

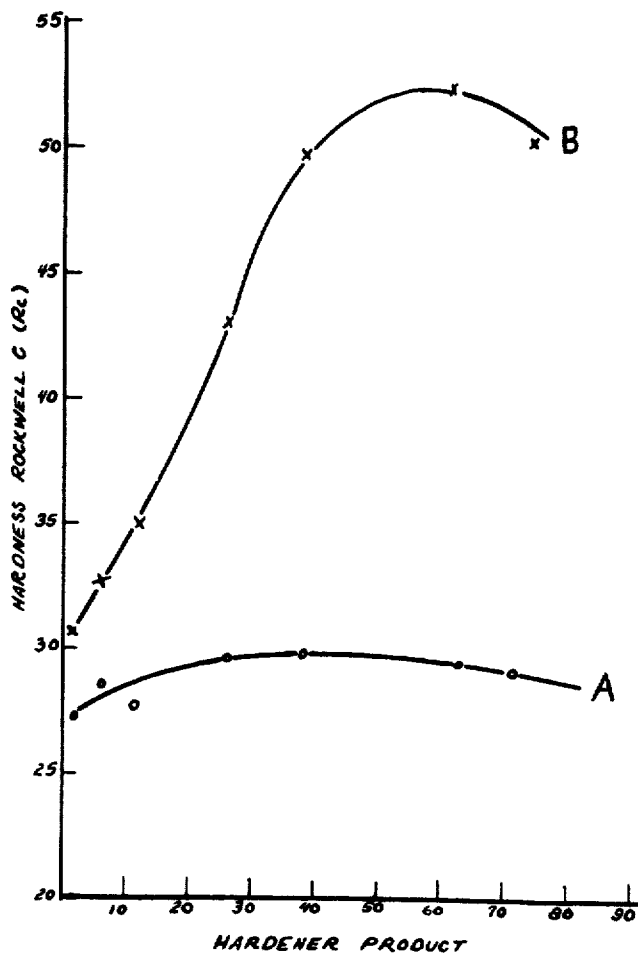
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AGE-HARDENABLE MARTENSITIC IRON-BASE ALLOYS

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**AGE-HARDENABLE, MARTENSITIC
IRON-BASE ALLOYS**

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The present invention relates to iron-base alloys and, more particularly, to ductile, tough, high strength iron-base alloys having an advantageous combination of mechanical characteristics.

Heretofore, the art has endeavored to provide a ductile, tough, high strength steel or iron-base alloy which is readily formable and readily weldable and which exhibits good resistance to stress-corrosion cracking and to crack propagation when stressed in the notched condition. Although attempts were made to provide a steel having such an advantageous combination of mechanical characteristics, none with tensile strength above 250,000 p.s.i., 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 specially controlling the amounts and character of alloying additions to a nickel-containing steel, a novel steel having an advantageous combination of mechanical characteristics in the martensitic, aged condition can be provided.

It is an object of the present invention to provide a novel, nickel-containing steel.

Another object of the invention is to provide a novel, nickel-containing, martensitic steel having an advantageous combination of hardness, ductility and useful mechanical characteristics.

The invention also contemplates providing a novel, nickel-containing iron-base alloy having high strength and ductility.

It is a further object of the invention to provide a method for producing steel structures having a high combination of mechanical characteristics.

The invention further contemplates providing structures, mechanical elements and the like having an advantageously high combination of strength, hardness, resistance to stress corrosion, ductility, toughness, formability, weldability and resistance to crack propagation induced by physical, mechanical or metallurgical notches.

A still further object of the present invention is to provide a novel cast alloy having an advantageously high combination of strength, hardness, resistance to stress corrosion, ductility and toughness.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which the FIGURE depicts graphically the relationship of a hardener product (hereinafter defined) upon the hardness of a typical base composition of the novel steels of the present invention.

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Generally speaking, the present invention contemplates steels or iron-base alloys containing by weight about 10% to about 27% nickel, about 1% to about 10% molybdenum and about 2% to about 30% cobalt where-in the product of the numerical value of the percentage of molybdenum times the numerical value of the percentage of cobalt (i.e., the hardener product) is about 10 to about 80 or even 100. The alloys of the present invention usually contain at least about 50% iron but can contain less than about 50% iron subject to the condition that iron is always present in an amount greater than any other element.

