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AGED STEEL

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The present invention relates to ferrous-base alloys and, more particularly, to nickel-containing ferrous-base alloys particularly adapted to be employed as high strength structures for cryogenic use.

It is well known that certain ferrous-base alloys, that is, alloys containing iron as their major constituent, can be produced with a martensitic matrix which can, by means of tempering and/or hardening heat treatments, provide in those alloys advantages combinations of high strength, wear resistance, hardness, etc. Particularly advantageous wrought age-hardenable martensitic ferrous-base alloys have been disclosed in the Bieber U.S. patent application Serial No. 839,296, field on September 11, 1959 (now U.S. Patent No. 3,093,518) and in the Decker et al. U.S. patent application Serial No. 80,381, filed on January 3, 1961 (now U.S. Patent No. 3,093,519). Among the alloys disclosed in the prior Bieber U.S. patent application Serial No. 839,296 are commercially available iron-base alloys containing, in percent by weight, about 18% to about 25% nickel, small interrelated amounts of carbon and columbium (niobium) and amounts of titanium and/or aluminum in the aggregate of at least about 1.5%. These wrought Bieber alloys can be subjected to an age-hardening heat treatment while in the martensitic condition to provide hitherto unattainable combinations of strength and ductility at room temperature and lower. The aforementioned Decker et al. U.S. application was concerned with wrought ferrous-base alloys containing about 10% to about 27% nickel together with interrelated amounts of cobalt and molybdenum which could also be age hardened while in the martensitic condition. The wrought alloys of both Bieber and Decker et al. are commercially available, have been widely publicized in metallurgical circles and are currently in the process of being tested for acceptance in many applications where strength coupled with toughness at ordinary temperatures is of paramount consideration. These wrought alloys, known as "maraging steels," are characterized on the whole by ease of formability both by hot-working and cold-working processes, by ease of weldability, through hardenability and by freedom from major distortion during hardening heat treatment.

Since the discovery of the remarkable combination of characteristics which can be provided in the known steels, considerable effort has been expended in an endeavor to provide a steel adapted to be employed as high strength structures for cryogenic usage. When an alloy is to be employed at cryogenic temperatures, i.e., temperatures below about −100° F., it is essential that the alloy exhibit not only good strength characteristics but also the alloy must exhibit good fracture toughness at such temperatures. Additionally, it is advantageous for such an alloy to possess high resistance to stress-corrosion cracking. Although attempts were made to overcome the foregoing difficulties and provide a commercially acceptable high strength steel suitable for use at cryogenic temperatures, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that by specifically controlling alloying elements including nickel, cobalt, molybdenum, titanium, and aluminum within special ranges of composition, a steel can be provided which exhibits

in the wrought and heat treated condition an advantageous combination of engineering characteristics at cryogenic temperatures.

It is an object of the present invention to provide a novel steel adapted to be employed at cryogenic temperatures.

Another object of the invention is to provide a novel high strength ferrous-base alloy suitable for use at cryogenic temperatures.

An additional object of the present invention is to provide a novel process for producing an ultra-high strength aged cryogenic steel.

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

Generally speaking, the present invention contemplates a steel containing, in percent by weight, about 17% to about 19% nickel, about 8% to about 9% cobalt, about 2.8% to about 3.5% molybdenum, about 0.05% to about 0.25% titanium, about 0.05% to about 0.15% aluminum, up to about 0.2% silicon, up to about 0.2% manganese, up to about 0.01% sulfur, carbon in unavoidable amounts up to about 0.03%, with the balance being essentially iron. When employed in this specification and claims, the term "balance essentially" is intended to include small amounts of impurities and incidental elements normally associated with the ingredients of the alloys.

