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NICKEL-CHROMIUM ALLOY

Filed March 14, 1961

2 Sheets-Sheet 1

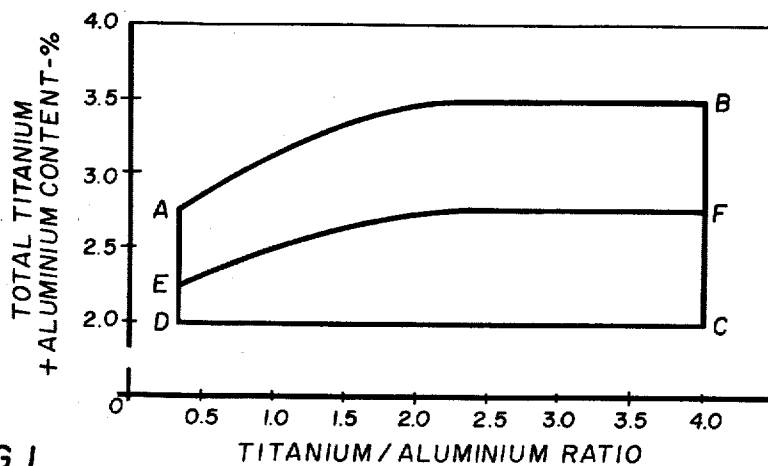


FIG. 1

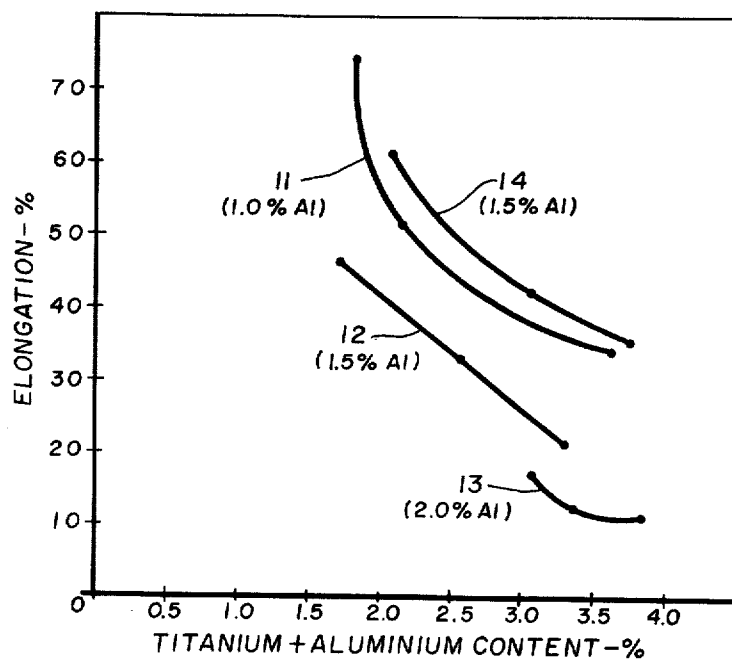


FIG. 2

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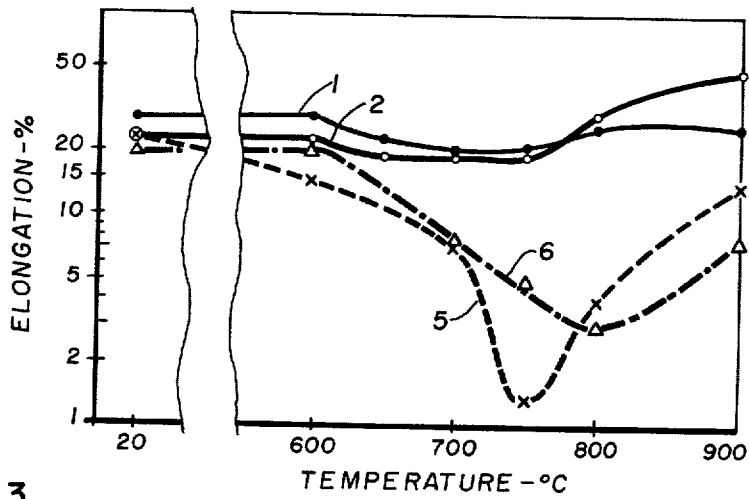


