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AGE HARDENABLE NICKEL-MOLYBDENUM FERROUS ALLOYS

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ABSTRACT OF THE DISCLOSURE

A ferrous alloy containing carbon and correlated amounts of nickel and molybdenum, the objective being to obtain upon simple heat treatment an alloy of both high strength and good toughness. Alloys also advantageously contain titanium and/or aluminum for special purposes such as to provide good deoxidation and malleabilization characteristics.

The present invention relates to ferrous alloys and more particularly to ferrous-base alloys which manifest a combination of strength and toughness of such magnitude that the alloys can be used in the fabrication of a host of high strength structural members.

As is known to those skilled in steel metallurgy, a number of different steels have been proposed for applications requiring tensile strengths of about 150,000 p.s.i. to 300,000 pounds per square inch (p.s.i.). Many quenched and tempered low alloy, carbon steels have been advanced and, indeed, have found commercial acceptance. Nonetheless, the well documented drawbacks attendant the quenching operation of such steels, to wit, dimensional change, distortion, etc., have underscored the need for improved steels.

Apart from problems associated with quenching, the toughness characteristics of prior art quenched and tempered steels have often been found wanting. This has been particularly evident from the consideration that as the strength levels of such steels increased, the toughness characteristics thereof correspondingly decreased. In this connection, it should be mentioned that "toughness," as contemplated herein, encompasses more than the standard yardsticks of tensile ductility and reduction in area values. It also includes the ability of a steel to exhibit a high ratio of notch tensile strength to ultimate tensile strength. Experience has shown that tensile ductility and reduction in area values arrived at from testing smooth (as opposed to notched) specimens are not always an unqualified indicator as to reliability.

Notch toughness is a reflection of the ability of a material to yield by plastic flow to localized stress. A crack, notch or other flaw is an initiating point of self-propagation and should a material be sufficiently resistant to the propagation of the flaw, i.e., if it is sufficiently "self-yielding," it is considered notch-ductile; if not, it is deemed notch-sensitive or prone to the development of deleterious brittle failure characteristics.

The propagation of a flaw leading to brittle fracture can be induced by a number of factors, including the heat treatment applied to the material, and is particularly acute in respect of high strength materials. It is known that as the level of yield strength increases 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, in 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 notch-tensile test is well known and is not dwelt upon herein; however, in

accordance herewith, the steels must manifest a ratio of notch-tensile strength to ultimate tensile strength of at least 1.0 (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.

It is also noteworthy of mention in attaining the foregoing objectives, that processing operations should be simple to minimize cost as well as to obviate processing difficulties. Thus, the near optimum would be the application of but a single heat treatment without the necessity of recourse to various cold treatments and/or intermediate conditioning treatments (e.g., a heat treatment subsequent to an annealing treatment and prior to a final aging treatment), or even the commonly used solution treatment. In achieving a high level of strength together with good toughness, the recently introduced maraging steels described in U.S. Patents Nos. 3,093,518 and 3,093,519 have received considerable attention and, in fact, have achieved rather spontaneous commercial acceptance. These steels generally require only a solution treatment followed by an aging treatment and thus obviate the above-described difficulties associated with quenching operations. While the alloys contemplated herein are of the maraging type, nonetheless they depart from certain accepted principles and do not even require the application of a solution treating step. In other words, subsequent to the normal hot working step to which all steels must be subjected beyond the cast stage, steels of the present invention require only an aging treatment. It is to be understood, as herein contemplated, that a heat treatment comprised of a solution treatment followed by aging is a two stage treatment.

It has now been discovered that ferrous-base alloys containing special and correlated amounts of certain elements, including nickel, molybdenum, manganese, silicon and carbon, can be provided which afford a highly satisfactory and commercially attractive level of strength and toughness.

It is an object of the present invention to provide a novel and improved ferrous-base alloy having a desirable combination of mechanical characteristics, including strength and toughness.