The steels of the present invention are produced by melting selected stock and/or scrap using conventional steel melting practice such as induction melting, consumable electrode melting and basic electric furnace melting with or without protective atmospheres. Prior to pouring, additions of titanium and aluminum are made together with malleableizing and/or deoxidizing amounts of one or more of silicon, manganese, boron, zirconium, mischmetal, lithium, magnesium, uranium, calcium, etc. The carbon content of the charge can be controlled by the use of oxygen. After all alloying and deoxidation and/or desulfurization additions have been made to the molten alloy, the metal is cast at temperatures of about 2700° F. to about 3000° F. The solidified alloy is then homogenized either prior to or during hot working operations. Thus, homogenization can be accomplished by heating for about 1 to about 4 hours at a temperature of about 2200° F. to about 2350° F., and/or by initially hot working in such fashion that the cast grain structure is thoroughly broken up by metal flow in more than one direction. Hot working can be accomplished by forging, rolling and the like at starting temperatures as high as about 2300° F. and finishing temperatures as low as about 1400° F. After hot working, or as the last step thereof, the alloy is solution annealed at a temperature of about 1500° F., e.g., a temperature of about 1450° F. to about 1800° F. Finish hot rolling of sheet and plate conducted so that the finishing temperature is about 1400° F. to about 1700° F., is essentially equivalent to solution annealing. The solution annealing is advantageously carried on for about 1 hour.

During cooling of the alloy to room temperature, i.e., a temperature in the vicinity of 70° F., after hot working and/or annealing, the alloy transforms to provide an alloy matrix having a structure comprising decomposition and/or transformation products of austenite. In this transformed condition, the alloy has a hardness of about 28 to about 32 in Rockwell C units (Rc) and can be readily cold worked.

After transformation by cooling to room temperature (or in certain cases to a temperature lower than room temperature), the alloy can be cold shaped by rolling, machining, hydrospinning, high velocity impact, deep drawing and the like. Thereafter, the alloy is hardened

by aging at a temperature of about 700° F. to about 1000° F. for about 1 hour to about 10 hours. A satisfactory aging treatment consists of heating for about 3 hours at a temperature of about 900° F.

In order to minimize microsegregation in alloy ingots as cast and to improve toughness in the age-hardened alloy, it is advantageous to limit the amount of titanium in the alloys to a maximum of about 0.25% and the amount of molybdenum to a maximum of about 3.5%. Cobalt within the range of about 8% to about 9%, in combination with the remainder of the alloy composition, provides in the hardened alloy an advanatgeous modulus of elasticity of about 27×10^6 pounds per square inch (p.s.i.). An advantageous nominal alloy composition in terms of weight percent is set forth in Table I.

Table I

Elements:	Nominal composition, (percent)
Nickel	18.0
Cobalt	8.5
Molybdenum	3.2
Titanium	0.2
Aluminum	0.1
Carbon	0.015
Zirconium	0.01
Boron	0.003
Iron	Balance

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative compositions in accordance with the present invention are set forth in Table II.

Table II

Alloy No.	Percent C	Percent Ni	Percent Mo	Percent Co	Percent Ti	Percent Al	Percent B	Percent Zr	Percent [1] Fe
1	0.017	17.55	2.85	8.10	0.19	0.11	0.0036	<0.01	Bal.
2	0.018	17.32	3.48	8.00	0.18	0.09	0.0053	<0.01	Bal.
3	0.014	18.00	3.40	8.50	0.17	0.083	[2] 0.003	<0.01	Bal.

[1] Iron includes small amounts of silicon, manganese and/or calcium in amounts within the ranges set forth hereinbefore together with small amounts of impurities and incidental elements.
[2] Amount added.

Alloy No. 1 was produced by vacuum melting and was rolled to sheet nominally 0.063 inch thick. Samples of this sheet were produced in two conditions. Condition "A" resulted from solution annealing the alloy at 1500° F. for one hour, air cooling to room temperature and thereafter aging the thus transformed alloy for three hours at 900° F. Condition "B" resulted from a solution anneal for one hour at 1500° F., air cooling to room temperature, cold working the thus transformed alloy by cold rolling to effect a 50% reduction and thereafter aging the transformed and cold worked alloy for three hours at 900° F. Various tensile values in thousands of pounds per square inch (k.s.i.), elongations in percent and notch to unnotch tensile ratios at room temperature and at −320° F., the temperature of liquid nitrogen, are set forth in Table III.

