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[54] **CAST NICKEL BASE ALLOY**
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ABSTRACT: An improved cast nickel base alloy has a combination of stability, high-temperature stress rupture strength and hot corrosion resistance primarily through control of such phases as sigma, eta, and the carbides. Control is achieved through the balance of the elements Al, Ti, Mo, W, Co, Cr and C in the proper relationships with a Ni base in the substantial absence of Fe.

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CAST NICKEL BASE ALLOY

The invention described and claimed in the U.S. Pat. application herein resulted from work done under United States Government contract FA-SS-66-6. The United States Government has an irrevocable, nonexclusive license under said application to practice and have practiced the invention claimed herein, including the unlimited right to sublicense others to practice and have practice the claimed invention for any purpose whatsoever.

Advancing technology and development of improved power-producing apparatus such as the gas turbine engine has identified the need for stronger alloys which are stable at relatively high operating temperatures such as up to 1,800° F. and yet can withstand the corrosive atmospheres in which they are intended to operate. Although a number of alloy systems including those based on the refractory metals have been evaluated for such applications, the nickel base alloy remains the type presently most widely used in such difficult applications.

One high-temperature nickel base alloy application of particular interest is the cast form of the alloy. However, known nickel base alloys in cast forms either are relatively weak or unstable during longtime operation or have insufficient resistance in hot corrosive atmospheres particularly in the 1,500° F.-1,800° range.

It is a principal object of this invention to provide an improved cast nickel base alloy having an unusual combination of strength and stability for longtime operation at elevated temperatures coupled with hot corrosion resistance.

A more specific object is to provide such an alloy of improved stability and having a stress rupture life in the as-cast condition of at least 25 hours under a stress condition of 27,500 p.s.i. at 1,800° F.

These and other objects and advantages will be more apparent from the following detailed description and typical representative examples within the broad scope of the appended claims.

It has been recognized that a cast nickel base alloy having an improved combination of high-temperature stability and hot corrosion resistance along with a stress rupture life of at least 25 hours under stress of 27,500 p.s.i. at Cr; F. can be attained through (1) the control of the type of precipitation of strengthening phases first with carbon, and second with the elements titanium and aluminum in a nickel matrix, (2) the control of the solution-strengthening mechanisms as a result of the presence of W and Mo in particular portions to precipitate desirable carbides, along with (3) the substantial elimination of the well-known embrittling and weakening phases such as sigma and eta. Broadly, the composition which defines such an alloy consists essentially of, by weight, 0.1-0.3% C; greater than 13% but less than 15.6% Cr; 4-6% Ti; 2-4% Al; 0.005-0.02% B; 3-6% W; 2.5-5% Mo; greater than 5% up to 15% Co; up to 0.1% Zr; with the balance nickel and incidental impurities provided that the ratio of Ti to Al is greater than 1 but less than 3:1, the sum of Ti and Al is $7.5-9\% \text{ Mo} + w/2$ is 5-7%.

In the alloy of the present invention, carbon, preferably in the range of about 0.15-0.2 percent provides for carbide formation which leads to improved strength particularly at high temperatures. Insufficient carbon, for example at about 0.08 percent is insufficient for high-temperature strength whereas an overabundance of carbon, for example, above about 0.3 percent results in lower life and embrittlement at lower temperatures as a result of excessive carbide formation in the grain boundaries.

The element chromium provides oxidation and hot corrosion resistance. However, in amounts of less than 13 percent there is insufficient hot corrosion resistance provided in the temperature range of about 1,500-1,800° F. Cr in amounts greater than 16 percent leads to the formation of sigma and other deleterious phases without proper phase control. Accordingly, the preferred Cr range is 13.5-14.5 percent to assure such phase control.

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As is the case with Cr, Co in excessive amounts can result in sigma phase formation. However, in the proper amounts described herein, Co adds to the gamma prime solubility and affects ductility of the alloy.