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

Generally speaking, the present invention contemplates providing ferrous alloys containing 10% to 16% nickel, 6% to 12% molybdenum, the sum of the nickel plus molybdenum being not greater than 27%, up to 1% titanium, up to 1% aluminum, carbon in an amount up to 0.1%, up to 1% cobalt, up to not more than 0.25% manganese, up to not more than 0.25% silicon, and the balance essentially iron. As will be readily understood by those skilled in the art, the term "balance" or "balance essentially" when used in referring to the amount of iron in the alloys does not exclude the presence of other elements commonly present as incidental elements, e.g., deoxidizing and cleansing elements, and impurities ordinarily associated therewith in small amounts which do not materially affect the basic characteristics of the alloys. In this connection, elements such as sulfur, phosphorus, hydrogen, oxygen, nitrogen and the like should be maintained at low levels consistent with commercial practice. However, supplementary elements may be present in the alloys is follows: up to 2% columbium, e.g., up to 1.5%; up to 4% tantalum, e.g., up to 3%; up to 0.1% boron, e.g., up to 0.05%; up to 0.25% zirconium, e.g., up to 0.15%; up to 2% vanadium, e.g., up to 1.5%; up to 0.1% calcium, e.g., up to 0.075%; up to 1% berryllium, e.g., up to 0.5%; and up to 4% copper, e.g., up to 2%. When used, it is preferred that the respective amounts of the aforementioned supplementary elements be as follows: up to 1% columbium, e.g., 0.1%

to 0.5%; up to 2% tantalum, e.g., 0.01% to 0.5%; up to 0.01% boron, e.g., 0.0005% to 0.0075%; up to 0.1% zirconium, e.g., 0.001% to 0.1% zirconium; up to 1% vanadium, e.g., 0.1% to 0.5%; up to 0.05% calcium, up to 0.1% beryllium, and up to 1% copper. The total sum of the supplemental elements should not exceed 10% and advantageously should not exceed 6%. Tungsten can be used to replace molybdenum in part on an atom for atom basis, two parts of tungsten by weight for one part of molybdenum, in an amount up to 8% by weight of tungsten. However, it is advantageous that the tungsten not exceed 6% and preferably should not exceed 4%, particularly since molybdenum, in contrast to tungsten, importantly contributes to improved forgeability and/or hot workability and also imparts enhanced ductility characteristics.

Chromium can adversely affect the characteristics of the alloys contemplated herein and should preferably be held to impurity levels, i.e., less than 1%. In no event should chromium, if present, exceed 5%.

In achieving an optimum combination of strength and toughness, the alloys advantageously contain 11% to 15% nickel, 8% to 11% molybdenum, the sum of the nickel plus molybdenum being not greater than 25%, at least one element selected from the group consisting of 0.1% to 1% titanium and 0.1% to 1% aluminum, the sum of the titanium plus aluminum being not greater than 1.5%, up to 0.05% carbon, not more than 0.15% manganese, not more than 0.15% silicon with the balance being substantially iron.

When heat treated, as will be set forth hereinafter, steels of the instant invention manifest yield strengths (0.2% offset) from upwards of 150,000 p.s.i. to 300,000 p.s.i. or above, together with tensile elongations of 5% to 20%, reduction in areas of at least 30%, e.g., 40% to 75%, a high notch-tensile strength, a ratio of notch-tensile strength to ultimate tensile strength of at least 1 and preferably of at least 1.2, and are also capable of absorbing substantial levels of impact energy.

The element nickel contributes, among other things, to achieving ductility, toughness and a desired martensitic structure upon cooling from hot working or, where used, solution treatment. The subject alloys are austenitic at high temperature and undergo transformation during cooling. However, with excessive amounts of nickel, e.g., 19%, retained austenite in deleterious amounts can ensue and/or there is danger of excessive austenite reversion upon aging. Austenite reversion can be minimized by using low aging temperatures, e.g., below 700° F., but this, in turn, would significantly impair the strength level of the steels. On the other hand, extremely low nickel contents invite the tendency for formation of ferrite or other undesirable and subversive phases and such phases can wreak havoc with various mechanical characteristics of the steels.