The iron-base alloys of the present invention, (i.e., alloys containing iron in an amount greater than any other element) which contain molybdenum and cobalt as hardeners, can advantageously contain up to about 8% chromium provided that when an effective amount of chromium is present the sum of the percentage of nickel plus the percentage of chromium is no greater than about 23%. More advantageously, the total percentage of nickel plus chromium is less than about 20%. Thus, the present invention contemplates iron-base alloys containing about 10% to about 14% nickel in combination with about 4% to about 8% chromium and alloys containing about 13% to about 18% nickel in combination with about 0.5% to about 5% chromium. It is to be noted that in alloys of the present invention containing about 10% to about 14% nickel and about 4% to about 8% chromium, it is advantageous to limit the amount of cobalt to a maximum of about 20%. Advantageously, in chromium-free alloys of the present invention the maximum nickel content is of the order of about 22% or 23%. Carbon is advantageously present in the alloys of the present invention in amounts up to about 0.15%, for example, about 0.005% to about 0.15% and, more advantageously, in amounts of about 0.01% to about 0.05%. When employed in the alloys of the present invention, carbon acts to increase hardness. Elements (hereinafter referred to as "auxiliary hardeners") such as beryllium, silicon, copper, tungsten, columbium, titanium, aluminum, vanadium, nitrogen, etc., which can be present in the alloys of the present invention in amounts up to about 10% in the aggregate can also cooperate with molybdenum and cobalt to harden the alloys. Some of these auxiliary hardeners can also react with carbon and/or nitrogen to form various simple and/or complex carbides, nitrides and/or carbonitrides. Titanium, columbium and vanadium are examples of elements which can perform these dual functions. The auxiliary hardeners can, if employed in excess, adversely effect the ductility of the alloys of the present invention to an undesirable degree. For this reason, it is advantageous to limit the amounts of each of the auxiliary hardeners when included in the alloys of the present invention singly to the maximum percentages by weight set forth in Table I.

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Table I

Element	Percent	Element	Percent
Be.....	1	Ti.....	3
Si.....	2	Al.....	3
Cn.....	6	V.....	6
W.....	10	N.....	0.2
Co.....	3	C.....	0.15

For the same reason, to wit, an adverse effect upon ductility, it is advantageous to maintain the aggregate amounts of these auxiliary hardeners within a maximum total of about 7% by weight.

Other elements such as manganese, sulfur, phosphorus, etc., which are normally encountered in steels are undesirable in the iron-base alloys of the present invention. Under special circumstances, manganese can be present in the alloys of the present invention in amounts up to about 5% by weight. Ordinarily, however, it is advantageous to maintain the manganese content of the alloys below about 1% by weight and even below about 0.25% by weight in order to assure that the alloys will have adequate toughness. Sulfur and phosphorus contents should be maintained below about 0.04% and even 0.02% by weight each. Advantageously, these elements should be at as low a percentage level as is consistent with economical commercial practice.

For purposes of deoxidation and/or synergistic coaction with the remainder of the components of the iron-base alloys of the present invention, elements such as calcium (or magnesium), boron and zirconium can be employed. The residual percentages of these elements can be up to about 0.1% by weight each of calcium and boron and up to about 0.25% by weight of zirconium.

The alloys of the present invention always contain molybdenum and cobalt. The hardening coaction of these elements in the alloys of the present invention is graphically illustrated in the drawing. Referring now thereto, it is to be noted that curve A is constructed by plotting the hardener product of certain alloys against their hardness in the annealed condition and thereafter correlating the plotted points by means of an average curve. Curve B is similarly constructed from data on the same alloys in the aged-martensitic condition. The compositions of these alloys is set forth in Table II:

Table II

Alloy No.	Ni percent	Co percent	Mo percent	Fe percent
A.....	20.4	1.72	1.75	Bal. E. ¹
B.....	19.9	3.44	1.93	Do.
C.....	20.0	5.04	2.23	Do.
D.....	18.9	7.04	3.76	Do.
E.....	18.9	7.04	5.44	Do.
F.....	18.5	7.5	8.3	Do.
G.....	18.5	7.3	9.9	Do.

¹ Bal. E=Balance essentially and includes small amounts of carbon, silicon, sulfur, phosphorus in amounts which do not affect the basic characteristics of each of the alloys.

The alloys A to G were melted under a blanket of argon, hot forged at 1800° F., soaked for one hour at 2300° F. in an argon atmosphere and finally forged at 1800° F. to square section. The total reduction in area from hot forging was 78%. After forging, samples of these alloys were solution treated at 1600° F. for one hour and air cooled to room temperature. Alloys F and G were also

