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AGE HARDENABLE NICKEL-IRON ALLOY FOR CRYOGENIC SERVICE

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ABSTRACT OF THE DISCLOSURE

Iron-base alloys having controlled expansivity, high strength and ductility in the age-hardened condition containing controlled amounts of nickel, columbium and titanium and the method for heat treating the same.

The present invention relates to iron-base alloys containing substantial amounts of nickel, e.g., 40% nickel, and, more particularly, to age-hardenable, weldable iron-nickel alloys and to structural products and articles made therefrom having characteristics of utility at low temperatures such as from room temperature down to cryogenic temperatures of minus 320° F., or even as low as minus 420° F., or lower.

Heretofore the art has endeavored to provide alloys having characteristics which would be satisfactory for structures that must endure use at low subzero temperatures, e.g., minus 320° F., and must withstand being subjected suddenly to wide fluctuations in temperature from room temperature down to low subzero temperatures. For instance, metal tanks, tubing and pump parts in structures for storing or transmitting liquefied gases at cryogenic temperatures are subjected to drastic temperature changes by being suddenly flooded with liquid nitrogen or liquid hydrogen. Among the problems to be overcome in providing an improved alloy for cryogenic service are needs for overcoming or avoiding such detrimental results of embrittlement, thermal shock or thermal fatigue cracking, metallurgical phase changes and excessive thermal expansion and contraction as commonly result when many of the heretofore known alloys are cooled to low subzero temperatures or cycled over wide ranges of low temperatures. Additionally, when metal products are to be provided for building large rugged structures that must bear heavy loads and survive hard industrial use in cryogenic service, sometimes requiring withstanding hard knocks and blows and other severe mechanical shock when at very low temperatures, as contrasted with use in small devices, for instance, for instrumentation purposes, it is very important that the alloy therefor be weldable with freedom from weld cracking and have good toughness including impact resistance and notch tensile strength at low subzero temperatures, in addition to having high strength and satisfactory ductility. Also needed for large scale production are other characteristics of advantage in commercial processing, such as good hot workability and cold workability, cleanliness in air melting and casting and homogeneous solidification characteristics for avoiding excessive segregation. For many uses it is also required that a

structural alloy be strengthenable by some means other than cold working, e.g. by an age-hardening heat treatment, in order that high strength can be obtained after welding. With regard to segregation difficulties, it should be noted that although alloying additions may be desirable for obtaining high strength in some alloys, iron-base alloys containing substantial amounts of nickel such as 35% to 45% nickel have been found particularly prone to develop detrimental segregation when alloying additions are incorporated therein and such difficulties are aggrevated with increase in the volume of an additional alloying element. Homogeneous solidification characteristics are, of course, very much needed where alloys must be produced in heavy sections for structural purposes.

Although many attempts were made to overcome the foregoing difficulties and other disadvantages, none, as far as I am aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that an alloy having a new and improved combination of characteristics including high strength, satisfactory ductility and toughness and low thermal expansion at room temperature and at low subzero temperatures when in the age-hardened condition and also having good commercial processing characteristics and good weldability with freedom from cracking is obtained with a new age-hardenable iron-nickel alloy composition containing specially controlled and balanced proportions of columbium and titanium, with or without tantalum.

It is an object of the present invention to provide a new age-hardenable iron-nickel alloy having in the age-hardened condition an enhanced combination of characteristics at low temperatures of from room temperature down to minus 320° F. and lower.

Another object of the invention is to provide wrought age-hardenable iron-nickel alloy sheet, bar, tubing, plate, billets, rod and like products characterized by good weldability enabling the alloy to be welded and age-hardened thereafter without cracking and by other characteristics of utility for use in cryogenic service.

It is a further object of the invention to provide an age-hardened iron-nickel alloy article characterized by high strength and toughness, metallurgical stability and low thermal expansion at temperatures from room temperature down to minus 320° F.

Still another object of the invention is to provide a new process for obtaining an age-hardened iron-nickel alloy having high strength and impact resistance and low thermal expansion at temperatures as low as minus 320° F. and lower.

The invention further contemplates weldments, welded structures and welding materials for cryogenic service.