Table III

Alloy No.	Condition	0.2% Yield Strength, (k.s.i.)	Ultimate Tensile Strength, (k.s.i.)	Elongation, Percent	Notch [1] Tensile Strength, (k.s.i.)	Notch Tensile Strength/ Ultimate Tensile Strength
1	[2] A	197	199	4	226	1.14
1	[2] B	230	230	2	245	1.06
1	[3] A	266	273	4	284	1.04
1	[3] B	301	302	2	283	0.94

[1] Measured on a sheet specimen having a notch acuity factor of 18.
[2] Test Temperature—Room Temperature.
[3] Test Temperature—−320° F.

Table III shows that alloy No. 1, an example of the advantageous alloys of the present invention, exhibits excellent tensile characteristics including ultimate tensile strength (U.T.S.), yield strength (Y.S.) and notch tensile strength (N.T.S.) at both room and cryogenic temperatures.

Room temperature tensile characteristics and room and cryogenic temperature Charpy V Notch (C.V.N.) impact characteristics of air melted bar samples of alloys Nos. 2 and 3 in condition "A" are set forth in Table IV.

Table IV

	Alloy No. 2	Alloy No. 3
0.2% Y.S., (k.s.i.)	200	204
U.T.S., (k.s.i.)	206	211
Elongation, percent	15	15
Reduction in area, percent	66	68
N.T.S., (k.s.i.)	334	335
C.V.N.[1]:		
Room Temperature	68	60
−320° F	31	29
−423° F		34

[1] Charpy V Notch values are in units of foot-pounds (ft.-lbs.).

U-bend samples of age-hardened alloys Nos. 2 and 3 stressed at their yield point have been exposed to ambient temperature sea water for about one year without fracture. This demonstrates that alloys in accordance with the present invention have excellent resistance to stress-corrosion cracking in the presence of sea water.

It is to be noted that the steels of the present invention are advantageous when compared to other materials of construction for cryogenic purposes. Thus, when comparing the engineering characteristics of the steels of the present invention at −320° F. with the characteristics of other materials taking into account density, yield strength and the notch to smooth tensile ratio calculated with notch values obtained on samples having a notch acuity factor greater than 18, the aged steels or alloys of the present invention are substantially superior to aluminum alloys such as the alloy designated as 2014–T6 and cold rolled steels such as those designated as AISI 301 and AISI 310. Under the same conditions, the aged steels of the present invention compare favorably with certain titanium-base alloys which are much more expensive both from the standpoint of material cost and from the standpoint of fabricating costs.

The alloys of the present invention are readily weldable and can be easily fabricated into structures for use at cryogenic temperatures. Such structures include missile motor cases and pressure vessels, liquid-gas storage vessels and pressure equipment and other fixtures and structural elements employed in service under critically stressed conditions at cryogenic temperatures.

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 steel for use as structures and structural elements subjected in use to stress at cryogenic temperatures consisting essentially of about 17% to about 19% nickel, about 8% to about 9% cobalt, about 2.8% to about 3.5% molybdenum, about 0.05% to about 0.25% titanium, about 0.05% to about 0.15% aluminum, up to about 0.2% silicon, up to about 0.2% manganese, less than about 0.01% sulfur and less than about 0.03% carbon with the balance being essentially iron together with small amounts of impurities, deoxidants and incidental elements normally associated therewith.

2. A steel as in claim 1 hardened by aging for about 1 to about 10 hours at about 700° F. to about 1000° F. after transformation.

3. A steel for use as structures and structural elements subjected in use to stress at cryogenic temperatures consisting essentially of about 18% nickel, about 8.5% cobalt, about 3.2% molybdenum, about 0.2% titanium, about 0.1% aluminum, about 0.015% carbon, about 0.01% zirconium, about 0.003% boron with the balance being essentially iron.

4. A steel for use as structures and structural elements subjected in use to stress at cryogenic temperatures consisting essentially of about 0.014% to about 0.018% carbon, about 17.32% to about 18.00% nickel, about 2.85% to about 3.48% molybdenum, about 8.00% to about 8.50% cobalt, about 0.17% to about 0.19% titanium, about 0.083% to about 0.11% aluminum, about 0.003% to about 0.0053% boron, less than 0.01% zirconium with the balance being essentially iron.

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