subjected to an additional refrigeration treatment at -105° F. for 18 hours after solution treatment. Further, alloy G was refrigerated at -320° F. for three hours. Hardness measurements upon the alloy samples were then conducted and these measurements were plotted. Subsequently, samples of these alloys forged, soaked, reformed, solution treated and cooled and/or refrigerated as set forth hereinbefore, were aged at 800-1000° F. for one to ten hours. Maximum hardness measurements taken after aging were then plotted. The drawing, in conjunction with the discussion set forth above, shows that when the hardener product, i.e., the numerical value of the product of the numerical values of the contents of molybdenum and cobalt (in weight percent) of an iron-base alloy containing nickel within the aforementioned composition range of about 10% to about 27% by weight exceeds about 15 or even about 10 and is below about 50 or even 80 or 100, an extraordinarily large increase in the hardness of the martensitic iron-base alloy occurs upon aging. Thus, it is within the contemplation of the present invention to age harden martensitic alloys of the present invention for minutes, e.g., 0.1 hour to about 100 hours at a temperature of about 500° F. to about 1100° F. An advantageous age hardening treatment in accordance with the present invention comprises heating the alloy for about one to about ten hours at temperatures of about 800° F. to about 1000° F. When used in this specification and/or claims, it is to be understood that the term "martensitic" refers to those alloys which have a matrix structure composed substantially of martensite. The term "martensite," as used in this specification, includes low temperature (i.e., usually less than about 700° C.) transformation products of austenite. The major portion of alloys within the present invention will be martensitic upon cooling to room temperature after hot-cold working or a solution treatment temperature of about 1300° F. to 2000° F. Thus, of the alloys of the present invention as set forth above in Table II, to wit, alloys C to G, alloys C to E are martensitic when cooled to room temperature from the solution treatment temperature. Certain alloys of the present invention such as the afore-listed alloys F and G which contain more than about 7% molybdenum, or other alloys containing more than about 21% nickel or more than about 20% nickel plus chromium are not wholly martensitic when cooled to room temperature after solution treatment. These certain alloys must therefore be subjected to a treatment which will induce a martensitic transformation. Satisfactory treatments include cold working up to about 95% reduction in an area and/or refrigeration at below room temperature down to about -320° F. for about 0.1 hour to about 24 hours. Heat and/or hardening treatments in accordance with the present invention include solution treatment at about 1300° F. to about 2000° F. for about 0.1 hour to about 10 hours followed by cooling and/or cold working to induce a martensitic transformation in addition to the aforementioned aging treatment of the martensitic iron-base alloy at temperatures of about 500° F. to about 1100° F. for about 0.1 hour to about 100 hours. It is to be noted that alloys which require refrigeration and/or cold working to induce a martensitic transformation after solution treatment can be advantageous in that, as cooled to room temperature, i.e., about 50° F. to about 80° F., these alloys are substantially austenitic and in this condition exhibit a hardness of the order of 10 Rockwell "C" (Rc). These alloys can be readily formed cold. In contrast, alloys of the present invention which are martensitic as cooled to room temperature after solution treatment exhibit hardnesses of the order of about 25 to

about 32 Rc. Martensitic alloys of the present invention which have been aged at temperatures of about 800° F. to about 1000° F. as set forth hereinbefore exhibit high strength, e.g., an ultimate tensile strength (U.T.S. of about 210,000 to about 320,000 pounds per square inch (p.s.i.) and a yield strength (Y.S.) of about 200,000 p.s.i. to about 310,000 p.s.i. Alloys of the present invention having up to about 270,000 p.s.i. U.T.S. are tough and ductile, exhibiting elongations of the order of about 12% and reductions in area of about 45% to about 60%. Tensile tests conducted upon notched bars (0.3-0.5 inch major diameter, $K_t=10$, where K_t =notch accuity factor) of the alloys usually result in notch tensile values which are of the order of about 120% to 150% of the value of the corresponding U.T.S. The special nickel contents of the alloys of the present invention contribute substantially to the toughness and ductility of the alloys.

In carrying the invention into practice, it is advantageous to employ compositions within the range as set forth in Table III when it is required that components made of the alloy be fabricated to form structures adapted to be subjected to high internal and/or external pressures or loads.

Table III

Element	Percent by weight	Element	Percent by weight
Ni.....	17-19.	Si.....	0.1 maximum.
Mo.....	4.6-5.1.	S.....	0.01 maximum.
Co.....	7-8.	P.....	Do.
Ti.....	0.3-0.5.	B.....	About 0.003 ¹ (0.0025).
Al.....	About 0.1.	Zr.....	About 0.02 ¹ (0.015).
C.....	0.01-0.03.	Ca.....	About 0.05 ¹ (0.01).
Mn.....	0.1 maximum.	Fe.....	Balance substantially.

¹ The first amounts of these elements are those amounts added. Under standard practice with a preliminary deoxidation with silico-manganese and calcium silicide and addition of aluminum, titanium, boron and zirconium just prior to casting the amounts of these elements in the parentheses are representative of retained percentages.

