the sum of 0.8 times the chromium content plus the nickel and molybdenum contents exceeded the herein specified maximum of 23%. Alloy A was, as a practical matter, completely austenitic upon cooling from the solution treatment as evident from the very low Rockwell hardness level of R_c 6 set for in Table II. In addition, this alloy had a high amount of retained austenite after cooling from the aging treatment. Concerning Alloys D and E, the yield strength of these alloys was good but the ratio of the notch tensile strength to ultimate tensile strength for these alloys was below unity; thus these steels lacked sufficient toughness. Alloys F and G contained too much nickel and, as mentioned above, the yield strengths did not satisfy the "high yield strength" minimum of 200,000 p.s.i.

In contrast to the alloys outside the invention, Alloys 1 to 4 formulated in accordance herewith all manifested a satisfactory level of properties. Alloys 3 and 4 which nominally contained an amount of chromium plus nickel plus molybdenum of 23% illustrate that a high level of properties can be obtained without any cold treatment, e.g., refrigeration and/or cold working, whatever. This aspect is quite beneficial where it is necessary to form large vessels. To form such vessels, a welding treatment would be necessary and this in turn would require a subsequent solution and aging treatment to restore the properties of the parent metal contiguous to the weld zone. Obviously, it would be quite desirable, if possible, to avoid subjecting such vessels to a refrigeration treatment prior to aging in view of the impracticality of so doing. Thus, in accordance with the invention, condition treatments are not only unnecessary but utilization of refrigeration techniques can be avoided where desired. A comparison of Alloy 1 with Alloys 2, 3 and 4 further shows the benefit of maintaining the sum of 0.8 times the chromium content plus the nickel and molybdenum contents at an amount not greater than about 22%.

Yield strengths below about 200,000 p.s.i., e.g., 150,000 p.s.i. to 200,000 p.s.i., are quite satisfactory for a host of commercial applications. In such instances, from 0.5% to 1% aluminum, e.g., 0.6% to 0.9%, aluminum can be used in the steels as referred to above herein. Such steels manifest a unique capability of absorbing extremely high levels of impact energy. This is illustrated by the alloys in Tables IV (composition) and V (test results), the alloys having been prepared and tested, except for heat treatment in the same manner as the alloys of Table I. The heat treatment consisted of solution treating at 1800° F. for 1 hour followed by air cooling and then aging at either 900° F. for 4 hours (Heat Treatment "D") or at 1000° F. for 2 hours (Heat Treatment "E"). The steels were neither refrigerated nor cold worked.

TABLE IV.—COMPOSITION*

Alloy No.	Percent						
	Cr	Ni	Mo	Al	Ti	Cb	Fe
5	12	10	2	0.8	0.2	N.A.	Bal.
6	12	9	2	0.8	0.2	N.A.	Bal.
7	12	9	2	0.8	N.A.	0.5	Bal.

*Not more than 0.03% carbon was added to the steels and each contained less than 0.15% of manganese and silicon, respectively.
N.A.—Not added.

TABLE V

Alloy No.	Heat, Treatment	Y.S., K.S.I.	U.T.S., K.S.I.	El., Percent	R.A., Percent	C.V.N.,* ft.-lbs.
5	D	192.4	203.4	16	67	72.5
	E	180	192.4	18	65	137.5
6	D	195	205	15	64.5	75.0
	E	183.3	194.7	16.5	66.5	119
7	D	200.8	210	15	65	55.5
	E	186.5	202	16.5	63.5	109

*C.V.N.—Charpy V-notch.

From the data in Tables IV and V, it will be noted that exceptionally high levels of resistance to impact energy, e.g., well over 50 ft.-lbs. and even over 100 ft.-lbs., can be obtained together with reasonably high yield strengths. While Alloys B, C, F and G of Table I exhibited yield strengths comparable to Alloys 5, 6 and 7, they do not afford the markedly high level of resistance to impact energy characteristic of Alloys 5, 6 and 7.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A precipitation hardenable stainless steel characterized by a yield strength (0.2% offset) of at least about 215,000 p.s.i., a tensile ductility of at least about 10%, a reduction in area of at least about 45% and a ratio of notch tensile strength to ultimate tensile strength of at least unity, said steel consisting essentially of a composition falling within the following ranges: about 11.5% to about 12.75% chromium, about 9.75% to 10.75% nickel, about 1.75% to 2.5% molybdenum with the proviso that the sum of 0.8 times the chromium content plus the nickel and molybdenum contents is at least 20.5% and not greater than 22%, at least one metal selected from the group consisting of titanium and columbium, the titanium being from 0.2% to 0.35% and the columbium being from about 0.1% to about 0.5%, about 1.1% to about 1.5% aluminum with the proviso that the sum of the aluminum and any co-present titanium does not exceed 1.8%, carbon in an amount up to 0.03%, up to 0.15% manganese, up to 0.15% silicon and the balance essentially iron.

