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AGE HARDENING MANGANESE-CONTAINING MARAGING STEEL

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The present invention relates to ferrous-base alloys and, more particularly, to ferrous-base alloys manifesting a combination of relatively high yield strength and satisfactory toughness characteristics of sufficient magnitude that they are suitable for use, inter alia, as steels for high strength structural applications.

As is well known to those skilled in the art, a number of mild carbon and low alloy steels have been developed and/or proposed for use as structural steels in structural applications. Generally, such steels are normally of the quenched and tempered variety and are characterized by yield strengths on the order of about up to 100,000 pounds per square inch (p.s.i.) or above. There are any number of carbon-containing low alloy steels which afford yield strengths of 150,000 to 200,000 p.s.i. or above, but they generally lack adequate toughness and/or are afflicted with other problems to be utilized for diversified structural applications on a substantial commercial basis. For example, there are the well known problems of warpage and dimensional change attendant the quench operation, particularly with respect to fairly high carbon-containing steels. Too, weldability problems arise and embrittlement problems on cooling from tempering temperatures become a source of difficulty.

A number of alloying constituents have been advanced to achieve high yield strengths together with adequate toughness in both the quenched and non-quenched steels. Manganese is an element which is probably present in all carbon and low alloy steels. However, notwithstanding its extensive use in steels, manganese (insofar as we are aware) has not been proposed for the purpose of achieving relatively high yield strengths combined with a reasonable degree of toughness in age-hardenable, non-quenched steels. As is known, manganese is found as a residual element and often used as a refining agent in steels. For example, manganese is utilized to tie-up detrimental sulfur, whereby the subversive influence of sulfur is rendered innocuous. Of course, manganese promotes hardenability characteristics, particularly in quenched steels and also has been used in substantial amounts in the AISI 200 series of stainless steels. In the latter instance, it is used to stabilize austenite, a function which it also performs in the high manganese steels (circa 13% manganese), generally known as the Hadfield steels. Too, the use of manganese has also been advanced for producing expansion members of bi-metallic elements.

However, it has now been discovered that when special amounts of manganese are incorporated in nickel-containing, ferrous base alloys, an age-hardenable steel is provided which affords, upon simple heat treatment, a satisfactory combination of yield strength and toughness. Further, alloys contemplated herein exhibit an unusually low hardness in the annealed condition. This renders the steels especially amenable to working and machining operations. This is in direct contrast to quenched steels wherein maximum hardness is obtained on quenching, a condition which is not favorable to ease of workability and machinability.

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The alloys of the present invention are of the class known as the "maraging steels" which were developed and introduced to the art several years ago. These steels have not only opened up a vast new area of steel metallurgy and technology but fundamentally differ from the carbon and low alloy steels in that upon heating (aging) in the martensitic condition, the maraging steels increase in hardness and strength as opposed to the softening response and decrease in strength attendant the carbon and low alloy steels. In this connection it should be mentioned that with the advent of the maraging steels, manganese, while it has been deemed to be a hardener in such prior steels, amounts thereof on the order of, say, 0.5% and above have resulted in a rather marked impairment of ductility. This is not the case in accordance with the instant invention.

It is an object of the present invention to provide a novel manganese-containing, age-hardenable steel capable of providing relatively high yield strengths in combination with an acceptable level of toughness in the aged condition.

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

Generally speaking, the present invention contemplates providing alloy steels which are martensitic in the solution annealed condition and which thereafter can be age hardened in the martensitic condition to provide satisfactory levels of both yield strength and toughness. The alloy steels consist essentially of (by weight) about 10% to 20% nickel, about 1.2% to 3.9% manganese, up to 5% chromium, with the sum of the nickel plus manganese plus chromium contents being controlled such that the total sum thereof is from 14% to 23%, e.g., 16% to 22%, carbon in an amount up to 0.03%, up to 1% titanium, up to 1% aluminum with the sum of the titanium plus aluminum not exceeding 1%, up to 1% silicon, and the balance essentially iron. To achieve an optimum combination of properties, including yield strength and toughness, the steels most advantageously contain about 16% to about 20% nickel, about 1.5% to 3% manganese, up to 1% chromium, the sum of the nickel plus manganese plus chromium contents being about 17.5% to about 23%, carbon in an amount up to 0.03%, up to 0.5% titanium, e.g., 0.02% to 0.2% titanium, up to 0.5% aluminum, e.g., 0.02% to 0.2% aluminum, up to 0.5% silicon and the balance essentially iron. When heat treated by aging, steels of the present invention exhibit yield strengths (0.2% offset) of from 150,000 to 225,000 pounds per square inch (p.s.i.) together with a highly satisfactory magnitude of toughness as determined by tensile elongation and reduction of area properties. The following auxiliary elements in a total aggregate of not more than 2% can be present: up to 2% cobalt, up to 2% molybdenum, up to 2% vanadium, up to 2% tungsten, up to 0.4% beryllium, up to 2% columbium, up to 2% tantalum and up to 2% copper.