Alloys within the composition range as set forth in Table III are martensitic as cooled from a solution treatment. Accordingly, satisfactory hardening treatments for these alloys include a solution treatment at about 1450° F. to about 1600° F. for about one to about four hours, air cooling to room temperature, aging for about one to about ten hours at about 800° F. to about 1000° F. followed by air cooling. Alloys of the present invention can sometimes be benefited by a degassing heat treatment, i.e., heating after aging at a low temperature, e.g., 300° F. for a period of hours, such as is well known in the treatment of common steels. The alloys of the present invention as set forth in Table III can be hot worked with ease and, in the pre-aged condition, can be cold worked, for example, by cold rolling with reductions in area up to 95%. During such cold working, the average solution treated hardness of 28-30 Rc can increase, for example, up to 35 Rc. After aging, the hardnesses of the alloys within the range as set forth in Table III are of the order of 50 Rc and higher. Both the yield strength and the ultimate tensile strength of aged alloys of the present invention as set forth in Table III exceed about 250,000 p.s.i. These aged alloys are ductile, exhibiting in the tensile tests, elongations and reductions in area of the order of about 10% and 50%, respectively. Notch tensile tests on 0.5 inch bar with $K_t=10$ of aged alloys within the range set forth in Table III give values of notch tensile strength (N.T.S.) of the order of 340,000 p.s.i. and higher. The fully heat treated (aged) alloys as set forth in Table III can be readily welded with no cracking in the heat affected zone. The properties in this

zone can be restored by a simple aging treatment at about 800° F. to 1000° F. for .1 hour to 10 hours.

The aforementioned alloy range as set forth in Table III exemplifies a basic concept of the present invention set forth hereinbefore, to wit, that the hardening of the martensitic nickel-containing iron-base alloys of the present invention through the cooperative action of specially restricted contents of molybdenum and cobalt during aging can be supplemented, enhanced and/or modified by other supplementary hardeners. In the case of the alloy range set forth in Table III, the effective supplementary hardener is titanium. That amount of titanium in excess of the amount required to combine with carbon and nitrogen in the alloy is available to assist in hardening the alloy.

In general, the amounts of supplementary hardeners employed in alloys of the present invention are closely controlled. Thus, in the aggregate, amounts of copper plus tungsten plus vanadium should not exceed about 10%, amounts of columbium plus titanium plus aluminum should not exceed about 5%, amounts of beryllium plus silicon should not exceed 2% and amounts of nitrogen plus carbon should be about 0.05% and should not exceed about 0.25%.

Advantageously, when employed, amounts of the supplementary hardeners, when used singly, are inversely related to the hardener product, for example, as set forth in Table IV.

Table IV

Hardener product	10-30	25-55	50-80
Percent Be.....	0.3-1	0.1-0.4	0-0.2
Percent Cu.....	2-6	1-4	0-2
Percent W.....	5-10	3-7	0-3
Percent Co.....	0.5-3	0.2-2	0-0.9
Percent Ti.....	0.5-3	0-2	0-0.9
Percent Al.....	0.5-3	0.2-1.5	0-0.4
Percent V.....	2-6	1-4	0-2
Percent N plus percent C.....	0-0.25	0-0.10	0-0.05

It is to be understood that at any given hardener product level any one or group of supplementary hardeners may not be employed and because of this the minimum percentage of a supplementary hardener or group thereof is always zero. Carbon, nitrogen and silicon can assist in hardening the alloys but detrimentally affect the ductility and therefore should not be employed in the larger amounts in alloys wherein ductility is a prime consideration. Care should also be taken to avoid excessive amounts of supplementary hardeners which are not available for hardening (i.e., associated with carbon and nitrogen) since this can lead to undesirably large amounts of carbides, nitrides, carbonitrides, etc., in the microstructure of the alloys. An additional factor which must be considered when employing supplementary hardeners is the fact that these elements like molybdenum and chromium tend to lower the temperature at which martensite starts to form during cooling the alloys of the present invention, i.e., the M_s temperature. For alloys of the present invention to be substantially martensitic when cooled to room temperature after solution treatment, the M_s temperature should be of the order of about 250° F. or above. In any event, the M_s temperature should be no lower than about 0° F. in order that refrigeration and/or cold working will be effective in inducing the initiation and/or substantial completion of the martensitic transformation reaction.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages of the invention, additional

illustrative examples of alloys within the ambit of the present invention are set forth in Table V:

tures of about 2000° F. to 2300° F., hot rolled at 1500° F. to 1900° F. and thereafter, with the exception of