Very critical to the alloy of the present invention are the elements W and Mo which generally are identified with the solution-strengthening mechanism of a nickel base alloy. However, it has been recognized that a complex control of both sigma phase and of precipitating carbides can be achieved through a careful balance of the amounts of W and Mo. As will be shown in detail in connection with the specific examples, it was unexpectedly recognized that if the total amount of W and Mo were maintained such that the sum of half of the W and all of the Mo were in the range of 5-7 percent, not only could the formation of sigma phase be inhibited but also the more stable M_6C carbide could be formed along with the $M_{23}C_6$ carbide rather than all $M_{23}C_6$. Although Mo has been included in substantial amounts in certain known nickel base alloys, it has been recognized that Mo on a weight percentage basis is a more potent sigma phase former. It has also been previously shown that W additions are beneficial to 1,500-1,800° F. stress rupture strength. Therefore, it is necessary that both Mo and W be present and that the ranges in which the above relationship is maintained is 3-6 percent W and 2.5-5 percent Mo in order to maintain optimum alloy strength and stability.

The elements Ti and Al have been described in connection with their function as the primary precipitation-strengthening elements in combination with nickel in forming $Ni_3(AlTi)$. Now it has been unexpectedly discovered that in the proper combination, they also function to improve hot corrosion (sulfidation) resistance particularly in the 1,500-1,800° F. range. This unique combination of Al and Ti along with that just described for Mo and W in their dual control function is one important aspect of the present invention not recognized in known nickel base alloys.

The present invention recognizes that Ti/Al ratio must be greater than 1 to provide such improved hot corrosion resistance but less than 3:1 to prevent the formation of the weakening eta (Ni_3Ti) phase. Al is preferably included in the range of about 2.5-3.5 percent because for one reason it can result in the formation of sigma phase somewhat more readily than does Ti; Al ties up more nickel from the matrix to form the $Ni_3(Al,Ti)$, sometimes referred to as gamma prime. This occurs because of the lower atomic weight of aluminum compared with titanium. As the gamma prime content increases, there is less nickel available in the gamma matrix. Therefore, there is a greater tendency for sigma phase formation due to the relatively larger amounts of Cr, Co, Mo, and W in the matrix. Accordingly, it is an objective to keep as much nickel as possible in the gamma matrix.

Hence, keeping close control and lowering the Al content relative to the Ti content will result in less tendency to form the embrittling sigma phase and the higher Ti/Al ratio will improve hot corrosion resistance.

The present invention recognizes the criticality of United States patent of aluminum and titanium not only from the standpoint of the ratio of aluminum and described above but also that at least 7.5 weight percent of the two elements is required but no more than 9 weight percent can be tolerated without seriously depleting the practiced matrix. The proper amount of Al stabilizes the gamma prime phase and prevents the Ni_3Ti formation. With too much Ti, the $Ni_3(Al,Ti)$ is metastable and breaks down to form the weakening Ni_3Ti .

Although iron has been included or tolerated in certain relatively large amounts in known nickel base alloys, the present invention recognizes that iron tends to form deleterious phases. Therefore, it is preferred that no iron be present although slight adjustment such as in the solid solution-strengthening elements can be made to tolerate small amounts of Fe.

Boron is included within the range of 0.005-0.02 percent for its beneficial effect on rupture strength and ductility. The

alloy including boron below that level is weak, whereas too high a boron content results in the formation of excessive borides leading to incipient melting on over temperature exposure.

It has been recognized in evaluation of the present invention that the elements Cb and Ta are not substitutes for W and Mo. It is believed that about half of the Cb or Ta goes into gamma prime formation, such as $Ni_3(A1, Ti, Cb, Ta)$, and to carbides. Both deplete the matrix and are undesirable in the balanced alloy defined by the present invention. Both can lead to the formation of sigma phase.

These unusual aspects of the present invention will be more clearly understood from the following detailed examples typical of alloys melted in the evaluation of the alloy of the present invention. The alloys were melted by the commercial vacuum-melting techniques widely used in the preparation of nickel base alloys. Heats ranging in size from about 12 pounds to about 1,000 pounds have been made, the latter being made on alloys within the range of the present invention. Test specimens were prepared either by casting directly from the melting furnace into precision casting specimen molds or by remelting and casting previously prepared alloy ingots.

The alloy forms representative of those melted within the scope of the present invention are shown in the following table I.