FIG. 3

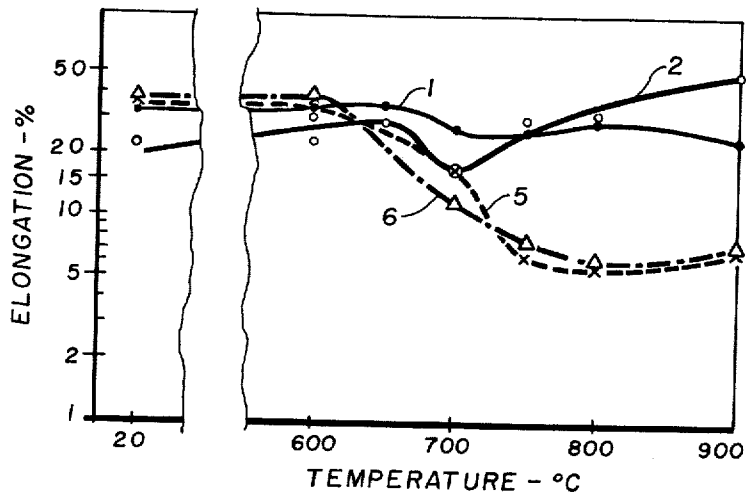


FIG. 4

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NICKEL-CHROMIUM ALLOY

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9 Claims. (Cl. 75-171)

The present invention relates to nickel-chromium alloys and, more particularly, to weldable nickel-chromium alloys including nickel-chromium-iron alloys.

Nickel-chromium and nickel-chromium-iron base heat- and creep-resistant alloys containing titanium and aluminum to provide a precipitable phase of the $Ni_3(Ti, Al)$ type and also containing molybdenum are now well known. In most alloys of this type, however, it is found that the ductility decreases with increasing temperature and is generally at a minimum in the temperature range 700° C.-850° C. While these alloys in the form of thin sheet not more than about 1/8 inch thick can be welded under mild conditions and without restraint, the ductility of the welded joints decreases to an even greater extent in this temperature range, so that the elongation of the welded joints in high-temperature tensile tests may fall below the commercially desirable minimum of 5% or 7%. To overcome this loss of ductility it has hitherto been necessary to apply high-temperature heat treatments after welding. The difficulty in fabricating components by welding is particularly acute when the alloys are in sheet form and are used to make components such as jet-pipes for aircraft gas turbines, since at the high temperatures that must be used for the heat treatments the components tend to collapse or distort. Moreover, it is often difficult or impossible to apply a post-weld heat treatment when the components are repaired in service under conditions where large-scale heat-treatment facilities are not available. Although attempts were made to overcome the foregoing difficulties and other disadvantages, 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 means of a specially restricted alloy composition it is now possible to provide alloy structural elements which are readily weldable.

It is an object of the present invention to provide a novel weldable alloy.

Another object of the invention is to provide a novel welding process.

The invention also contemplates providing novel welded structures.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which:

FIGURE 1 is a graph illustrating the relationship between titanium and aluminum contents which are characteristic of alloys in accordance with the present invention;

FIG. 2 graphically depicts the effect of aluminum and titanium contents on the elongation of alloys;

FIG. 3 shows graphically the elongation characteristics at various temperatures of welded alloys set forth in the specification; and

FIG. 4 graphically illustrates the elongation characteristics at various temperatures of unwelded alloys set forth in the specification.

Generally speaking, the present invention contemplates providing heat- and creep-resistant alloys that largely retain their strength and ductility after welding with a simple or no post-weld heat treatment. This object is achieved by adding critical amounts of the elements car-

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bon, titanium, aluminum, molybdenum, boron and zirconium to nickel-chromium or nickel-chromium-iron base alloys containing about 20% chromium.