Table V

No.	Percent Ni	Percent Co	Percent Mo	Percent Ti	Percent Al	Percent Ca	Percent C	Percent B	Percent Zr	Percent Si	Percent others ¹
1	18.6	6.8	4.9	0.35	0.12	0.02	0.011			<0.10	
2	(18.5)	6.8	4.8	0.42	0.08	(0.02)	0.014	(0.003)	(0.02)	0.11	
3	18.2	6.8	4.9	0.40	0.07	0.02	0.008	(0.003)	(0.02)	0.08	0.014 S
4	18.5	7.0	5.1	0.42	0.08	0.02	0.019	(0.003)	(0.02)	0.11	0.013 S
5	(18.5)	7.2	5.0	0.44	0.11	0.01	0.016			0.12	0.008 S
6	19.0	6.8	5.2	0.40	0.11	0.02	0.020			0.11	0.026 S
7	19.0	(7)	5.2	0.40	0.08	0.02	0.018			0.12	0.026 S
8	18.1	6.8	5.0	0.12	<0.05	0.02	0.013			<0.10	
9	18.6	6.8	5.1	0.64	0.12	0.02	0.023	(0.003)	(0.02)	0.17	
10	18.3	6.6	5.0	0.70	0.11	0.02	0.027	(0.003)	(0.02)	0.12	
11	19.0	6.6	5.1	0.89	0.12	0.02	0.021			0.10	
12	16.9	7.0	5.0	0.41	0.10	0.01	0.019	(0.003)	(0.02)	0.17	
13	18.5	6.9	5.1	0.42	0.09	0.02	0.024	(0.003)	(0.02)	0.11	
14	20.2	6.7	5.2	0.40	0.12	0.02	0.028	(0.003)	(0.002)	0.16	
15	21.8	7.0	(5)	(0.5)	(0.1)	0.02	(0.02)	(0.003)	(0.002)		
16	18.4	6.6	5.1	0.41	0.12	0.01	0.021	(0.003)	(0.02)	0.12	(1) Cr
17	18.5	6.6	5.1	0.41	0.12	0.01	0.024	(0.003)	(0.02)	0.18	(2) Cr
18	(18.5)	(7)	5.0	0.15	0.12	0.04	0.014	(0.003)	(0.02)	0.20	2.0 Cu
19	(18.5)	(7)	5.0	0.19	0.10	0.02	0.019	(0.003)	(0.02)	0.13	(2) W
20	18.5	(7)	5.1	0.20	0.4	0.02	0.010	(0.003)	(0.02)	0.15	
21	18.5	7.5	4.6	0.40	0.16	<0.01	0.023	(0.003)	(0.02)	0.13	
22	18.7	(7)	4.6	0.08	0.06	0.02	0.004	(0.003)	(0.02)	0.06	0.36 Cb
23	(18.5)	(7)	5.1	0.17	0.13	(0.02)	0.018	(0.003)	(0.02)	0.95	
24	(18.5)	(20)	(1)	(0.5)	(0.1)	(0.02)	(0.02)	(0.003)	(0.02)		
25	(18.5)	(25)	(1)	(0.5)	(0.1)	(0.02)	(0.02)	(0.003)	(0.02)		
26	(18.5)	(30)	(1)	(0.5)	(0.1)	(0.02)	(0.02)	(0.003)	(0.02)		
27	(15)	(7)	(5)	(0.5)	(0.1)	(0.02)	(0.02)	(0.003)	(0.02)		(2) Cr
28	(13)	(7)	(5)	(0.5)	(0.1)	(0.02)	(0.02)	(0.003)	(0.02)		(5) Cr
29	(10)	(7)	(5)	(0.5)	(0.1)	(0.02)	(0.02)	(0.003)	(0.02)		(8) Cr
30	(16.5)	(9.5)	(7)	0.24	0.12	0.01	0.014	(0.003)	(0.02)	0.22	

¹ In each alloy in accordance with the present invention the balance of the composition is substantially iron. The alloys set forth in Table V contain less than about 0.15% manganese.

NOTE.—Numbers in parentheses indicate nominal percentages.

These alloys were made by melting nickel, chromium, iron and cobalt together in an air induction furnace under an argon blanket, deoxidizing the melt with carbon, deoxidizing with silico-manganese and calcium silicide, adding molybdenum, further deoxidizing the melt with aluminum, adding titanium to the melt, thereafter immediately prior to casting, adding to the melt boron and zirconium and finally casting the melt. Other auxiliary hardeners were added in the base charge or after calcium silicide. The resultant castings were forged at tempera-

40 alloys No. 3, 23 and 30, each of the alloys were solution treated for one hour at 1500° F. Alloy No. 3 was not solution treated after forging and prior to aging. Alloys 23 and 30 were solution treated at 1600° F. for one hour.

45 Some mechanical characteristics of some of the example of alloys in accordance with the present invention, the compositions of which were set forth in Table V, are set forth in Tables VI and VIA together with the aging conditions and the post aging heat treatment.