TABLE I

[Composition in weight percent]

Alloy includes 0.014-0.016% B; 0.03% Zr, balance Ni and incidental impurities. Ti+Al=8-8.1; Ti/Al=1.6-1.7; Mo+W/2=5.4-6							
	C	Cr	Co	Mo	W	Ti	Al
Alloy:							
1.....	.17	14.0	9.9	4.0	3.9	5.0	3.0
2.....	.16	14.0	9.6	4.0	4.0	5.0	3.0
3.....	.19	14.2	14.9	4.0	4.0	5.0	3.1
4.....	.18	14.1	7.5	4.0	4.0	5.0	3.0
5.....	.18	14.0	12.3	4.0	4.0	5.0	3.0
6.....	.19	13.9	10.0	3.0	6.0	5.0	3.0
7.....	.18	13.5	10.0	4.0	4.0	5.0	3.0
8.....	.26	14.0	9.8	4.0	4.0	5.0	3.1
9.....	.19	14.0	10.0	2.9	5.0	4.9	3.1
10.....	.15	14.1	9.4	4.1	4.0	5.0	3.1

Other alloys made and tested during the evaluation of the alloy of the present invention include those shown in the following table II, outside the scope of the present invention.

TABLE II

[Composition in weight percent]

Alloy includes 0.014-0.017% B; 0.03-0.04% Zr with the balance Ni and incidental impurities

	C	Cr	Co	Mo	W	Ti	Al	Ti/Al	Ti+Al	Mo+W/2
Alloy:										
11.....	.14	16.1	10.7	3.2	2.9	3.8	4.0	1.0	7.8	4.7
12.....	.14	15.5	10.7	3.1	2.7	2.9	5.0	0.6	7.9	4.5
13.....	.16	15.4	10.3	4.0	3.8	4.5	2.6	1.7	7.1	5.9
14.....	.16	15.6	10.2	4.0	3.9	4.9	2.9	1.7	7.8	6.0
15.....	.20	13.0	10.0	4.0	4.0	4.9	3.0	1.6	7.9	6.0
16.....	.08	14.1	9.9	4.0	4.0	5.0	3.1	1.6	8.1	6.0
17.....	.19	14.1	5.0	4.0	4.0	4.9	3.1	1.6	8.0	6.0
18.....	.18	14.0	0	3.9	4.0	4.9	3.1	1.6	8.0	5.9
19.....	.18	13.9	10.0	6.1	3.0	5.0	3.0	1.7	8.0	7.6
20.....	.19	14.1	9.8	4.9	4.9	5.0	3.0	1.7	8.0	7.4

The improved characteristics of the present invention are particularly measured by combination of high-temperature stress rupture life and stability along with hot corrosion resistance. This improvement as it relates to longtime stability is related to the suppression of the formation of such embrittling phases as sigma and eta. These phases are greatly suppressed or are entirely eliminated according to the alloy of the present invention. When certain known case alloys are exposed to elevated temperatures, the gamma phase and carbides, which are found in the primary gamma prime phase, agglomerate. At temperatures in the range of about 1,300° F.-1,800° F., sigma plates form in matrix areas surrounding the gamma prime. This formation, which is accelerated by stress, appears to relate to excessive chromium in the primary gamma prime and surrounding matrix areas, first reacting with carbon to form

grain boundary $M_{23}C_6$ carbides. Then when all the available carbon is thus reacted, it appears that excessive chromium in the matrix combines with such elements as Co, Mo, etc. to form a Cr-Co-Mo type sigma. Long time stability testing such as at 1,500° F. at a stress of 55,000 p.s.i. identifies the strength-reducing nature of sigma phase. The terminal nature of such sigma phase has been reported by Boesch and Slaney in Metals Progress, July 1964, pages 109-111.

Although sigma phase may be removed by heat treatment, it will recur when the alloy experiences the same time and temperature conditions under which sigma was originally formed. The alloy of the present invention identifies a different kind of alloy which inhibits original sigma phase formation and results in the improved combination of higher temperature strength and stability along with hot corrosion resistance as a result of a different surface reaction product.

In order to understand more fully the present invention and its individual components as they affect the strength and stability of the alloy of the present invention, the following tables have been prepared. These compare the alloy forms both within and outside the scope of the present invention, as shown in full compositions in tables I and II. The element content referred to in the tables as well as throughout this specification is in weight percent and the term "ksi" refers to thousands of pounds per square inch.