Alloys according to the invention contain in percent by weight chromium about 15% to 25% and preferably 16% to 20%, iron 0% to 45%, carbon about 0.04% to 0.15%, titanium about 0.7% to 2.5%, aluminum about 0.7% to 1.5%, molybdenum about 3% to 6%, and preferably 3.5% to 4.5%, boron 0.01% to 0.009%, zirconium 0.01% to 0.1%, silicon 0% to about 0.5%, manganese 0% to about 0.5%, cobalt 0% to about 1%, the balance (apart from impurities in an amount not exceeding 0.5%) being nickel in an amount not less than 35%. In addition, the total titanium and aluminum content is 2% to 3.5%, the ratio titanium/aluminum is 0.5 to 4 and the Ti+Al content is so correlated with the Ti/Al ratio that the alloy lies within the area ABCDA in FIGURE 1 of the accompanying drawing.

It is found that within these preferred ranges of composition little or no formation of sigma phase occurs on welding or on exposure in service to temperatures of 600° C.-800° C. for times up to about 1000 hours.

The exact proportions of each of the added elements is of great importance in achieving satisfactory properties in the welded alloy.

The carbon content should be at least 0.04% in order to obtain an acceptable level of ductility. However, at carbon contents higher than 0.15%, free carbides are formed in the alloy during working that reduce the creep resistance at elevated temperatures and also make it difficult to form the alloy into sheet or shape the sheet into components. Prolonged exposure to temperatures above 600° C. leads to precipitation of carbides at carbon contents of less than 0.15%, and at carbon contents of above 0.08% these carbides tend to be deposited at the grain boundaries in a form that may ultimately lead to embrittlement of the alloys, after say 500 hours or more. This effect is particularly pronounced at temperatures of less than 700° C. For applications involving very long periods of heating at such temperatures carbon contents in the range of 0.05% to 0.08% are therefore preferred. On the other hand for short-time applications in which to 0.12% may advantageously be used.

The greatest ductility is required the carbon contents up to 0.12% may advantageously be used. Both the total content of titanium and aluminum and the Ti/Al ratio are important. The effect of increasing the Ti+Al content is to increase the strength of the alloy and at the same time decrease its tensile ductility, both at room temperature and at elevated temperatures. At Ti+Al contents below 2% the strength is inadequate, while above a Ti+Al content depending on the Ti/Al ratio and defined by the line A-B in FIGURE 1 of the drawings the alloys have very low ductilities at elevated temperatures, particularly after welding. Alloys having Ti+Al contents corresponding to points above the line A-B but less than 3.5% have undesirably low ductility at high temperatures after welding; and at Ti+Al contents greater than 3.5% their room temperature ductility also rapidly falls off to such an extent that fabrication of the alloy in the form of sheet becomes impractical. For applications where the greatest ductility is required and strength is of rather less importance, it is advantageous to make use of alloys within the area EFCDE. The optimum combination of strength and ductility is obtained within the area ABFEA at Ti+Al contents below 3%, while if the highest strength is required at the expense of some sacrifice in ductility alloys within the portion of the area ABFEA that corresponds to Ti+Al contents above 3% should be used.

The effect of increasing the ratio of titanium to aluminum at a given Ti+Al content is to increase the ductility at elevated temperatures, as is shown in the curves in the

graph forming FIG. 2 of the accompanying drawing. Referring now thereto, the curves marked 11, 12 and 13 show the variation in percentage elongation to fracture at 750° C. of alloys of the nominal composition: 20% Cr, 0.11% C, 0.003% B, 0.05% Zr, 3% Mo, <0.5% Si, <0.5% Mn, balance Ni, containing different amounts of titanium and aluminum. Curve 11 refers to alloys containing 1% Al, curve 12 to alloys containing 1.5% Al and curve 13 to alloys containing 2% Al. These curves also demonstrate the decrease in high-temperature ductility that occurs as the total Ti+Al content is increased at all Ti/Al ratios.

The effect of increasing the iron content of the alloys within the broad range 0% to 45% is to increase the high-temperature ductility. This effect is shown by comparing the curve 12 in FIG. 2 of the drawing with the curve 14, which shows the variation of the elongation at 750° C. with total Ti+Al content of alloys nominally containing 1.5% Al together with 18% Cr, 0.11% C, 37% Ni, 3% Mo, 0.003% B, 0.05% Zr, <0.5% Si, <0.5% Mn, balance Fe. Curve 14 also shows that the ductility of the iron-containing alloys falls with increasing Ti+Al content in the same way as for the substantially iron-free alloys of curve 12. All four of the curves 11 to 14 refer to alloys that had been heat treated by heating at 1100° C. for 8 minutes, cooling in air and finally ageing for 4 hours at 750° C.