2. A precipitation hardenable stainless steel characterized by a good combination of strength and toughness and consisting essentially of about 11% to 13% chromium, about 9% to about 11% nickel, about 1.5% to 3% molybdenum with the proviso that the sum of 0.8 times the chromium content plus the nickel and molybdenum content is at least about 20% and not more than about 23%, at least one metal selected from the group consisting of titanium and columbium, the titanium being from about 0.1% to not more than 0.5% and the columbium being from 0.1% to 1%, about 1% to 1.6% aluminum with the proviso that the sum of the aluminum and any co-present titanium does not exceed 1.9% and with the further proviso that the ratio of nickel to the sum of aluminum and any co-present titanium is at least 5 to 1, carbon in an amount up to 0.03%, up to 0.2% manganese, up to 0.2% silicon, up to 0.5% vanadium, up to 1% tantalum, up to 0.5% copper, up to 0.1% beryllium, up to 0.01% boron, up to 0.05% zirconium and the balance essentially iron.

3. The alloy as set forth in claim **2** in which the sum of 0.8 times the chromium content plus the nickel and molybdenum contents does not exceed about 22% and is not less than 20.5%, the manganese and silicon contents are not greater than 0.15% each and the titanium content does not exceed 0.35%.

4. A precipitation hardenable stainless steel characterized by a good combination of strength and the ability to absorb high levels of impact energy, said steel consisting essentially of 11% to 13% chromium, from 9% to 11% nickel, about 1.5% to 3% molybdenum with the proviso that the sum of 0.8 times the chromium content plus the nickel and molybdenum contents is at least 20% and not more than 23%, at least one element selected from the group consisting of titanium and columbium, with the titanium content being about 0.1% to 0.5% and the columbium content being about 0.1% to about 1%, about 0.5% to 1% aluminum with the proviso that the sum of the aluminum plus any co-present titanium being not greater than 1.4%, carbon in an amount up to about

0.03%, up to 0.15% manganese, up to 0.15% silicon, and the balance essentially iron.

5. The alloy as set forth in claim **4** in which the sum of 0.8 times the chromium content plus the nickel and molybdenum contents does not exceed about 22% and is not less than 20.5%, the aluminum content is from 0.6% to 0.9% and the manganese and silicon contents do not exceed 0.15% each.

6. A precipitation hardenable stainless steel characterized by a good combination of strength and toughness and consisting essentially of about 11% to 13% chromium, about 9% to about 11% nickel, about 1.5% to 3% molybdenum with the proviso that the sum of 0.8 times the chromium content plus the nickel and molybdenum contents is at least about 20% and not more than about 23%, at least one metal selected from the group consisting of titanium and columbium, the titanium being from about 0.1% to not more than 0.5% and the columbium being from 0.1% to 1%, about 0.5% to 1.6% aluminum with the proviso that the sum of the aluminum and any co-present titanium does not exceed 1.9% and with the further proviso that the ratio of nickel to the sum of aluminum and any co-present titanium is at least 5 to 1, carbon in an amount up to 0.03%, up to 0.2% manganese, up to 0.2% silicon, up to 0.5% vanadium, up to 1% tantalum, up to 0.5% copper, up to 0.1% beryllium, up to 0.01% boron, up to 0.05% zirconium and the balance essentially iron.

7. An alloy in accordance with claim **2** in which the sum of the chromium, nickel and molybdenum does not exceed 23.5%.

8. An alloy in accordance with claim **7** containing about 0.2% to about 0.5% columbium.

9. An alloy in accordance with claim **4** in which the sum of the chromium, nickel and molybdenum does not exceed 23.5%.

10. An alloy in accordance with claim **9** containing about 0.2% to about 0.5% columbium.

11. An alloy in accordance with claim **6** in which the sum of the chromium, nickel and molybdenum does not exceed 23.5%.

12. An alloy in accordance with claim **6** containing at least 0.2% titanium.

13. An alloy in accordance with claim **6** containing at least 0.1% columbium.

14. An alloy in accordance with claim **11** containing about 0.2% to about 0.5% columbium and with any titanium not exceeding 0.35%.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,342,590 September 19, 1967

Clarence George Bieber

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 34, for "is", first occurrence, read -- in --; line 66, for "ductibility" read -- ductility --; column 2, line 7, for "responsive" read -- responsible --; line 60, for "strength" read -- strengths --; line 62, for "ductibility" read -- ductility --; column 3, lines 41 and 42, for "high-tensile" read -- high notch-tensile --; line 59, for "judicial" read -- judicious --; column 5, line 37, for "application" read -- applications --; column 6, line 41, for "160° F." read -- 1600° F. --; column 9, line 3, for "for" read -- forth --.

Signed and sealed this 29th day of October 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.
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