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

Generally speaking, the present invention is directed to an age-hardenable iron-base alloy containing specially controlled amounts of nickel, columbium and titanium resulting in a special combination of characteristics providing new and improved utility for making structures and components which are subjected to cryogenic temperatures when in use. The alloy can also contain small amounts of tantalum, such as are often associated with columbium obtained from commercial sources. These

small amounts of tantalum are generally up to about 20%, e.g., about 1% to 20%, or, more usually, about 10% to 15%, of the total columbium plus tantalum in the alloy. In weight percentages the new iron-base alloy, i.e., alloy having a greater percentage of iron than of any other single element in the alloy, contains 36% to 42% nickel, advantageously 38% to 42% nickel, columbium with or without small amounts of tantalum in percentages such that the total of the per cent columbium plus one-half the percent of tantalum is 1.8% to about 4% of the alloy, 1% to about 2% titanium, the proportions of nickel, columbium, titanium and any tantalum present being additionally controlled to be in accordance with the alloy-balance relationship

Percent Ni-percent (Cb-½ (percent Ta)-percent Ti=33% to 36.4%

up to about 0.5% aluminum, up to about 0.1% carbon, advantageously not more than 0.05% carbon, with balance essentially iron. Small amounts of impurities, auxiliary deoxidizers, malleabilizers, etc., which may be present along with the balance of iron include up to about 1% cobalt, up to about 0.5% silicon and up to about 0.5% manganese. Chromium, molybdenum and tungsten are undesirable impurities and any amounts thereof in the alloy should not exceed 0.5% each. Moreover, the total of all elements other than iron, nickel, columbium, titanium and any tantalum in the alloy does not exceed about 1.5% and is advantageously not above 1%. The new alloy can be heat treated to have at room temperature and at low subzero temperatures a highly useful combination of characteristics including high tensile strength, toughness, very satisfactory ductility and metallurgical stability and low thermal expansion, e.g., yield strength of at least 90,000 pounds per square inch (p.s.i.) and up to 140,000 p.s.i. and higher, notch tensile strength at least equal to yield strength at the same temperature and an average coefficient of thermal expansion (from minus 320° F. to plus 70° F.) not greater than about 2.0, e.g., 1.5 to 1.9, times 10 to the minus six power per degree Fahrenheit ($\times 10^{-6}$/° F.). The thermal expansion coefficient is substantially constant (linear) from minus 320° F. to 70° F. Particularly important processing characteristics which contribute to utility for making structural products and welded structures include clean air-meltability and castability, homogeneous solidification characteristics without serious segregation tendencies, excellent hot workablity and cold workability and good weldability with high resistance to weld cracking even when welded under conditions of severe restraint and when age hardened after welding.

Heat treatment for strengthening the alloy of the invention when in relatively soft conditions, such as present after annealing, hot working or moderate cold work, comprises age hardening by heating the alloy at about 1200° F. to about 1375° F. for 1 hour to about 24 hours. Air cooling from age hardening or annealing temperatures is satisfactory. Age hardening usually lowers the thermal expansion coefficient of the alloy although the coefficient is near and may be less than 2×10^{-6}/° F. when the alloy is in hot worked, cold worked or even annealed conditions. An annealing treatment of heating at about 1800° F. to about 2000° F. for about ½ hour to about 2 hours, applied prior to age hardening the alloy, is generally beneficial for obtaining good characteristics in the age hardened condition, particularly for obtaining good toughness and ductility and especially when the alloy has been previously cold worked. For providing the alloy in an advantageous age hardened condition characterized at minus 320° F. by high impact strength of at least about 20 foot-pounds (ft.-lbs.) impact energy as determined with the Charpy V-notch specimen, it is advantageous to anneal the alloy from the hot worked condition, air cool to room temperature, and thereafter age harden the alloy for two to sixteen hours at 1200° F. to 1325° F., with subsequent air cooling.