Molybdenum confers strengthening and hardening characteristics and, as mentioned above herein, also contributes to good forgeability and ductility. It is preferred that the nickel and molybdenum be correlated such that the sum thereof does not exceed 27% and most advantageously does not exceed about 25% or 26%. This correlation greately contributes to achieving the formation of a satisfactory martensitic condition upon cooling from hot working without the necessity of using additional treatments, such as cold treating. However, it is to be understood that cold treatments as by, for example, refrigeration and/or cold working, are not excluded from the scope of the invention in achieving the desired degree of transformation to martensite.

Titanium and/or aluminum serve to provide good deoxidation and malleabilization characteristics. Titanium, for example, serves to fix elements, such as oxygen, nitrogen and carbon. The respective amounts of titanium or aluminum should not exceed about 1%, the total thereof not exceeding 1.5%. While carbon can be present up to 0.1%, for optimum results it should not be present in amounts greater than 0.05%, e.g., not more than about 0.03%.

The silicon and manganese contents of the steels are of vital significance and, in accordance herewith, should be kept to a minimum; otherwise, toughness can be most adversely affected. For example, silicon and manganese levels even as low as, say, 0.5% seriously impair the notch ductility of the steels. It is preferred that the total amount of these elements not exceed 0.30% and it is most advantageous to keep each of 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.

In carrying the invention into practice, air or vacuum melting practice can be utilized, preferably followed by consumable electrode melting for optimum effects. It is advantageous to utilize materials of good purity to thereby minimize the occurrence of inclusions, contaminants, etc. In processing, the initially formed cast ingots should be thoroughly homogenized, as for example, by soaking, at a temperature of about 2200° F. to about 2300° F. for about one hour per inch of cross section. Thereafter, the alloys are hot worked (as by forging, pressing, rolling, etc.) and, if desired, cold worked to desired shape. A plurality of heating and hot working operations can be used and are advantageous to assure thorough homogenization of the cast structure through diffusion and to break up the cast structure. Hot working can be satisfactorily carried out over a temperature range of 2300° F. or 2200° F. down to 1400° F., e.g., 2150° F. to 1500° F., with suitable finishing temperatures being about 2000° F. down to about 1500° F. Cooling from hot working is preferably accomplished by air cooling although furnace cooling, quenching, etc., can be employed.

Subsequent to cooling from the hot working temperature to effect a transformation to the martensitic condition, the steels can be directly aged (no other processing or heating step being necessary, although solution treating or annealing over the range of 1400° F. to 2200° F. can be used if desired) by heating at a temperature of about 750° F. to 1100° F. for about 100 hours to 0.1 hour, the longer aging periods being used in conjunction with the lower aging temperatures. Aging at 950° F. to 900° F. for about one to four hours has been found quite satisfactory. With aging times above about an hour or so, temperatures above about 1100° F. should not be used since deleterious austenite reversion can occur. On the other hand, temperatures appreciably below 750° F. are not recommended in view of the long aging times required, e.g., more than 100 hours, to obtain maximum strength and hardness. However, where especially hard surfaces, particularly in combination with softer cores, are required, the steels can be heated at a temperature as high as 1400° F., e.g., about 1200° F. to 1375° F. and preferably at 1250° F. to 1350° F., for a period of time of not greater than about 30 minutes, e.g., up to 15 minutes, the longer time being associated with the lower temperature. A period of from a few seconds, e.g., 15 seconds, up to five minutes is satisfactory for the temperature range of 1250° F. to 1350° F.

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:

In Table I a substantial number of nominal alloy compositions are given, Alloys Nos. 1 through 10 being within the invention and Alloys A through J being outside the scope thereof. Cast ingots of Alloys Nos. 1 through 10 and A were homogenized (soaked) at about 2200° F. to 2300° F., hot worked, machined and thereafter subjected to one or more of the following heat treatments (none of these steels being solution treated):

Heat Treatment A

Aged at about 900° F. for about four hours, air cooled.

the tensile elongation (el., percent) and reduction in area (R.A., percent) in percent. Also set forth is the notch tensile to ultimate tensile ratio, N.T.S./U.S.T.