TABLE III

Alloy:	Element variation, Wt. percent	As-cast stress rupture life (hrs.)		Sigma
		1,500° F./ 65 K. s.i.	1,800° F./ 27.5 K. s.i.	
18.....	0 Co	1 230	None.
17.....	5 Co	1 481	Do.
6.....	10.0 Co	744	49 Do.
5.....	12.3 Co	896	50 Do.
3.....	15.0 Co	836	33 Small.
14.....	15.6 Cr	588	38 Large.
6.....	13.9 Cr	744	49 None.
15.....	13.0 Cr	588	30 Do.
16.....	0.08 C	512	45 Small.
8.....	0.18 C	896	50 None.
8.....	0.26 C	670	43 Do.

¹ Heat treated: 2,200° F. -2 hrs.; 2,000° F. -4 hrs.; 1,550° F. -16 hrs.; 1,400° F. -16 hrs.

As shown in table III, in the alloy of the present invention, cobalt below about 15 weight percent does not lead to the formation of sigma phase. Although at 15 percent Co, a small amount of sigma is beginning to form, this can be tolerated as the upper limit because the strength and stability characteristics have been reduced only a slight amount. However, above about 15 weight percent, excessive sigma will form resulting in a different kind of alloy of reduced properties. Because the alloy formed at 5 percent Co was significantly weaker than desired, the higher temperature tests were not run.

With respect to the chromium variation shown in table III, the detrimental effect of the formation of heavy amounts of sigma on longtime stability is shown by alloy 14 at 15.6 percent Cr. The identification of large amounts of sigma shows

alloy 14 to be of a different kind than that of alloy 6 within the scope of the present invention. Alloy 15 at 13 percent Cr and only 0.9 percent lower than alloy 6, shows a reduction in strength even though all the elements of alloy 15 are within the range of the present invention. Therefore, the alloy of the present invention includes less than 15.6 percent but greater than 13 percent Cr.

With respect to the carbon variation in table III, it can be noted that at 0.08 percent C, insufficient carbon is present to react with Cr within the range of the present invention to prevent Cr from forming sigma platelets. The reduction in long time stability as represented by the 1,500° F. tests should be noted in this regard. Although amounts of carbon approaching about 0.3 percent can be included, it is preferred that carbon at about 0.2 weight percent be maintained in order to assure the unusually fine properties of the preferred form of the alloy of the present invention.

Although the elements W and Mo have been included in known nickel-base alloys singly or interchangeably as solution-strengthening elements, the present invention recognizes additional critical roles played by these two elements. Both are involved in the complex control of precipitating carbides and sigma phase formations, although Mo is a more potent sigma phase former. The following table IV shows the effect and interrelationship of these elements on the alloy of the present invention.

TABLE IV

Alloy	Element variation (weight percent)			As-cast stress rupture life (hrs.)		
	Mo	W	(Mo+W/2)	1,500° F./5 k. s.i.	1,800° F./27.5 k. s.i.	Sigma
19	6.1	3.0	7.6	(0)	21	Medium.
6	3.0	6.0	6.0	744	49	None.
20	4.9	4.9	7.4	439	47	Medium.
9	2.9	5.0	5.4	746	37	None.

¹Based on a 200 hour life 1,500° F—68 k. s.i. rupture test.

except for the element variation listed, which in the case of alloy 19 is Mo and in the case of alloy 20 is (MO+W/2).

The elements Ti and Al contribute to the alloy of the present invention in several ways. This invention recognizes that the proper amount and interrelationship between these elements can control the short time strength, the alloy stability through sigma phase inhibition and, very importantly, provide hot corrosion resistance.

The problem of hot corrosion resistance involves resistance to sulfidation in the range of about 1,500–1,800° F. Above and below that range, hot corrosion resistance is not as significant a problem in the type of alloys to which the present invention relates because such alloys include the element aluminum. Aluminum oxide which forms on the surface as a reaction product will form a reasonably protective oxidation resistant barrier. The problem of oxidation resistance is different from that of hot corrosion resistance. Normally for oxidation resistance it would be better to have a Ti/Al ratio of greater than 1. The higher ratio is desirable because TiO₂ is formed on the surface. The more TiO₂ available, the better is the hot corrosion resistance. However, Ti in amounts which would produce a Ti/Al ratio of about 3:1 or more, cannot be tolerated in the alloy of the present invention.

The effect of the elements Al and Ti on the alloy of the present invention as it relates to as-cast stress rupture life and stability is shown in the following table V.