Table VI

No.	Aging temp., ° F.	Time, hours	Y.S., p.s.i.	U.T.S., p.s.i.	Elong., percent	Red. in area, percent	N.T.S.	
							0.5 inch bar, p.s.i.	0.3 inch bar, p.s.i.
1	900	3	242,000	254,000	11	57		381,000
2	800	1	219,000	231,000	14	59		350,000
3	900	3	256,000	260,000	10	58		396,000
4	900	3	266,000	275,000	11	56	356,000	374,000
5	900	3	249,000	261,000	11	48	333,000	377,000
6	900	3	246,000	257,000	11	51	309,000	359,000
7	900	3	248,000	260,000	11	50	306,000	342,000
8	900	3	218,000	227,000	12	56		341,000
9	900	3	280,000	285,000	10	43	291,000	
10	900	3	286,000	291,000	8	44	302,000	
11	900	3	281,000	292,000	10	48		380,000
12	900	3	256,000	262,000	14	53	319,000	
13	900	3	272,000	279,000	12	56	342,000	
14	1900	3	279,000	290,000	11	50		369,000
15	1900	3	261,000	281,000	10	52	275,000	
16	1900	3	283,000	287,000	10	52	316,000	
17	1900	3	272,000	285,000	10	48	314,000	
18	900	3	254,000	265,000	9	47	280,000	
19	900	3	256,000	268,000	11	38	277,000	
20	900	3	263,000	275,000	12	48	277,000	
21	900	3	248,000	256,000	12	54	362,000	374,000
22	900	3	237,000	244,000	11	51		347,000
23	900	3	250,000	260,000	8	24		186,000
30	900	3	313,000	321,000	4	20		198,000

¹ Refrigerated at -105° F. for 16 hours before aging. All baked 16 hours at 300° F.

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Table VIA

Alloy No.	Hardness as annealed (Rc)	Hardness as aged 3 hrs. at 960° F. (Rc)
24.....	28	45
25.....	30	50
26.....	29	56
27.....	27	46
28.....	31	47
29.....	33	43

The foregoing Tables V, VI and VIA show that in the aged condition, alloys in accordance with the present invention exhibit advantageous mechanical characteristics. The effect of the auxiliary hardeners upon the characteristics of the aged iron-base martensitic alloys of the present invention is clearly shown by a comparison of Examples 4, 8, 9, 10 and 11. Each of these alloys differs from the others primarily in titanium content. As the titanium content rises from about 0.1% to about 0.9%, the ductility gradually decreases. Increasing the titanium content from about 0.1% to about 0.4% increases the strength and notch toughness of the alloy. Further increases in titanium content above 0.4% results in increase in strength and some decrease in the notch toughness of the alloy. Examples 18, 19, 20 and 22 show that copper, tungsten, aluminum and columbium can advantageously be employed to supplement hardening. Example 17 is an example of an alloy which must be refrigerated and/or cold worked in order to induce a martensitic transformation. These alloys are advantageous in that after annealing they are relatively soft and can be cold worked with ease. Additionally, Example No. 17 exemplifies alloys of the present invention which possess substantial resistance to corrosive media.

Table VII illustrates the cooperative action of cobalt and molybdenum in the alloys of the present invention. Each of the alloys in Table VII contains about 18-20% nickel and about 0.02% carbon, 0.4% titanium, with the balance of the alloy being essentially iron.

Table VII

Alloy	Co, percent	Mo, percent	Hardness as aged 3 hrs. at 960° F. (Rc)
M.....	7	None	27
N.....	None	4.72	39
E.....	7.04	5.44	50

The base with neither cobalt nor molybdenum is 25-28 Rc after aging. Table VII shows that cobalt by itself scarcely affects the hardness of aged martensite while molybdenum has a definite hardening effect. An alloy within the present invention, containing both cobalt and molybdenum, exhibits an unusually large hardening response not attributable to either molybdenum or cobalt alone but rather to some synergistic interaction between these elements.

Alloys in accordance with the present invention, for example, alloys Nos. 2, 3 and 4 exhibit good impact resistance both at room temperature (R.T.) and at temperatures as low as -320° F. Table VIII which contains the results of Charpy V-notch tests shows the good impact resistance of the aged alloys of the present invention.