TABLE II

	Ni, percent	Mo, percent	Ti, percent	Al, percent	Mn, percent	Si, percent	U.T.S., K s.i.	Y.S., K s.i.	El., percent	R.A., percent	N.T.S., U.T.S
Alloy No.:											
1	14	10	0.2	0.2	0.05	0.05	270.2	255.6	11	55	1.29
9	16	6	0.2	0.2	<0.15	<0.15	219.5	209.3	11	57	N.D.
11*	14	10	----------	0.2	0.05	0.05	260.5	284.6	12	37.5	N.D.
K	14	10	0.2	0.2	0.5	0.5	304.0	273.0	8	31	0.68

*4% tungsten added.
NOTE.—N.D. Not determined.
Alloy No. 1 aged 8 hours at 900° F., all others 4 hours at 900° F.

Heat Treatment B

Aged at about 900° F. for about eight hours, air cooled.

Heat Treatment C

Aged at about 1000° F. for about one hour, air cooled.

Heat Treatment D

Heat treated for four hours at 1200° F., air cooled. Alloys B through J were small cast specimens and were annealed at 2100° F. and then aged at 900° F. for about three hours. Hardness determinations (Rockwell C, Rc,) were made in both the hot worked and aged conditions for Alloys Nos. 1 through 10 and A, and in both the solution annealed and aged conditions (Heat Treatment E) for Alloys B through J. The hardness data is also reported in Table I. In addition to the constituents reported in Table I, not more than about 0.03% carbon nor more than about 0.15% of either silicon or manganese was added to the steels, the balance otherwise being iron plus impurities.

While Alloys Nos. 1, 9 and 11 reflect the highly satisfactory combination of properties characteristic of the invention, Alloy K is illustrative of the strikingly adverse effects of using what might otherwise be considered as small amounts of manganese and silicon. As indicated herein, the respective amounts of these constituents should not exceed 0.25% and it is preferred that the total thereof not exceed 0.3%.

In addition to the fact that alloys within the invention afford a high degree of strength and/or hardness as well as being ductile, alloys contemplated herein are also resistant to stress corrosion cracking. The alloys are useful in the production of such items as bar, rod, plate, castings, wire, etc., and products made therefrom, including fasteners, e.g., bolts. Desired shapes are best obtained prior to aging, i.e., in the hot worked or annealed condition since the alloys are comparatively soft and thus are more amenable to shaping operations such as cold working. Further, to minimize processing time, aging temperatures from 850° F. to 950° F. are deemed the

TABLE I

	Ni, percent	Mo, percent	Ti, percent	Al, percent	Hardness, Rockwell "C"						
					HW	A	B	C	D	E	F
Alloy No.:											
1	14	10	0.2	0.2	37	51	56	------	45	------	------
2	10	10	0.2	0.2	38	46	57	------	46	------	------
3	12	10	0.2	0.2	35	50	------	------	------	------	------
4	13	9	0.2	0.2	36	52	53	50	------	------	------
5	15	9	0.2	0.2	35	49	51.5	48	------	------	------
6	14	8	0.2	0.2	36	49	50	47	------	------	------
7	10	12	0.2	0.2	39	54	57	56	------	------	------
8	15	7	0.2	0.2	35	48	49	46	48.5	------	------
9	16	6	0.2	0.2	34	45	47	43	46	------	------
10*	12	10	0.2	0.2	33	50	------	------	------	------	------
A	15	15	0.2	0.2	17	19	------	------	21	------	------
B	5	3	0.2	------	------	------	------	------	------	15	15
C	10	3	0.2	------	------	------	------	------	------	19	18
D	15	3	0.2	------	------	------	------	------	------	20	22
E	19	3	0.2	------	------	------	------	------	------	20	29
F	5	5	0.2	------	------	------	------	------	------	21	20
G	9	5	0.2	------	------	------	------	------	------	22	25
H	4	10	0.2	------	------	------	------	------	------	25	27
I	18	10	0.2	------	------	------	------	------	------	0	0
J	22	10	0.2	------	------	------	------	------	------	0	0

* 1% columbium added.
NOTE.—HW=Hot worked condition; A=Aged condition, Heat Treatment A; B=Aged condition, Heat Treatment B; C=Aged condition, Heat Treatment C; D=Aged condition, Heat Treatment D; E=Annealed condition; F=Aged condition, Heat Treatment E.