TABLE V

Alloy:	Weight percent				As-cast stress rupture life (hrs.)		
	Ti	Al	(Ti+Al)		1,500° F./55 k. s.i.	1,800° F./27.5 k. s.i.	Sigma
			Ti/Al	Ti/Al			
11	3.8	4.0	7.8	1.0	309	35	Medium
12	2.9	5.0	7.9	0.6	251	25	Large.
13	4.5	2.6	7.1	1.7	560	19	None.
5	5.0	3.0	8.0	1.7	896	60	Do.

In alloy 19, even with Mo as high as 6.1 percent, there is insufficient strengthening to provide adequate high-temperature stress rupture strength. More importantly, however, is the fact that the total amount of Mo and W is sufficiently high to result in sigma phase formation as measured by the atomic relationship between those elements of (Mo+W/2) of as high as the 7.6 percent. The present invention contemplates that relationship to be within the range of 5–7 percent to inhibit sigma phase formation and precipitation of the proper carbides as described before. Alloy 20, a different kind of alloy and outside the scope of the present invention, includes Mo and W within the invention range but with the improper relationship one to the other as shown by the (Mo+W/2) of 7.4 percent. The formation of medium amounts of sigma resulted in significantly reduced stability as measured by the 1,500° F. stress rupture test. Alloy forms 6 and 9, within the scope of the present invention, have the proper balance of W and Mo and are a different kind of alloy because of the absence of the sigma structure. This results in improved stability and strength.

In the above tables III and IV, it should be noted that the alloy forms identified with numbers greater than 10 have compositions within the range of the alloy of the present invention

Although alloys 5, 11 and 12 include about the same amount of the sum of titanium and aluminum, it should be noted that alloy 5 forms no sigma phase whereas alloys 11 and 12 form medium to large amounts of sigma phase. This can be attributed to the improper relationship between the two elements. The fact that different kinds of alloys are formed between alloy 5 and alloys 11 and 12 is further substantiated by the stress rupture life, particularly the stability data represented by the 1,500° F. tests. Further, it should be noted that the alloy 13, although having the proper ratio between Ti and Al, does not have sufficient amounts of these elements to provide the required strength. Therefore, the alloy of the present invention defines the relationship between Ti and Al such that the sum of those elements is in the range of about 7.5–9 percent and that the Ti/Al ratio is greater than one but less than 3:1.

One important characteristic of the alloy of the present invention which distinguishes it from known alloys presently intended for the same use is its significantly improved hot corrosion resistance. A series of comparison tests to determine the hot corrosion resistance of a variety of alloys was conducted on such known nickel base super alloys as those listed in the following table VI.

TABLE VI

[Known alloys in weight percent]

Alloys include .01-.02 B, balance Ni and incidental impurities

	C	Cr	Co	Mo	W	Ti	Al	Zr	Others
Alloy:									
A.....	.18	9.5	15.0	3.0	-----	4.2	5.5	.06	1. V
B.....	.07	14.2	15.0	4.2	-----	3.4	4.3	-----	
C.....	1.3	6.0	7.5	2.0	6.0	1.0	5.5	1.3	9 Ta, 0.5 Hf, 0.5 Cb, 0.5 Re.
D.....	.08	15.0	22.0	4.4	-----	2.4	4.4	-----	
E.....	.14	13.0	-----	4.5	-----	0.75	6.0	.10	2.3 Cb+Ta

Because the alloys tested were intended for use in a gas turbine engine, test apparatus simulating conditions in the turbine section of a gas turbine was constructed. The apparatus burned jet fuel, for example JP-5 in a 30-1 air-fuel mixture and injected sea water having a composition within the range of ASTM specification D-665-60. The sea water was diluted with distilled water to five parts per million. The tests run were cyclic tests over a period of 1,000 hours including 18 intermittent colling cycles to room temperature with an air blast. The specimens tested were cast bars ground to a diameter of about 0.130 inch and about 1.25 inches long. Results of such a comparative test are shown in the following table VII.

TABLE VII
Hot Corrosion Resistance 1000 hrs. cyclic test

Alloy	Depth of Attack (Mils)*	
	1600F	1750F
2.....	4/10/12	3/8/9
B.....	35/44/47	26/36/44
A.....	(^a)	(^a)
C.....	(^a)	39/42/43
D.....	32/44/47	10/18/20
E.....	(^a)	30/36/39

* Expressed as 1/2 (surface loss/avg. penetration/max. penetration).
^a Specimen corroded throughout.