The composition of the alloy is closely controlled in accordance with the foregoing compositional ranges and alloy-balance relationship for percentages of nickel, columbium, titanium and tantalum in the alloy in order to obtain all the good results referred to hereinbefore as provided by the invention. (All alloy compositional percentages referred to herein are by weight.) The titanium content of the alloy is at least 1% and the sum of the percentage of columbium present plus one-half the percentage of any tantalum present (referred to hereinafter as the columbium plus one-half tantalum percentage) is at least 1.8% in order that the alloy be characterized in the age-hardened condition by high yield strength of at least 90,000 p.s.i. at room temperature. (Yield strength referred to herein is determined by the 0.2% offset method.) The titanium content of the alloy is maintained not greater than 2%, advantageously only up to 1.8%, and greater amounts of titanium are avoided in order to insure having homogeneous solidification characteristics, satisfactory cleanliness in air melted and cast alloy products, good toughness and ductility at low temperatures and freedom from weld cracking, including post-weld cracking when age-hardened. Amounts of columbium or tantalum individually greater than 4% would give rise to serious segregation problems and thus are not present in the alloy of the present invention. Moreover, high percentages of columbium plus one-half tantalum in excess of about 4% would also be detrimental to the toughness and crack resistance of the alloy when age-hardened. When small amounts of tantalum are present, the alloy usually contains about 1.6% to 3.9% columbium and about 0.1% to 0.8% tantalum. Control of the composition according to the alloy-balance relationship and the nickel range of 36% to 42% is especially needed for obtaining the low thermal expansion coefficient which characterizes the alloy in the age-hardened condition and is thus beneficial for avoiding thermal shock and thermal fatigue cracking and avoiding other difficulties arising from high differential expansion of unevenly cooled or heated articles and structures in cryogenic service. As will be pointed out in more detail hereinafter, even small, and perhaps seemingly minor, departures from the herein required nickel range and/or alloy-balance relationship can result in substantial unsatisfactory increases in the thermal expansion coefficient. Moreover, the good metallurgical stability of the alloy, which remains austenitic and does not form martensite when cooled to low subzero temperatures, thus avoiding detrimental changes in dimensions and characteristics, would be impaired if the nickel content were decreased excessively low or if the proportion of elements from the hardener metal group titanium, columbium and tantalum were excessively increased. Carbon in amounts greater than 0.1% detrimentally detracts from the strength of the alloy when heat treated for age-hardening and interferes with the alloy-balance relationship of the elements in the new alloy. Chromium, molybdenum, aluminum and/or cobalt are disadvantageous to obtaining high tensile strength in the present alloy.

In carrying the invention into practice it is advantageous for obtaining an enhanced combination of toughness, crack resistance and strength, including very high yield strength of at least 125,000 p.s.i. at room temperature in the age-hardened condition, along with obtaining other advantageous characteristics, to further control the alloy composition to contain 1.3% to 1.8% titanium, 2.7% to 3.5% columbium or columbium-plus-one-half tantalum, 37% to 41% nickel, up to 0.05% carbon, up to 0.5% aluminum, e.g., about 0.15% to 0.3% aluminum, and the balance essentially iron. Controlling the amounts of titanium, columbium and any tantalum in the alloy to be in proportions such that the percentage of columbium plus one-half tantalum is about 2, e.g., 1.7 to 2.3, times the percentage of titanium in the alloy is beneficial for

minimizing post-weld parent-metal cracking and segregation difficulties at any required total hardener content for the alloy. Stated more algebraically, the immediately foregoing advantageous compositional columbium-tantalum-titanium relationship for the alloy is:

$$\frac{\text{Percent Cb}+1/2\ (\text{percent Ta})}{\text{Percent Ti}}=1.7 \text{ to } 2.3$$

Portions of the alloy can be welded together autogenously or with matching filler wire made of the new alloy. Inert gas protection, e.g., with argon or helium, is recommended for welding. Where the portions to be welded are severely restrained it is advantageous to have the alloy in a relatively soft condition, e.g., the annealed condition, when being welded in order to avoid post-weld cracking when age-hardening the heat effected zone. In the absence of severe restraint the alloy can be welded in the age-hardened condition and re-aged without cracking, inasmuch as the alloy has at least moderately good crack resistance in the age-hardened condition. In situations where furnace heat treatment for two hours or more is difficult or impossible, reasonably good age-hardening can be achieved by heating for about one hour at about 1375° 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 of the invention, the following illustrative examples are given.

Chemical compositions of alloys 1 through 4, which are in accordance with the invention, are set forth in Table I.