The data in Table I reflect the substantial increase in hardness illustrative of steels within the invention as opposed to those alloys without the ambit thereof. With the possible exception of Alloy E, none of the steels outside the invention manifested any significant increase in hardness. In this connection, the strength level of Alloy E would be too low to further consider.

In Table II mechanical characteristics for Alloys Nos. 1 and 9 are given together with another alloy within the invention, Alloy No. 11. Also included in Table II is Alloy K, an alloy quite similar in chemistry to Alloy No. 1 except 0.5% each of silicon and manganese was used in the former as opposed to the low amount (<0.15%) employed in respect of the latter. The ultimate tensile strength (U.T.S.) and yield strength (Y.S., 0.2% offset) are given in thousands of pounds per square inch (K s.i.),

most satisfactory, the aging period not exceeding about ten hours.

As will be readily understood by those skilled in the art, the terms "martensite" or "substantially martensite" include the decomposition and/or transformation products of austenite obtained upon cooling from the hot working operation (or, where used, a solution annealing treatment). These terms also include transformation products of austenite resulting from the application of a cold treatment, e.g., refrigeration at a temperature down to minus 300° F. and/or cold working.

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.

We claim:

1. An iron-base alloy in the martensitic condition and characterized by a good combination of strength and toughness in the aged condition, said alloy consisting essentially of about 10% to about 16% nickel, about 6% to 12% molybdenum, the sum of the nickel plus molybdenum being not greater than 26%, up to 1% titanium, up to 1% aluminum, carbon in an amount up to 0.1%, up to not more than 0.25% manganese, up to not more than 0.25% silicon, up to 1% cobalt, up to 2% columbium, up to 4% tantalum, up to 0.1% boron, up to 0.25% zirconium, up to 2% vanadium, up to 0.1% calcium, up to 1% beryllium, up to 4% copper, the sum of the columbium, tantalum, boron, zirconium, vanadium, calcium, beryllium and copper being not greater than 10%, up to 1% chromium, and the balance essentially iron, said martensitic condition being achieved in the absence of any intermediate conditioning heat treatment prior to the aging treatment.

2. The alloy set forth in claim 1 wherein the sum of molybdenum plus nickel does not exceed 25%, the manganese plus silicon does not exceed a total of 0.3%, and wherein the sum of columbium, tantalum, boron, zirconium, vanadium, calcium, beryllium, and copper does not exceed 6%.

3. An iron-base alloy in the martensitic condition and characterized by a good combination of strength and toughness in the aged condition, said alloy consisting es-

sentially of about 11% to 15% nickel, about 8% to 11% molybdenum, the sum of the nickel plus molybdenum being not greater than 25%, at least one element selected from the group consisting of 0.1% to 1% titanium and 0.1% to 1% aluminum, the sum of the titanium plus aluminum being not greater than 1.5%, up to 0.05% carbon, not more than 0.15% manganese, not more than 0.15% silicon, and the balance essentially iron, said martensitic condition being achieved in the absence of any intermediate conditioning heat treatment prior to the aging treatment.

4. The alloy as set forth in claim 1 wherein the molybdenum is partially replaced by an equal atomic percentage of tungsten up to a maximum tungsten content of 8%.

5. The alloy as set forth in claim 3 wherein the carbon content does not exceed about 0.03%.

6. The alloy as set forth in claim 5 wherein the manganese and silicon contents do not exceed about 0.1%, respectively.

References Cited

UNITED STATES PATENTS

3,093,519	6/1963	Decker et al.	75—123 X
3,123,506	3/1964	Tanczyn	75—123 X
3,262,777	7/1966	Sadowski	75—124

OTHER REFERENCES

Transactions of the ASM, vol. 55, 1962 relied on pages 58–76.

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