From table VII, it is easily seen that at all temperatures tested, alloy 2 within the scope of the present invention is remarkably more resistant to hot corrosion than are all of the other tested known alloys, most of which are presently in use in the hot section of gas turbine engines.

Another measure of hot corrosion resistance involved a study of specimen weight loss rather than surface penetration or thickness loss. Another series of tests resulting in data of which the date of table VIII is a typical were performed on alloys both within and outside the scope of the present invention.

TABLE VIII
Hot Corrosion Resistance 1750° F for 500 hrs.

Alloy	Wt. Loss (mils/dia.)	
	Gross	Max.
10.....	0.3	3.
11.....	5.	16.
12.....	6.	14.
D.....	3.	10.
E.....	50.	53.

Alloy 10 within the scope of the present invention shows significant and remarkable resistance to weight loss after 500 hours at 1,700° F. as compared with alloys known or outside the scope of the present invention.

The significantly improved hot corrosion resistance of the alloy of the present invention is based on the fact that it is a different kind of alloy. Hence a different kind of reaction product is formed on the surface of the alloy of the present invention under oxidizing conditions than is formed on the surfaces of certain known nickel base alloys intended for the same purpose. As an example of such difference, an X-ray diffraction study was made on such surfaces after exposure for

400 hours at elevated temperatures. The results of one such comparison is shown in the following table IX.

TABLE IX.—X-RAY DIFFRACTION DATA AFTER 400 HRS. EXPOSURE

	1,700° F.	1,800° F.
Alloy:		
2.....	TiO ₂ (S) plus Cr ₂ O ₃ (M) plus matrix (W).	TiO ₂ (M) plus Cr ₂ O ₃ (M) plus spinel (M).
B.....	Matrix (VS) plus Al ₂ O ₃ (W) plus TiO ₂ (W).	Matrix (S) plus Al ₂ O ₃ (M) TiO ₂ (VW).

NOTE.—(S)=strong, (M)=medium, (W)=weak, (V)=very.

Alloy 2 within the scope of the present invention and having a remarkable resistance to hot corrosion had a substantial amount of TiO₂ in its surface reaction product. Only a small amount of that oxide is found in the reaction product of the alloy B. Thus the two alloys are of a different kind.

What is claimed is:

1. A cast nickel base alloy of improved stability, strength and corrosion resistance, consisting essentially of, by weight:
 - about 0.15-0.3 percent C, said carbon percentage being greater than that required for deoxidation and in addition being sufficient for forming grain boundary carbides;
 - greater than 13 percent but less than 15.6 percent Cr;
 - greater than 5 up to 15 percent Co;
 - 2.5-5 percent Mo;
 - 3-6 percent W;
 - 4-6 percent Ti;
 - 2-4 percent Al;
 - 0.005-0.02 percent B;
 - up to about 0.1 percent Zr;
 - with the balance essentially nickel and incidental impurities the ratio Ti/Al being in the range of greater than 1:1 to less than 3:1;
 - the sum of Ti and Al being in the range of 7.5-9 percent; and
 - the sum of Mo and half of the W being in the range of 5-7 percent; and further characterized by the substantial absence of sigma phase and a stress rupture life in the as-cast condition of at least about 25 hours under a stress of 27,500 p.s.i. at 1,800° F.
2. The alloy of claim 1 in which:
 - the C is 0.15-0.2 percent;
 - the Cr is 13.5-14.5 percent;
 - the Co is 7.5-12.5 percent;
 - the Mo is 3.5-4.5 percent;
 - the W is 3.5-4.5 percent;
 - the Ti is 4.5-5.5 percent;
 - the Al is 2.5-3.5 percent;
 - the B is 0.01-0.02 percent;
 - the Zr is 0.005-0.1 percent; and
 - the Ti/Al ratio is 1:1-2:1.
3. The alloy of claim 2 in which:
 - the Cr is 13.7-14.3 percent;
 - the Co is 9-10 percent;
 - the Mo is 3.7-4.3 percent;
 - the W is 3.7-4.3 percent;
 - the Ti is 4.8-5.2 percent;
 - the Al is 2.8-3.2 percent; and
 - the Zr is 0.02-0.04 percent.