TABLE I

Alloy No.	Ni, percent	Cb+Ta[1], percent	Ti, percent	C, percent	Al, percent	Si, percent	Mn, percent	Fe[2]
1	39.14	3.91	1.46	.01	.18	.01	.01	Balance.
2	40.27	2.89	1.51	.03	.19	.05	<.01	Do.
3	38.00	2.89	1.47	.03	.18	.10	<.01	Do.
4	39.56	2.90	1.46	.01	.22	.12	.22	Do.

Alloys 1, 2 and 3 were vacuum induction melted and cast into ingots and the metal thereof was satisfactorily clean and homogeneous without detrimental segregation. Alloy 4 was induction melted and cast in air and was also satisfactorily clean and free from harmful oxides, slag, dirt, etc. Good solidification characteristics of the alloy were further confirmed by obtaining satisfactory homogeneity and freedom from segregation with alloy 4 in ingots which were as large as 18 inches square by 48 inches long. The alloy had excellent hot workability when forged and rolled at about 2150° F.

Yield strengths at 0.2% offset (Y.S.) and ultimate tensile strengths (U.T.S.) in units of one thousand pounds per square inch (K s.i.), and also percent elongation (Elong., percent) resulting from room temperature tensile tests of wrought alloys 1 through 4 in the age hardened condition are set foth in Table II. For obtaining the results in Table II, tensile specimens of alloys 1, 2 and 3 were taken from 2-inch square bar stock in orientations transverse to the length of the bars and the tensile specimen of alloy 4, from hot rolled sheet, was taken with the specimen length oriented transversely to the direction of rolling. Heat treatments of the specimens are indicated by heat treatment numbers (H.T. No.) shown in Table II and are set forth in Table III. In all instances of annealing or age hardening referred to herein in connection with examples of the invention, specimens were air cooled after annealing or aging unless otherwise noted. Average thermal coefficients of expansion (C.O.E.) from minus 320° F. to 70° F. obtained with alloys 1 through 4 in the age hardened condition are also included in Table II, along with heat treatments pertaining thereto.

TABLE II

	Heat Treatment No.	Y.S., K s.i.	U.T.S., K s.i.	Elong., percent	C.O.E. (in./in./° F.)
Alloy No.:					
1	1	181.0	193.5	8	1.95×10^{-6}
2	1	149.5	169.0	9	[1] 1.62×10^{-6}
3	2	13.95	166.0	13	1.74×10^{-6}
4	4	147.5	169.5	16	1.68×10^{-6}

After H.T.-2 instead of H.T.-1.

TABLE III

	Anneal	Aging treatment
H.T. No.:		
1	1 hour at 1,950° F	8 hours at 1,300° F., F.C.+A.C.
2	do	8 hours at 1,375° F., F.C.+A.C.
3	do	8 hours at 1,350° F., F.C.+A.C.
4	½ hour at 1,800° F	8 hours at 1,325° F., F.C.+A.C.
5	do	8 hours at 1,275° F., F.C.+A.C.
6	do	8 hours at 1,375° F., F.C.+A.C.
7	½ hour at 1,900° F	8 hours at 1,275° F., F.C.+A.C.
8	None	8 hours at 1,250° F., F.C.+A.C.
9	½ hour at 1,800° F	8 hours at 1,225° F.+A.C.
10	do	16 hours at 1,200° F.+A.C.
11	do	16 hours at 1,225° F.+A.C.
12	do	8 hours at 1,200° F.+A.C.
13	do	8 hours at 1,325° F.+A.C.
14	None	8 hours at 1,225° F.+A.C.

NOTE.—F.C.+A.C.=Furnace Cooled at 100° F. per hour (hr.) to 1,200° F., held 8 hours at 1,200° F., and then air cooled.