In carrying the invention into practice, the nickel content is advantageously from 16% to 20%, e.g., 18%. Lower amounts of nickel result in lower strength levels whereas higher amounts promote retention of austenite

upon cooling from solution annealing temperature to about room temperature, i.e., the structure obtained on cooling from solution (annealing) treatment may not be as completely martensitic as would otherwise be the case, thus necessitating, for example, a sub-zero cooling treatment to effect as complete a transformation to martensite as possible.

The amount of manganese employed has been found to be most important. When the manganese content is less than about 1.2%, yield strength is adversely affected whereas with manganese contents above about 3.9%, toughness is detrimentally impaired. For the best combination of properties, the manganese content advantageously should be within the range of 1.5% to 3%. However, the total content of nickel plus manganese should not exceed 23% since as referred to hereinabove, retained austenite can ensue. Retained austenite, assuming that too much of this phase is not present, can be transformed by refrigerating or cold working at sub-zero temperatures before aging. It is preferred that at least small amounts, e.g., 0.02% to 0.2%, of titanium and/or aluminum be present in the steels to achieve optimum toughness characteristics.

The amount of carbon advantageously should not exceed 0.03%. With carbon contents characteristics of various carbon and low alloy steels, toughness is impaired and higher strength levels are not attained. The steels should be substantially devoid of elements such as sulfur, phosphorus, oxygen, nitrogen, lead, etc., as is consistent with commercial steelmaking practice. Such constituents merely serve to give rise to problems involving processing of the steels, e.g., workability, and result in a deterioration of properties.

A most advantageous range of composition for steels contemplated herein is as follows: 17.5% to 18.5% nickel, e.g., 18% nickel, about 1.75% to 2.75% manganese, e.g., 2.5% manganese, carbon in an amount up to 0.02%, e.g., 0.01%, and the balance essentially iron.

A further attribute of the steels of the instant invention is that they can be prepared using standard air melting techniques. While vacuum melting treatments can be employed, air melting practice results in a satisfactory level of properties. Materials of relatively high purity and/or selected scrap should be used as the basic melting charge, and such metals as boron, zirconium, calcium, lithium, magnesium and the like can be used as suitable malleableizing and/or deoxidizing constituents. Titanium also can be employed for this purpose. Cast ingots obtained upon solidification of the melt should be rather thoroughly homogenized by soaking at temperatures of about 2200° F. to about 2400° F. followed by hot working and, if desired, by cold working to size and/or shape.

Prior to aging, the steels should be solution annealed at temperatures of from about 1400° F. to about 1600° F. High annealing temperatures up to 2300° F. can be employed but the higher annealing temperatures result in a loss of tensile strength although hardening is still possible with the utilization of such temperature levels. Upon cooling from the solution annealing treatment, the alloys transform from austenite to martensite. It is important that as complete a martensitic structure be obtained prior to aging in order to achieve the high strength levels characteristic of the steels. As used herein, the term martensite (or martensitic) refers to steels having a structure of martensite (or substantially martensitic) in both the solution annealed condition and in the aged condition. The transformation from austenite to martensite is normally accomplished by cooling through the M_s–M_f transformation range to room temperature (from the annealing temperature). As indicated above, in some instances and in order to attain as complete a transformation as possible, it may be desirable to cool the steels below room temperature, e.g., down to minus 100° F., as by, for example, refrigeration. To illustrate, should the total content of nickel plus manganese plus any amount of chromium present exceed about 22%, sub-zero cooling would be beneficial. Cold working prior to aging can also be used to effect the completion of transformation to martensite.

The aging treatment should be conducted over the temperature range of 700° F. to about 900° F. and preferably 750° F. to 850° F. for about 1 to 50 hours, e.g., 3 to 24 hours at 800° F. Aging temperatures appreciably above 900° F. should be avoided; otherwise, retention of undesired austenite can occur. Since aging temperatures of 700° F. require undesirably longer aging times, it is advantageous to use the aging temperature range of about 750° F. to 850° F.

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

A series of alloys having compositions given in Table I (Alloys A and B being outside the invention and Alloys 1 and 2 being within the invention) were prepared by air melting, small amounts of silicon, aluminum and titanium being used as refining additions.

TABLE I

Alloy No.	Percent						
	Ni	Mn	Si	Al	Ti	C	Fe
A	17.4	0.07	0.02	0.04	0.06	0.019	Bal. Ess.
B	18.2	0.80	<0.01	<0.05	0.08	0.008	Bal. Ess.
1	18.1	1.72	0.02	<0.05	0.06	0.012	Bal. Ess.
2	18.0	2.50	0.02	<0.05	0.04	0.011	Bal. Ess.

Bal. Ess.=balance of alloy was essentially iron.