Table VIII

Alloy No.	Y.S.	Foot pounds at R.T.	Foot pounds at -320° F.
21.....	250,000	18.5	12.5

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In addition, aged alloys of the present invention having yield strengths of 250,000 p.s.i. are resistant to stress corrosion. Thus, beam loaded specimens loaded at 250,000 p.s.i. of an alloy having substantially the same composition as alloy No. 4 aged for three hours at 900° F. remained unbroken for 100 days in aerated artificial sea water when tested in accordance with the method described in J. P. Fraser, G. G. Eldredge and R. S. Treseder, "Laboratory and Field Methods for Quantitative Study of Sulfide Corrosion Cracking," Corrosion, 14, 517t, 1958. As mentioned hereinbefore, alloys of the present invention containing about 2% chromium have good resistance to atmospheric corrosion. Alloys of the present invention containing about 5% chromium are resistant to oxidation up to temperatures of the order of about 1000° F. It is to be noted that the chromium-containing alloys can be made so that they are either martensitic or austenitic as cooled from solution treatment.

Table IX shows typical nickel and chromium ranges for each of the embodiments of chromium-containing alloys.

Table IX

Chromium Level	Martensitic as cooled from solution temp., percent nickel	Retains austenite after cooling from solution temp., percent nickel
2% chromium alloy.....	15	18.5
5% chromium alloy.....	13	16.5

It is to be understood that alloys having a chromium level of 2% include alloys containing about 1.5% to about 2.5% chromium and likewise alloys having a 5% chromium level include alloys containing about 4.5% to about 5.5% chromium. All of the alloys of the present invention including chromium-free alloys, 2% chromium alloys, 5% chromium alloys and alloys containing other amounts of chromium up to 8% which are austenitic when cooled to room temperature after a solution treatment must be refrigerated and/or cold worked to induce transformation to martensite prior to aging.

Additional advantageous characteristics of the alloys of the present invention include the fact that the alloys are readily air melted and form a fluid, readily castable melt. The alloys can also be vacuum melted and/or degassed. Crucible refractory life when melting alloys of the present invention is substantial. Cast ingot surface is good. The alloys possess a low coefficient of expansion. Thus, alloy Example No. 2 after aging has an average linear coefficient of expansion of about 5.6×10^{-6} inch/inch/° F. over a temperature range of about 70° F. to about 900° F. Alloys of the present invention which are martensitic when cooled to room temperature after solution (annealing) treatment are readily cold worked and exhibit a low work-hardening rate. Thus, samples of alloy Example No. 1 which were cold worked prior to aging exhibited low increases in base hardness as shown by Table X.

Table X

Percent reduction in area by cold working	Hardness Rc
0	28
25	31
35	31.5
50	32
95	34

In addition, alloys of the present invention such as alloy Example Nos. 2, 3 and 4 (as aged to provide yield strengths of at least about 220,000 p.s.i. and even 266,000 p.s.i.) when tested for ductility and crack propagation tendencies at -80° F. (as described in the Welding Research, Supplement to The Welding Journal, May 1959, pages 209S to 218S), show excellent ductility and resistance to crack propagation.

The present invention is particularly applicable to the production of components which in service are highly stressed. Thus, the alloys of the present invention can be employed as highly stressed skin members for load bearing components, machine parts subject to stress, fasteners, e.g., bolts and the like, subject in use to high stresses, and plate members for structures subjected in use to high internal and/or external pressures. The chromium-containing alloy embodiments of the present invention which contain more than about 1.5% chromium are employable in uses where some resistance to atmospheric corrosion coupled with high strength is required. Alloys of the present invention containing more than about 4.5% chromium are resistant to scaling and are adapted to be employed for structures subjected in use to oxidizing and/or other mildly corrosive atmospheres at temperatures up to about 1000° F. and higher. It is to be noted that in this specification percentages and specific percentage values when used in connection with alloy compositions are percentages by weight of the total alloy.

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 age-hardenable, martensitic iron-base alloy containing interrelated and coacting amounts of molybdenum and cobalt as essential elements and consisting essentially of about 17% to 19% nickel, about 4.6% to 5.1% molybdenum, about 7% to 8% cobalt, about 0.01% to 0.03% carbon, about 0.3% to 0.5% titanium, up to 0.15% aluminum, up to about 0.1% silicon, up to about 0.1% manganese, up to about 0.1% boron, up to about 0.25% zirconium, up to about 0.1% calcium, and the balance essentially all iron, said martensitic iron-base alloy having a martensitic structure in both the aged and non-aged condition and said alloy having, after aging in the martensitic condition to obtain yield strength levels over 200,000 p.s.i. and up to at least 300,000 p.s.i., an unusually high combination of toughness, resistance to stress-corrosion cracking, resistance to crack propagation in the notched condition and weldability at such high strength levels.