Results set forth in Table II illustrate high yield strengths of at least 125,000 p.s.i. and higher in combination with high ultimate tensile strength and satisfactory ductility which were obtained with advanatgeous embodiments contemplated herein containing at least 1.4% titanium and at least 2.5% columbium plus ½ tantalum along with amounts of nickel, iron and other elements in accordance with the invention. Furthermore, results in Table II, when viewed in conjunction with the heat treatments in Table III, illustrated that the high strength and low thermal expansion coefficient which characterize the alloy are obtainable with age hardening treatments over a range of temperatures from 1200° F. to 1375° F., which is highly desirable where an alloy is to be used for large commercially produced products. The thermal expansion tests of alloys 1 through 4 also confirmed that the thermal expansion coefficient of the new alloy is linear over the low temperature range tested. Furthermore, in these tests and in additional tests, including cycling alloys 4 eight times from room temperature to minus 320° F., it was confirmed that the alloy is metallurgically stable throughout this temperature range, inasmuch as the alloy did not undergo phase changes or other metallurgical transformations and the thermal expansion coefficient results were within about 5% of the norm without consistent upward or lower trend during the repeated cycling. Tests of alloy 4 when in the annealed condition obtained by heating ½ hour at 1800° F. showed room temperature characteristics of 50,000 p.s.i. yield strength, 92,300 p.s.i. ultimate tensile strength and 47% elongation and also showed an average thermal expansion coefficient of about 2×10^{-6}/° F., e.g., 2.05, from minus 320° F. to 70° F. Inasmuch as age hardening lowers the expansion coefficient of the present alloy, results clearly show that a low average thermal expansion coefficient of less than 2×10^{-6}/° F. at subzero temperatures is readily obtainable with the new alloy and that in regard to obtaining such a low

coefficient the alloy has a good tolerance for production variations in heat treatment within the scope of the invention.

Additional test results at room temperature, minus 320° F. and minus 423° F. which illustrates highly satisfactory characteristics of alloy 4 when produced in a variety of wrought product forms including hot rolled sheet, cold rolled sheet, hot forged bar and hot extruded tubing and when heat treated over a range of times and temperatures in accordance with the invention are set forth in Table IV. Sheet metal specimens, including smooth sided specimens, notch tensile strength (N.T.S.) specimens and Charpy V-notch impact specimens were taken transverse to the direction of rolling; bar specimens were taken parallel to the length of the bar and; the test bars from the tube, which was of 6-inch outside diameter with a one-inch wall, were taken both circumferentially and longitudinally as indicated in Table IV. Charpy impact specimens were half size specimens since the sheet was only about ¼ inch or less in thickness. Impact specimens from bar stock were full size. Notch tensile specimens from the sheet had edge notches with stress concentration factors (K_t) of 20. Bar stock was notch tested with a round bar notched to $K_t=10$. Heat treatments were as indicated in Table IV and set forth in Table III. In instances where Table III shows no annealing treatment was applied, the alloy was aged directly from the as-rolled or as-extruded condition.

TABLE IV

Specimen No.	Product	Heat treatment No.	Test temp., °F.	Y.S., K s.i..	U.T.S., K s.i.	Elong., percent	N.T.S., K s.i.	Impact, ft.-lb.
1	Hot Rolled Sheet	8	R.T.	159.0	179.0	10		
2	do	5	R.T.	141.0	175.5	16		
3	do	6	R.T.	136.5	162.0	16		
4	do	7	R.T.	145.0	175.0	15		
5	Cold Rolled Sheet	9	R.T.	139.5	167.0	20	163.0	[1] 21
6	do	9	−320	172.0	223.5	23	196.0	[1] 13
7	do	9	−423					[1] 12.5
8	do	10	R.T.	137.5	174.0	17	171.8	[1] 17
9	do	10	−320	176.5	236.0	22	190.0	[1] 11
10	do	10	−423					[1] 11
11	do	11	R.T.	154.0	175.0	16	173.0	[1] 14
12	do	11	−320	190.5	226.0	11	202.5	[1] 11
13	do	11	−423					[1] 10.5
14	Hot Forged Bar	9	R.T.	129.5	178.5	19	245	
15	do	9	−320	194.0	238.5	20	312.0	
16	do	12	−320					24
17	do	13	−320					24
	Extruded Tubing							
18	Longitudinal	14	R.T.	128.0	163.0	16		
19	Circumferential	14	R.T.	131.0	166.0	15		
20	Longitudinal	9	R.T.	121.5	163.0	17		
21	Circumferential	9	R.T.	129.0	164.5	17		

[1] Results from tests of half size Charpy V-Notch specimens taken according to Federal Test Method 151a.