The effect upon the room-temperature ductility of varying the Ti+Al content and the Ti/Al are shown by the results in Table I. These results were obtained from tensile tests made at room temperature on bar samples of alloys of base composition: 0.08% C, 18% Cr, 5% Mo, 37% Ni, 0.003% B, 0.005% Zr, balance (apart from Ti and Al) substantially all Fe.

The bars were heat-treated before testing by heating for 30 minutes at 1150° C. air cooling, heating for 16 hours at 850° C. and again air cooling.

Table I

Ti, percent	Al, percent	Ti+Al, percent	Ti/Al	Elongation, percent
1.3	0.99	2.29	1.35	26
2.25	0.47	2.72	4.78	17
1.3	1.57	2.87	0.82	23
3.1	0.24	3.34	12.9	2
3.0	0.68	3.68	4.4	0.5
3.15	1.02	4.17	3.09	0.4
3.2	1.55	4.75	2.07	0.4

Replacement of nickel iron does, however, result in some decrease in the tensile strength at high temperatures and alloys with a low iron content for example 0% to 5% of iron, are therefore advantageous for applications where the highest tensile strengths are required. Alloys with say 30% to 40% iron, on the other hand, can be used where the highest ductilities are required but the tensile strength is not of such great importance.

It is important that the nickel content should not be reduced below 35%, otherwise severe embrittlement occurs after long exposure to temperatures in the range 650° C.-850° C.

The presence of molybdenum improves the creep resistance of the alloys at temperatures and for this purpose at least 3% molybdenum should be present. On the other hand, the molybdenum content must not exceed 6%, as at higher levels the corrosion resistance becomes seriously impaired and forging is almost impossible. Within the range 3% to 6% the effect of molybdenum on the high-temperature strength of the alloys is complementary to that of Ti+Al. At a given Ti+Al content, increasing the molybdenum content increases the high-temperature strength and the fall in strength that occurs on reducing the Ti+Al content from a given level can be partly or wholly compensated by increasing the molybdenum content by 0.5% for every 0.1% that the Ti+Al content decreases.

We have surprisingly found that very small amounts of boron improve the tensile ductility of the alloys at high temperatures and a content of boron within the very narrow range 0.001% to 0.009% is essential if welded joints formed in the alloys are to have adequate ductility at elevated temperatures and are to be satisfactorily hot-workable. At boron contents below 0.001%, the ductility of the alloys after welding is low and so is the stress-rupture life. On the other hand if the boron content is increased above 0.009% the alloys tend to crack on welding, particularly in thick sections exceeding say $\frac{3}{8}$ inch, and preferably it does not exceed 0.004%. A particularly suitable content is 0.003%. The effect of the boron content on the ductility of welded joints at temperatures between 600° C. and 800° C. is shown by the following comparative figures for alloys of the nominal composition (apart from boron): 0.05% C, 20% Cr, 5% Mo, 2.6% (Ti+Al), Ti/Al 1.5, Zr 0.02%, Ni balance. The tests were carried out on sheet specimens 0.048 inch thick butt-welded without restraint by the argon-arc process.

Table II

Temperature, °C.	Elongation, percent	
	<0.001% B	0.002% B
600	26	34
700	13	33
800	24	29

Zirconium contributes to the creep resistance of the alloys and for this purpose it should be present in the range 0.01% to 0.1%, preferably 0.05%. Greater amounts of zirconium than 0.1% again may lead to cracking on welding.

The alloys may be melted in any convenient manner. It is common practice in air-melting nickel-chromium alloys to deoxidize them by an addition of calcium or magnesium. When this technique is used for the present alloys, particularly those containing less than 5% iron, care should be taken that the residual calcium or magnesium content is as low as possible, preferably not exceeding 0.005%, as otherwise cracking may occur on welding thick sections or under restrained conditions, and the high-temperature ductility of the welded joints may be impaired.