2. An age-hardenable, martensitic iron-base alloy containing interrelated and coacting amounts of molybdenum and cobalt as essential elements and consisting essentially of about 10% to 23% nickel, about 1% to 10% molybdenum, about 2% to 20% cobalt with the amounts of molybdenum and cobalt being interrelated such that the hardener product determined as the product of the numerical values of the weight percentages of molybdenum and cobalt is from 10 to about 80, up to about 0.15% carbon, not more than 0.25% manganese, up to 5% chromium with the total nickel and chromium contents being less than 23%, up to about 0.1% boron, up to about 0.25% zirconium, up to about 0.1% calcium, up to 0.2% nitrogen, up to 6% copper, up to 7% tungsten, up to 6% vanadium, up to 3% columbium, up to 3% titanium, up to 3% aluminum, up to 1% beryllium and up to 0.2% silicon, the total amount of nitrogen, copper, tungsten, vanadium, columbium, titanium, aluminum, beryllium and silicon not exceeding about 7% in the aggregate,

and the balance essentially iron with the iron being present in an amount above 50%, said martensitic iron-base alloy having a martensitic structure in both the aged and non-aged condition and said alloy having, after aging in the martensitic condition to obtain yield strength levels over 200,000 p.s.i. and up to at least 300,000 p.s.i., an unusually high combination of toughness, resistance to stress-corrosion cracking, resistance to crack propagation in the notched condition and weldability at such high strength levels.

3. An age-hardened alloy having a composition as set forth in claim 2 and having a structure of aged martensite.

4. An age-hardenable, martensitic iron-base alloy containing interrelated and coacting amounts of molybdenum and cobalt as essential elements and consisting essentially of about 10% to 21.8% nickel, about 1% to 5.2% molybdenum, about 6.6% to 30% cobalt with the amounts of molybdenum and cobalt being interrelated such that the hardener product determined as the product of the numerical values of the weight percentages of molybdenum and cobalt is from 10 to about 50, about 0.008% to 0.028% carbon, not more than 0.25% manganese, up to 0.89% titanium, up to 5% chromium with the total nickel and chromium contents being less than 20.5% when chromium is present, up to about 0.003% boron, up to about 0.02% zirconium, up to about 0.4% aluminum, up to about 0.02% calcium, up to about 2% copper, up to about 2% tungsten, up to about 0.4% columbium, up to 1% silicon, and the balance essentially iron with the iron being present in an amount above 50%, said martensitic iron-base alloy having a martensitic structure in both the aged and non-aged condition and said alloy having, after aging in the martensitic condition to obtain yield strength levels over 200,000 p.s.i. and up to at least 300,000 p.s.i., an unusually high combination of toughness, resistance to stress-corrosion cracking, resistance to crack propagation in the notched condition and weldability at such high strength levels.

5. An age-hardenable, martensitic iron-base alloy containing interrelated and coacting amounts of molybdenum and cobalt as essential elements and consisting essentially of about 10% to 21.8% nickel, about 1% to 10% molybdenum, about 2% to 30% cobalt with the amounts of molybdenum and cobalt being interrelated such that the hardener product determined as the product of the numerical values of the weight percentages of molybdenum and cobalt is from 11 to 72, about 0.008% to 0.028% carbon, not more than 0.15% manganese, up to 0.9% titanium, up to 5% chromium with the total nickel and chromium contents being less than 20.5% when chromium is present, up to about 0.003% boron, up to about 0.02% zirconium, up to about 0.4% aluminum, up to about 0.02% calcium, up to about 2% copper, up to about 2% tungsten, up to about 0.4% columbium, up to 0.2% silicon, and the balance essentially iron with the iron being present in an amount above 50%, said martensitic iron-base alloy having a martensitic structure in both the aged and non-aged condition and said alloy having, after aging in the martensitic condition to obtain yield strength levels over 200,000 p.s.i. and up to at least 300,000 p.s.i., an unusually high combination of toughness, resistance to stress-corrosion cracking, resistance to crack propagation in the notched condition and weldability at such high strength levels.

6. An age-hardenable, martensitic iron-base alloy containing interrelated and coacting amounts of molybdenum and cobalt as essential elements and consisting essentially of about 10% to 23% nickel, about 1% to 6.5% molybdenum, about 2% to 20% cobalt with the amounts of molybdenum and cobalt being interrelated such that the hardener product determined as the product of the numerical values of the weight percentages of molybdenum and cobalt is about 25 to 55, up to about 0.1% carbon, not more than 0.25% manganese, up to about 5% chro-

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mium with the total nickel and chromium contents being less than 23%, about 0.2% to 1.5% titanium, and the balance essentially iron with the iron being present in an amount above 50%, said martensitic iron-base alloy having a martensitic structure in both the aged and non-aged condition and said alloy having, after aging in the martensitic condition to obtain yield strength levels over 200,000 p.s.i. and up to at least 300,000 p.s.i., an unusually high combination of toughness, resistance to stress-corrosion cracking, resistance to crack propagation in the notched condition and weldability at such high strength levels.

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