Among the many good results illustrated in Table IV it is to be particularly noted that all the notch tensile strength results show notch strength higher than yield strength at the same temperatures, which results are particularly good in view of being obtained with edge-notched specimens taken transversely from cold rolled sheet, especially when tested at minus 320° F. Also of note are the isotropic ductility characteristics illustrated by the results from the longitudinally and transversely oriented specimens of the tube made of the new alloy. It will be understood that the impact test results pertaining to the cold rolled and age hardened sheet illustrate high impact resistance equivalent to at least about 20 ft.-lbs. and higher if obtained with full size Charpy V-notch specimens inasmuch as the present results were obtained with half size specimens.

Good weldability and high weld-crack resistance of the new alloy was confirmed by tests including the following tests made in welding tube and cold rolled sheet products of the new alloy. The ends of two pieces of cold drawn tube (of about 5-inch outside diameter with 0.14 inch wall thickness) of alloy 4 in the age hardened condition were butt-welded together with matching filler using the tungsten-argon inert arc welding method. The resulting tube weldment was age hardened by heat treatment. Subsequently metallurgical examination showed no cracks in the weld metal or parent metal. For additional tests, of a type sometimes referred to as a patch weld test, circular cutouts about 2 inches in diameter were made in three cold rolled sheet (0.062 inch thick) specimens of alloy 4, two of the specimens being in the annealed condition and the other in the as-cold rolled condition. Each of the three specimens having the open circle were welded at their outer edges to a heavy metal plate (strong-back). The cutout circle pieces were then replaced in the circular openings and welded back into their respective parent sheets by autogenous tungsten-argon arc welding. The welded specimens were then given age-hardening heat treatments of 8 hours to 16 hours at 1225° F. and metallurgical examination thereafter showed no cracking of the alloy. In view of the foregoing tests, it is apparent that the new age hardenable alloy has very good resistance to weld cracking and post-weld cracking and is highly satisfactory for making age hardenable weldments that can be age hardened to obtain high strength across the weld without cracking upon heat treatment after welding.

In order to further illustrate advantages of the new alloy composition, particularly in providing the low expansion characteristic which is of great benefit for overcoming thermal expansion problems otherwise existent in cryogenic service, chemical compositions and average thermal expansion coefficients (from minus 320° F. to 70° F.) of alloys A, B and C, which are not in accordance with the invention, are set forth in Table V hereinafter. Alloys A, B and C were vacuum melted, cast and forged, and thermal expansion specimens were taken therefrom by the same techniques employed for obtaining the thermal expansion specimens for the results in Table II pertaining to alloys 1, 2 and 3. Heat treatments were as indicated in Table V and set forth in Table III.

TABLE V

Alloy	Ni, percent	Cb+Ta [1], percent	Ti, percent	Al, percent	C, percent	Fe [3]	H.T. No.	C.O.E. ×10⁻⁶/° F.
A	43.61	3.94	1.48	0.17	0.01	Balance	1	2.61
B	35.98	2.98	1.46	0.19	0.03	do	2	3.09
C	41.07	2.98	1.46	0.19	0.01	Balance [2]	2	3.69

[1] Contains tantalum in amount about ⅛ to 1/10 of total columbium plus tantalum content.
[2] Also contains 6.48% cobalt.
[3] Balance includes about 0.04% copper, up to about 0.01% silican, up to about 0.01% manganese and about 0.008% sulfur.

The composition of each of alloys A, B and C is outside the compositional requirements for the alloy of the invention in at least one respect. Thus, the nickel content of alloy A is too high; neither alloy A nor alloy B satisfy the requisite alloy-balance relationship whereby

Percent Ni-percent Cb-½ (percent Ta)-percent Ti=33% to 36.4%

in alloys of the invention; and the cobalt content of alloy C is too high, inasmuch as alloy C contains 6.48% cobalt whereas the alloy of the invention contains not more than 1% cobalt. Table V also shows that alloys A, B and C when in the age hardened conditions indicated in the table have unsatisfactory high thermal expansion coefficients which are very substantially greater than 2×10^{-6}/° F. and thus the compositions thereof are not satisfactory for achieving all the objects of the present invention.