To develop the optimum properties in the alloys, it is essential that they should be given an age hardening heat treatment consisting of solution heating followed by ageing at a lower temperature. Advantageously, this treatment consists of heating at 1020° C.-1150° C., followed by cooling in air and ageing at 650° C.-850° C. For thin sections, say less than $\frac{3}{16}$ inch, the first treatment should be for 2-30 minutes and the second treatment for 2-16 hours. For thicker sections the first treatment should be for a longer time, say 2-8 hours. All the statements in this specification about the properties of the alloys refer to specimens that have been age hardened in this way. It is to be observed that "welding" as employed in this specification refers to a process wherein elements, structures and the like are joined by means of a fusion process during which a liquid metallic contact is established while at least the adjacent surfaces of the structures, elements, etc., to be joined are at a temperature in excess of the incipient fusion temperature of the alloy or metal from which the structures or elements are made. Subsequent cooling during which contact is maintained establishes the weld bond by freezing of the liquid contacting metal.

If the alloys are to be welded, a solution heating should be applied before the welding operation is carried out but ageing before welding is unnecessary. After welding, no further solution heat treatment is in general necessary but where maximum strength is required, it can be desirable to carry out a post-weld ageing treatment

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consisting of heating for 2-16 hours at 650° C. to 850° C. or 900° C. for preference in the higher part of this temperature range.

In the following table, alloys Nos. 1 to 3 are examples of alloys according to the invention, whereas alloys Nos. 4 to 6 are outside the invention.

Table III

Element	Alloy No. 1, percent	Alloy No. 2, percent	Alloy No. 3, percent	Alloy No. 4, percent	Alloy No. 5, percent	Alloy No. 6, percent
Carbon	0.05	0.1	0.1	0.11	0.05	0.08
Chromium	20.1	18.2	17.95	17.7	20	19.6
Titanium	1.03	1.33	2.46	1.57	2.32	2.44
Aluminum	1.13	1.31	1.03	1.83	1.48	1.49
Molybdenum	4.93	5.16	3.1	5.2		
Nickel	Bal.	37.6	36.4	37.3	Bal.	
Boron	0.003	0.0025	0.005	0.003	0.007	0.008
Zirconium	0.02	0.035	0.05	0.05	0.065	0.04
Iron	0.37	Bal.	Bal.	Bal.	0.46	0.68
Cobalt	0.7		0.1	0.1	0.89	17.2
Silicon	0.29	0.29		0.43	0.56	0.84
Manganese	0.03	0.05		0.18	0.05	0.06
Ti+Al	2.16	2.69	3.49	3.40	3.8	3.93
Ti/Al	0.91	1.01	2.38	0.835	1.57	1.64

Percent=percent by weight.

Samples of each of the alloys in the form of sheet 0.048 inch thick were solution heated, alloys Nos. 1, 3, 4, 5 and 6 by heating at 1150° C. for 8 minutes and alloy No. 2 at 1020° C. for 20 minutes, and then autogenously butt-welded without restraint by the argon-arc process and finally aged for 4 hours at 750° C. Table IV shows the strength and elongation of welded samples, tested with the weld at the center of the gauge length at a temperature of 750° C.

Table IV

Properties at 750° C.	Alloy Nos.					
	1	2	3	4	5	6
U.T.S. (long tons/in. ²)	37	36	33	32	41	41
Elongation (percent)	21	19	14	1.5	1.3	4.6

The variation of the elongation with temperature of alloys Nos. 1, 2, 5 and 6 is shown in FIG. 3 of the accompanying drawing. Referring now thereto, this figure shows that whereas there is a very pronounced trough in the elongation temperature curves of alloys 5 and 6 in the temperature range 700° C.-900° C., which is responsible for their poor properties in the welded state, the alloys 1 and 2 of the invention experienced only a very slight drop in ductility.

As shown in FIG. 4, similar differences are present in the elongation temperature curves of the alloys in the unwelded state, though the fall in ductility with increases in temperature is not so great as in the welded alloys.

The molybdenum in the alloys can be wholly or partly replaced by an equal atomic percentage of tungsten.

The alloys are suitable for use both in the sheet and wrought forms and can be used in the manufacture of welded structures, including composite welded structures comprising sheet components with wrought stiffening members welded to them. Examples of such structures are parts of aircraft gas turbines such as jet pipes, flame tubes and jet silencers.