The steels were homogenized, hot forged and thereafter hot rolled to ¾ inch diameter bar stock. Specimens were solution annealed at 1500° F. for one hour and thereafter refrigerated for 16 hours at minus 105° F. to assure, as a precautionary measure, complete transformation to martensite. Thereafter the steels were aged at either 700° F., 800° F., or 900° F. for various periods and the data in Table II illustrate the hardness behavior thereof.

TABLE II

Alloy No.	Temp., ° F.	Hardness, Rockwell "C" Time (hours)				
		1	2	3	8	24
A	900	30	----------	----------	----------	----------
B	900	22	----------	19	21	21
1	800	----------	----------	39	----------	38
	900	26	----------	27	26	24
2	700	35	----------	----------	46	47
	800	----------	47	45	46	41
	900	39	----------	31	30	26

The foregoing hardness data illustrate that prolonged heat particularly at a temperature of 900° F. results in overaging and possible formation of retained austenite, factors which should be, as noted above herein, avoided. Alloy B reflects that with manganese contents of 0.8%, an amount quite representative of many carbon and low alloy steels, the response to age hardening treatment is minimal. The hardness characteristics of this alloy were such that further testing with regard thereto was not conducted.

The yield strength (Y.S., 0.2% offset) and ultimate tensile strength (U.T.S.) in thousands of pounds per square inch (K.S.I.), tensile elongation (El., percent) and reduction of area (R.A., percent) characteristics are given in Table III for alloys A, 1 and 2. In this regard, the steels were aged at 800° F. for a period of time as noted in Table III. The properties of alloy A are also given in the as-refrigerated condition.

TABLE III

Alloy No.	Aging Time, hours	Heat Treatment, °F	0.2% Offset [1] Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El., percent	R.A., percent
A		[2]	119	144	16	73
	1	800	123	126	18	74
	8	800	128	132	20	73
1	3	800	165	173	8	36
2	3	800	212	218	13	49
	24	800	215	224	11	47

[1] 0.252 inch diameter, 1 inch gage length.
[2] As refrigerated.

The present invention is particularly applicable to the production of high strength structural elements, assemblies and the like. The aged alloys of the invention can be used as sheet, plate, rods, bars, extrusion, etc. A particular advantage of the contemplated alloys is that they can be readily machined and/or otherwise shaped or formed while in the annealed condition and can thereafter be age hardened without the incurrence of detrimental distortion or dimensional change being induced by the age-hardening treatment. The necessity of utilizing further processing steps to obviate distortion and/or dimensional change has been characteristic of prior art carbon and low alloy steels.

As will be readily understood by those skilled in the art, the term "balance" as used herein in referring to the iron content of the alloys does not preclude the presence of other elements, e.g., deoxidizing and cleansing elements, and impurities normally associated therewith in small amounts which do not adversely affect the basic characteristics of the alloys.

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. A martensitic steel characterized in that it transforms substantially to martensite at room temperature or above and further characterized in the aged condition by a combination of relatively high yield strength together with a satisfactory level of toughness, said steel consisting essentially of about 16% to about 20% nickel, about 1.5% to about 3% manganese, up to 1% chromium, with the sum of the nickel plus manganese plus chromium contents being about 17.5% to about 23%, up to 0.03% carbon, up to 0.5% titanium, up to 0.5% aluminum, up to 0.5% silicon, and the balance essentially iron.

2. The alloy as set forth in claim **1** in which both titanium and aluminum are present in an amount of 0.02% to 0.2%, respectively.

3. A martensitic steel characterized in that it transforms substantially to martensite at room temperature or above and further characterized in the aged condition by a combination of relatively high yield strength together with a satisfactory level of toughness, said steel consisting essentially of about 10% to 20% nickel, from 1.2% to 3.9% manganese, up to 5% chromium, the sum of the nickel plus manganese plus chromium contents being about 14% to 23%, carbon in an amount up to 0.03%, up to 1% titanium, up to 1% aluminum, up to 1% silicon, up to 2% cobalt, up to 2% molybdenum, up to 2% vanadium, up to 2% tungsten, up to 0.4% beryllium, up to 2% columbium, up to 2% tantalum, up to 2% copper, with the proviso that the total summation of cobalt, molybdenum, vanadium, tungsten, beryllium, columbium, tantalum and copper is not greater than 2%, and the balance essentially iron.

4. A martensitic steel characterized in that it transforms substantially to martensite at room temperature or above and further characterized in the aged condition by a combination of relatively high yield strength together with a satisfactory level of toughness, said steel consisting essentially of about 17.5% to about 18.5% nickel, about 1.75% to about 2.75% manganese, up to 0.02% carbon, and the balance essentially iron.

References Cited by the Examiner

UNITED STATES PATENTS

963,123	7/1910	Dempster	75—128
2,048,164	7/1936	Pilling	148—142
2,683,677	7/1954	Walters	148—142

OTHER REFERENCES

The Journal of the Iron and Steel Institute, No. II, 1920, volume CII, article by Hanson et al., pages 41 and 49–59.

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