In view of the high strength, notch toughness, impact reistance, low thermal expansion and other useful characteristics obtainable at room temperature and at low subzero temperatures with the new alloy described herein, and the good weldability thereof, the present invention is particularly applicable to providing weldable, age hardenable wrought products, including tubing, plate, sheet, rod and wire, useful in making welded structures for storing, transmitting and processing liquefied gases at subzero temperatures and for other cryogenic service. Further, the invention is applicable for providing age hardenable and age hardened pipes, tubing, impellers and other pump parts, valve parts including yokes, bonnets, gates and valve bodies, storage tanks, pressure vessels, shafts, bearings, nozzles and other articles including weldments for service at low temperatures from room temperature down to cryogenic temperatures as low as minus 320° F., or minus 423° F., and lower.

While the present invention has been described as including alloys containing columbium and alloys containing columbium and small amounts of tantalum, the scope of the invention also includes alloys wherein tantalum replaces columbium in whole or in part but does not exceed 4% of the alloy. Thus, the invention provides alloys containing up to about 4% columbium and/or up to about 4% tantalum in proportions such that the total of the columbium plus one-half the percent tantalum is 1.8% to about 4% of the alloy, along with nickel, titanium and iron in the aforedescribed proportions and amounts such that the total of nickel, columbium, titanium, iron and any tantalum in the alloy is at least about 98.5%. However, the presence of tantalum in large amounts greater than 1%, e.g., 2% to 4%, is disadvantageous inasmuch as such large amounts of tantalum usually give rise to segregation difficulties nad may require difficult care in melting and casting, e.g., possibly requiring frequent stirring and/or forced-cooling solidification if homogeneous alloys are required.

I claim:

1. An alloy consisting essentially of 36% to 42% nickel, columbium and tantalum in amounts such that the total of the percent of columbium plus one-half the percent tantalum is from 1.8% to about 4% of the alloy, with the weight of tantalum being from about 1% to about 20% of the total weight of columbium plus tantalum in the alloy, 1% to 2% titanium, with the percentages of nickel, columbium, tantalum and titanium being correlated in accordance with the relationship

Percent Ni-percent Cb-½ (percent Ta)-percent Ti=33% to 36.4%

up to about 0.1% carbon, up to about 1% cobalt, up to about 0.5% aluminum, up to about 0.5% silicon, up to about 0.5% manganese with the balance essentially iron.

2. Wrought age-hardenable products including sheet, plate, strip tubing, bar, and wire made of the alloy set forth in claim 1.

3. An alloy having the composition set forth in claim 1 and being in the age-hardened condition characterized at low temperatures from minus 320° F. up to room temperature by yield strength of at least 90,000 p.s.i., notch tensile strength at least equal to the yield strength at the same temperature and an average thermal coefficient of expansion not greater than 2.0×10^{-6} per degree F.

4. An alloy as set forth in claim **1** containing 38% to 42% nickel.

5. An alloy as set forth in claim **1** containing 1.6% to about 3.9% columbium and about 0.1% to about 0.8% tantalum.

6. An alloy as set forth in claim **1** wherein the total of the percent columbium plus one-half the percent tantalum is at least 2.5% and the titanium content is at least 1.4%.

7. An alloy as set forth in claim **1** wherein the sum of the percent columbium plus one-half the percent tantalum is from 1.7 to 2.3 times the percent titanium in the alloy.

8. An alloy as set forth in claim **1** containing 37% to 41% nickel, columbium and tantalum in amounts such that the total of the percent columbium plus one-half the percent tantalum is 2.7% to 3.5% of the alloy, 1.3% to 1.8% titanium and up to 0.05% carbon.

9. Wrought age-hardenable products including sheet, plate, strip, tubing, bar, and wire made of the alloy set forth in claim **8**.

10. An alloy having the composition set forth in claim **8** and being in the age-hardened condition characterized at low temperatures from minus 320° F. up to room temperature by yield strength of at least 125,000 p.s.i., notch tensile strength at least equal to the yield strength at the same temperature and an average thermal coefficient of expansion not greater than 2.0×10^{-6} per ° F.