The alloys containing a high proportion of iron, for example, more than 30%, e.g., up to 40% iron, are resistant to corrosion in reducing atmospheres containing carbon and sulphur and are suitable for use in chemical plants where exposure to these conditions occurs.

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 under-

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stand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. An alloy consisting essentially by weight of about 15% to about 25% chromium, up to about 45% iron, about 0.04% to about 0.15% carbon, about 0.7% to 2.5% titanium, about 0.7% to 1.5% aluminum, an element selected from the group consisting of tungsten and molybdenum in an amount equivalent in atomic concentration in the alloy to about 3% to 6% molybdenum, 0.001% to 0.009% boron, 0.01% to 0.1% zirconium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 1% cobalt with the balance being substantially nickel, in an amount not less than about 35%, the sum of said titanium percentage and said aluminum percentage being 2% to 3.5% and the ratio of said titanium percentage to said aluminum percentage being 0.5 to 4 and the said sum being correlated with said ratio so that when the values of said sum and ratio are plotted, the resultant point lies within the area ABCDA set forth in FIGURE 1 of the accompanying drawing.

2. An alloy consisting essentially by weight of about 15% to about 25% chromium, up to about 45% iron, about 0.04% to about 0.15% carbon, about 0.7% to 2.5% titanium, about 0.7% to 1.5% aluminum, about 3% to 6% molybdenum, 0.001% to 0.009% boron, 0.01% to 0.1% zirconium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 1% cobalt with the balance being substantially nickel, in an amount not less than about 35%, the sum of said titanium percentage and said aluminum percentage being 2% to 3.5% and the ratio of said titanium percentage to said aluminum percentage being 0.5 to 4 and the said sum being correlated with said ratio so that when the values of said sum and ratio are plotted, the resultant point lies within the area ABCDA set forth in FIGURE 1 of the accompanying drawing.

3. An alloy as set forth and defined in claim 2 wherein when the values of said ratio and sum are plotted, the resultant point lies within the area ABFEA set forth in FIGURE 1 of the accompanying drawing.

4. An alloy as set forth and defined in claim 2 wherein the chromium content is 17% to 20%.

5. An alloy as set forth and defined in claim 2 wherein the iron content is up to 5%.

6. An alloy as set forth and defined in claim 2 wherein the boron content is 0.001% to 0.004%.

7. An alloy as set forth and defined in claim 2 wherein the carbon content is 0.05% to 0.08%.

8. A welded structure of a kind subjected in use to prolonged stress in the temperature range 700° C. to 850° C. having at least one welded element made of an alloy consisting essentially by weight of about 15% to about 25% chromium, up to about 45% iron, about 0.04% to about 0.15% carbon, about 0.7% to 2.5% titanium, about 0.7 to 1.5% aluminum, about 3% to 6% molybdenum, 0.001% to 0.009% boron, 0.01% to 0.1% zirconium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 1% cobalt with the balance being substantially nickel in an amount not less than 35%, the sum of said titanium percentage and said aluminum percentage being 2% to 3.5% and the ratio of said titanium percentage to said aluminum percentage being 0.5 to 4 and the said sum being correlated with said ratio so that when the values of said sum and ratio are plotted, the resultant point lies within the area ABCDA set forth in FIGURE 1 of the accompanying drawing.

9. A jet pipe for a gas turbine engine having a weld joint and at least one element made of an alloy consisting essentially by weight of about 15% to about 25% chromium, up to about 45% iron, about 0.04% to about 0.15% carbon, about 0.7% to 2.5% titanium, about

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0.7% to 1.5% aluminum, about 3% to 6% molybdenum, 0.001% to 0.009% boron, 0.01% to 0.1% zirconium, up to about 0.5% silicon, up to about 0.5% manganese, up to about 1% cobalt with the balance being substantially nickel in an amount not less than 35%, the sum of said titanium percentage and said aluminum percentage being 2% to 3.5% and the ratio of said titanium percentage to said aluminum percentage being 0.5 to 4 and the said sum being correlated with said ratio so that when the values of said sum and ratio are plotted, the resultant point lies within the area ABCDA set forth in FIGURE 1 of the accompanying drawing.

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