11. An alloy consisting essentially of 36% to 42% nickel, up to about 4% columbium, up to about 4% tantalum, with the total of the percent columbium plus one-half the percent tantalum being 1.8% to about 4% of the alloy, 1% to 2% titanium, with the percentages of nickel, columbium, tantalum and titanium being correlated in accordance with the relationship

Percent Ni-percent Cb-½ (percent Ta)-percent Ti=33% to 36.4%

up to about 0.1% carbon, up to about 1% cobalt, up to about 0.5% aluminum, up to about 0.5% silicon, up to about 0.5% manganese with the balance essentially iron.

12. An alloy as set forth in claim **11** containing at least 1.8% columbium.

13. An alloy as set forth in claim **11** containing 2.7% to 3.5% columbium.

14. An alloy as set forth in claim **11** containing 37% to 41% nickel, 2.7% to 3.5% columbium, 1.3% to 1.8% titanium and up to 0.05% carbon.

15. A process for obtaining an age hardened alloy characterized at low temperatures from minus 320° F. up to room temperature by yield strength of at least 90,000 p.s.i., notch tensile strength at least equal to the yield strength at the same temperature and an average thermal coefficient of expansion not greater than 2.0×16^{-6} per ° F. comprising providing an alloy consisting essentially of 36% to 42% nickel, up to about 4% columbium, up to about 4% tantalum, with the total of the percent columbium plus one-half the percent tantalum being 1.8% to about 4% of the alloy, 1% to 2% titanium, with the percentages of nickel, columbium, tantalum and titanium being correlated in accordance with the relationship

Percent Ni-percent Cb-½ (percent Ta)-percent Ti=33% to 36.4%

up to about 0.1% carbon, up to about 1% cobalt, up to about 0.5% aluminum, up to about 0.5% silicon, up to about 0.5% manganese with the balance essentially iron and heating said alloy for about 1 hour to about 24 hours at 1200° F. to 1375° F. and thereafter air cooling

the alloy, to thereby obtain the alloy in the age hardened condition having the aforesaid characteristics.

16. A process as set forth in claim **15** wherein the alloy contains at least 1.8% columbium.

17. A process as set forth in claim **15** wherein the alloy contains 2.7% to 3.5% columbium.

18. A process as set forth in claim **15** wherein the alloy consists essentially of 36% to 42% nickel, columbium and tantalum in proportions such that the weight of tantalum in the alloy is about 1% to about 20% of the total weight of columbium plus tantatum in the alloy and with the sum of the percent columbium plus one-half the percent tantalum being 1.8% to 4% of the alloy, 1% to 2% titanium, up to 0.1% carbon, up to 0.5% aluminum and the balance essentially iron.

19. A process as set forth in claim **15** wherein the alloy obtained has a yield strength of at least 125,000

p.s.i. and wherein the alloy contains 37% to 41% nickel, columbium and tantalum in amounts such that the total of the percent columbium plus one-half the percent tantalum is 2.7% to 3.5% of the alloy, 1.3% to 1.8% titanium and up to 0.05% carbon.

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RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

75—124, 128, 170, 171; 148—31, 142

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,514,284 Dated May 26, 1970

Inventor(s) HERBERT L. EISELSTEIN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 15, for "Percent Ni-percent (Cb-1/2 (percent Ta)- percent Ti=33% to 36.4%" read --Percent Ni - percent Cb - 1/2(percent Ta) - percent Ti = 33% to 36.4%--.

Column 5, Table I, in line with Alloy No. 3, under Si percent, for ".10" read --.01--; lines 41 and 42, insert footnotes to Table I -- 1-Contains tantalum in an amount about 1/10 to 1/5 of total columbium plus tantalum contents. 2-Balance includes about 0.04% copper and about 0.008% sulfur.--;

Column 6, Table II, in line with Alloy No. 3, under Y.S., for "13.95" read --139.5--.

Columns 7 & 8, Table IV, in line with Specimen No. 5, under N.T.S. for "163.0" read --163.9--.

Column 8, line 9, for "Subsequently" read --Subsequent--; line 76, for "silican" read --silicon--.

Column 9, line 51, for "nad" read --and--.

Column 10, line 59, (line 6 of claim 15), for "2.0×16^{-6}" read --2.0×10^{-6}--.

Signed and sealed this 30th day of November 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents