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④ **IMPROVEMENTS IN OR RELATING TO NICKEL-, COBALT-, AND IRON BASED ALLOYS.**

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## Improvements in or relating to nickel-, cobalt- and iron based alloys

This invention relates to nickel-, cobalt- and iron-based alloys comprising those suitable for use at high temperatures under oxidising conditions or corrosive conditions, and more particularly, but not exclusively, is concerned with directionally solidified nickel-based alloys for use in these conditions.

Alloys capable of resisting oxidation, corrosion and high mechanical stresses at elevated  
 5 temperatures are increasingly required, particularly in the gas turbine field. In these applications slight increases in permissible blade temperature have a considerable and very favourable effect upon engine output and efficiency. It is an unfortunate characteristic of gas turbine alloy development, however, that changes in alloy composition which lead to improved high temperature strength tend also to reduce the oxidation resistance of the alloys. Many of the strongest gas turbine alloys presently known have a  
 10 relatively low resistance to oxidation and corrosion, so that they must be protected against high temperature attack, ie corrosion and oxidation, by coatings which either remain on the surface of the alloy components or are caused to diffuse into the body of the components on which they are deposited. It is a disadvantage of the various coating processes employed that they are costly, and that they tend also to have a deleterious effect upon the high temperature mechanical properties of the  
 15 components to which they are applied.

Typical coatings of the kind which cover the surface of alloy components or diffuse into the surface thereof are discussed in US—A—3 918 139 wherein is disclosed and claimed an improved overlay coating composition of the MCrAlY type consisting essentially of 8—30 wt% Cr, 5—15 wt% Al, up to 1 wt% reactive metal selected from a group comprising yttrium and other rare earth elements, the  
 20 balance being selected from nickel, cobalt and nickel-cobalt, to which 3—12 wt% of a noble metal is added selected from a group comprising platinum.

The present invention, by contrast, seeks to provide, for fabrication into alloy components, high temperature nickel, cobalt and iron-based alloys incorporating a strengthening phase dispersed throughout the microstructure wherein oxidation and corrosion resistance is conferred by controlled  
 25 alloying additions thereto which, in combination, do not have any substantial adverse effect on the high temperature mechanical strength of the alloys, and which, at least in some cases, lead to enhanced oxide scale adhesion. The presence of the strengthening phase, to confer high temperature strength, requires that the controlled additions shall not adversely affect this phase.

It is known that Pt-group metal additions have frequently been made over a period of many years to  
 30 Ni-Co- and Fe- base alloys with the object of improving their resistance to oxidation and corrosion, and this is further demonstrated in US—A—3 918 139. Substantial quantities of Pt-group metals have however generally been required to achieve significant improvements and on account of the high cost this method of improving the oxidation resistance of high temperature alloys has not been considered feasible. Even in US—A—3 918 139, where there is an addition of a Pt-group metal to an overlay  
 35 coating composition containing reactive metal, no measurable benefit in the hot corrosion resistance is claimed for noble metal contents of < 3 wt% and, preferably, additions of 5—10 wt% are said to be needed. It has now been unexpectedly discovered however that provided the Pt-group metal and the reactive metal are present together in controlled proportions quantities of Pt-group metal substantially less than 3 wt% can be quite effective.

It is further known that Pt-group metal additions made to alloys containing carbide or  
 40 intermetallic compound strengthening phases cause disruption of the strengthening phase and a weakening of the high temperature strength. It is also known that reactive metal such as yttrium have a similar effect when they are added by themselves to alloys having a high temperature strengthening phase. It has now been unexpectedly discovered, however, that provided the Pt-group metals and the  
 45 reactive metals are present together in controlled proportions the disruptive effect is substantially obviated.

Accordingly there is provided by a first aspect of the present invention an alloy consisting of at least 5 wt% of chromium, from 0 to 3 wt% of carbon, a component X, a component Z, and a balance of one or more of nickel, cobalt and iron together with incidental elements and impurities if any, wherein  
 50 component X is one or more of:

(i) at least 2 wt% in total of one or more of aluminium, titanium, tantalum and niobium, (ii) at least 5 wt% in total of one or both of tungsten and molybdenum, and (iii) at least 60 wt% of nickel; and having a strengthening phase selected from either a transition metal carbide or an  
 55 intermetallic transition metal compound; and component Z comprises  $m_p$  wt% of one or more platinum-group metals (as herein defined) together with  $m_c$  wt% of one or more platinum-complementing metals (as herein defined), where the limits for  $m_p$  and  $m_c$  are set by the expressions

60  $0.1 \leq m_p + m_c \leq 5$  and

$0.3 \leq m_p/m_c \leq 20$

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the weight percentages being expressed in terms of the total alloy weight.

According to a second aspect of the present invention there is provided a method of modifying the oxidation resistance and corrosion resistance of a nickel-based, cobalt-based or iron-based alloy having a strengthening phase selected from either a transition metal carbide or an intermetallic transition metal compound which comprises including in the alloy composition an amount  $m_p$  wt% of one or more platinum-group metals (as herein defined) and an amount  $m_c$  wt% of one or more platinum-complementing metals (as herein defined), and wherein the limits for  $m_p$  and  $m_c$  are set by the expressions

$$0.1 \leq m_p + m_c \leq 5 \text{ and}$$

$$0.3 \leq m_p/m_c \leq 20$$

the weight percentages being expressed in terms of the total weight of the modified alloy.

In this specification, the expression "platinum group metal" should be taken to mean one of osmium, iridium, platinum, ruthenium, rhodium and palladium, and the expression "platinum-complementing element" should be taken to mean one of the following:— titanium, scandium, yttrium, lanthanum, hafnium, tantalum, zirconium, niobium, and any of the lanthanide elements (Ce to Lu).

"Incidental elements and impurities" can comprise elements such as silicon, manganese and boron or, to a lesser extent vanadium, which elements are usually found in commercial iron-based alloys, and will also generally comprise small amounts of oxygen, nitrogen, hydrogen, phosphorus and sulphur.

Nickel-, cobalt- and iron-based gas turbine alloys depend for their high temperature strength on carefully controlled micro-structures which generally contain, among several other phases, carbides based on Ti(Mo)C, Ti(Nb)C or other transition element compounds. Otherwise, the micro-structures may contain less stable components, such as  $Cr_3C_2$ . (It has been proposed to provide  $Cr_3C_2$  in a directionally solidified alloy in the form of slender reinforcing fibres). If these strengthening carbides are to retain their integrity and reinforcing ability at high temperatures, the matrix of the alloy must have a low affinity either for carbon or for the metal from which the carbide is formed. Certain metals known for their solution strengthening capabilities have a high affinity for one or the other of the components of these strengthening carbides. Their addition has been shown to render the reinforcing carbides less stable. Thus zirconium, for example, which strengthens solid solutions very effectively in other alloy systems, cannot, in general, be added safely to superalloys because of its very high affinity for carbon, which tends to decompose any titanium or niobium carbides in its vicinity.

It is well known that reactive metals such as Y and La, when present in suitable concentrations, can improve the high temperature oxidation and corrosion resistance of nickel-, cobalt- and iron-based alloys. However, these elements have, like zirconium, a high affinity for carbon. When they are present above a critical concentration level they have a tendency to attack the reinforcing constituents of the alloy in which they are incorporated. For example, consider a Ni-Ni<sub>3</sub>Al-Cr<sub>3</sub>C<sub>2</sub> directionally solidified eutectic alloy which depends for its high temperature strength upon fine longitudinal fibres of Cr<sub>3</sub>C<sub>2</sub>. The Applicants have found that rare earth metals such as yttrium, when present in excess in the alloy, tend to decompose these reinforcing fibres, thus limiting the high temperature mechanical properties of this material, although its oxidation resistance is improved.

Relatively small additions of one of the six platinum group metals (Os, Ir, Pt, Ru, Rh, Pd) are known by the present Applicants to enhance the oxidation and corrosion resistance of specific nickel-, iron- and cobalt-based alloys, particularly when the alloy to which additions are made is one of those which form a protective layer of aluminium oxide. Substantial additions of platinum group metals can rarely be made to such materials, however, because these metals have a tendency to decompose any carbides upon which the superalloy depends for mechanical reinforcement. This decomposition is caused, not because of the affinity of the platinum metals for carbon, which is very small, but because of their exceedingly high affinity for the metals which form stable carbides. It is known, for example, that platinum and iridium are capable of decomposing lanthanum carbide at temperatures as low as 1000°C. When platinum additions are made, therefore, to the directionally solidified Ni-Ni<sub>3</sub>Al-Cr<sub>3</sub>C<sub>2</sub> eutectic composite mentioned above, the aligned Cr<sub>3</sub>C<sub>2</sub> reinforcing fibres are partly decomposed and carbon is released in the form of graphite flakes. This leads to a deterioration in mechanical properties.

Considerations such as those outlined above appear therefore, at first glance, to preclude the use of the strongly carbide-forming elements and of the carbide-decomposing elements as beneficial additions to existing high temperature nickel-, cobalt- and iron-based alloys.

It has been found that, in accordance with the present invention, the above-mentioned carbide-forming and carbide-decomposing groups of metals can in certain circumstances be jointly added to superalloys in quantities up to a total of 5% by weight without any deleterious effect upon structure or mechanical properties, and with some improvement in their resistance to oxidation and corrosion at high temperatures.

It is thought that this is possible because the platinum group (carbide-decomposing) metals have an affinity for the carbide-forming elements which is comparable to and in most instances higher than

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the affinity of these carbide-forming elements for carbon. The strengthening carbides can thus remain stable, and the platinum group metals can therefore be safely added without detriment to the high temperature properties of nickel, cobalt- or iron-based alloys, provided that they are suitably associated with one or more of the platinum complementing elements titanium, scandium, yttrium, lanthanum, hafnium, tantalum, zirconium, niobium and any of the lanthanide elements (Ce to Lu).

While the most beneficial effects are obtained when the composition of the component Z is stoichiometrically adjusted to provide for example the compounds listed below in Table 1, precise adjustment is not essential, and preferably component Z contains between 50 and about 93% by weight of the platinum group metals. In any case, there must be more than about 0.023 wt% of a platinum group metal present in component Z (corresponding to a lower limit of 0.3 in the quantity  $m_{p/m_c}$ , given a lower limit of 0.1 in the quantity  $(m_p + m_c)$ ).

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TABLE I

5	Balanced Additive	Optimum Composition		Preferred Composition Range (Percentage by Wt of Platinum Metal)
		Compound	% by Wt of Pt Metal	
10	Rh Sc	Rh <sub>3</sub> Sc	87.5	50-90
	Rh Y	Rh <sub>2</sub> Y	70.0	
	Rh La	Rh <sub>2</sub> La	59.7	
15	Rh Hf	Rh <sub>3</sub> Hf	63.3	
	Rh Nb	Rh <sub>3</sub> Nb	76.9	
	Rh Zr	Rh <sub>3</sub> Zr	77.3	
20	Rh Lanthanide	Rh <sub>2</sub> (Ce-Lu)	59.6-54.0	
25	Pd Sc	Pd <sub>3</sub> Sc	87.6	50-90
	Pd Y	Pd <sub>3</sub> Y	78.1	
	Pd La	Pd <sub>3</sub> La	69.7	
30	Pd Hf	Pd <sub>3</sub> Hf	64.0	
	Pd Nb	Pd <sub>3</sub> Nb	77.4	
	Pd Zr	Pd <sub>3</sub> Zr	77.8	
35	Pd Lanthanide	Pd <sub>3</sub> (Ce-Lu)	69.6-64.6	
40	Ir Sc	Ir <sub>2</sub> Sc	91.8	50-93
	Ir Y	Ir <sub>2</sub> Y	81.2	
	Ir La	Ir <sub>2</sub> La	73.4	
	Ir Hf	Ir <sub>3</sub> Hf	76.3	
45	Ir Nb	Ir <sub>3</sub> Nb	86.2	
	Ir Zr	Ir <sub>3</sub> Zr	86.3	
	Ir Lanthanide	Ir <sub>2</sub> (Ce-Lu)	73.3-68.8	
50	Pt Sc	Pt <sub>3</sub> Sc	93.0	50-95
	Pt Y	Pt <sub>5</sub> Y	91.7	
	Pt La	Pt <sub>5</sub> La	87.3	
55	Pt Hf	Pt <sub>3</sub> Hf	76.6	
	Pt Nb	Pt <sub>3</sub> Nb	86.3	
	Pt Zr	Pt <sub>2</sub> Zr	86.6	
60	Pt Lanthanide	Pt <sub>3</sub> (Ce-Lu)	81.4-84.5	

65 The present invention will now be illustrated by the following Examples:—

## 0 0 0 6 9 5 1

### Example 1

To an alloy having a nominal composition (expressed in wt%) as set out below (incidental elements and impurities mounting to 1 wt%)

	Ni	Al	Cr	C
	78.0	6.9	12.33	1.77

various additions were made to give alloys A, B, C and D as shown in Table 2.

TABLE 2

Designation of Alloy	Additive Z comprising:—		Oxidation Resistance	Time to rupture (hours) when tested in air at 1000°C under a tensile stress of 100 MPa
	Pt m <sub>p</sub> wt %	Y m <sub>c</sub> wt %		
Basic Alloy	0	0	Poor	200 – 317
A	0	0.5	Better than above, but Al <sub>2</sub> O <sub>3</sub> skin not completely tenacious	1026
B	1.96	0	Better than A but the Al <sub>2</sub> O <sub>3</sub> skin not completely resistant to handling	14
C	1.96 (Stoichiometric Pt <sub>5</sub> Y)	0.18	Oxide skin very tenacious and resistant to handling at room temperature	907
D	1.96 (Pt <sub>5</sub> Y + 0.5 wt % Y)	0.68	Oxide skin very tenacious and resistant to handling at room temperature	42

Alloys C and D are according to the invention. The basic alloy and alloys A and B are for comparison.

The observations set out below were made on the five alloy compositions given in Table 2.

#### Microstructure

Directional solidification of the basic alloy at a rate of 300 mm/hour in a temperature gradient of about 13°Kmm<sup>-1</sup> produced an ingot in which were present Cr<sub>3</sub>C<sub>2</sub> fibres well aligned within a gamma nickel matrix which contained equi-axed particles of gamma prime (Ni<sub>3</sub>Al). The alloys A and D contained yttrium in excess of that required for the formation of Pt<sub>5</sub>Y and, in addition to the phases mentioned above, these two alloys also exhibited an elongated eutectic-like constituent which tended to run parallel to the aligned carbide fibres. This irregular constituent is thought to contain an yttrium-carbon compound.

The alloy to which 1.96% by weight of platinum(alloy B) had been added contained a quite different irregular phase. This phase is thought to be pure graphite deposited due to the release of carbon on the formation of a highly stable platinum-chromium compound.

No additional phases or micro constituents were observed in the alloy to which the platinum and yttrium in the ratio needed to form the compound Pt<sub>5</sub>Y (alloy C) had been added. (If the compound Pt<sub>5</sub>Y retained its separate identity when added to the alloy it must, presumably, have been in the form of a dispersion too fine to resolve with the optical microscope). The alloy displayed a regular aligned eutectic structure with thin fibres of Cr<sub>3</sub>C<sub>2</sub> supported in a matrix consisting of nickel containing finely distributed particles of the compound Ni<sub>3</sub>Al.

Oxidation Resistance

The basic alloy to which no addition had been made had a relatively poor resistance to oxidation when exposed to air at high temperatures either cyclically or under isothermal conditions. The initially formed scale of Al<sub>2</sub>O<sub>3</sub> spalled readily and oxidation continued with the formation of Cr<sub>2</sub>O<sub>3</sub>, nickel-chromium spinels, and with internal oxidation.

The addition of yttrium alone (alloy A) improved the oxidation resistance significantly by stabilising the layer of Al<sub>2</sub>O<sub>3</sub> which formed initially. Even so, the Al<sub>2</sub>O<sub>3</sub> scale which formed was not completely tenacious, and spalling occurred under tests carried out in a high velocity gas stream approximating in composition and speed to the hot gas passing over the first stage blading in a gas turbine, when the alumina scale was removed as rapidly as it was formed leaving behind the more tenacious skin of nickel-chromium oxide.

The alloy to which the stoichiometrically adjusted Pt<sub>5</sub>Y addition has been made (alloy C) developed an oxidation testing in air a protective skin of alumina which was resistant to spalling when cycled in temperature and also when handled at room temperature. After exposure to air at atmospheric pressure for 1000 hours at 1000°C no measurable oxide skin was observed and the carbide fibres retained their integrity to the specimen surface.

Hot salt corrosion resistance

Specimens (in the form of cylinders 6 mm dia x 44 mm) of alloys A and C and of the basic alloy were tested in a gas burner rig in conditions of hot salt corrosion at a temperature of 850°C. A commercial superalloy designated IN 713 LC was also tested for purposes of comparison. Two specimens of each alloy were tested.

The principal impurities in the fuel used in the burner were 0.15 ppm sulphur and 50 ppm sodium, the latter being introduced in the form of sodium carboxylite. In addition 50 ppm of sodium chloride was injected into the air feed in the form of sea water. The specimens were removed and examined at 24 hr intervals and the tests were run for a total of 300 hrs.

At the end of the tests all the alloys showed distinct evidence of attack although all of the eutectic-based alloys retained a more regular cylindrical shape than the IN 713 LC specimens. The latter was subject to internal attack along grain boundaries giving both more rapid and irregular corrosion than with the former which degraded by regular surface attack. The depths of penetration of the corrosion products, determined from transverse sections of the specimens are given in Table 3 below, from which it will be seen that the most corrosion resistant alloys are the basic (eutectic) alloy and the alloy C according to the invention.

TABLE 3

Alloy	Penetration of corrosion products below original surface (mm)
Basic Alloy	0.25; 0.20
Alloy A	0.78; 0.30
C	0.20; 0.27
IN 713 LC	1.22; 1.74

Creep Behaviour

Table 2 above shows the results of creep tests performed in air on the various alloys at 1000°C under a direct tensile stress of 100 MPa. The alloy C retained the mechanical properties of the yttrium doped alloy (alloy A) and both were substantially stronger at high temperatures than those containing either Pt or Y (alloys B and D respectively) above the level required to form stoichiometric Pt<sub>5</sub>Y.

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### Example 2

The nominal compositions of the alloys studied are shown in Table 4. Alloy K is according to the invention and the remaining alloys are for comparison.

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TABLE 4

	Alloy	Cr	Al	Pt	Hf	wt%
10	J	10	11	1	—	)
	K	10	11	0.9	0.3	)
	L	10	11	—	—	)
15	M	10	11	—	1	)
	N	10	11	—	0.3	) balance cobalt

Oxidation experiments were carried out in static air at 1 atmosphere pressure in a horizontal tube furnace. Thermogravimetric measurements were performed in a Sartorius automatic recording micro-balance at 1100°C. Results are as set out below and as shown in Table 4.

#### Alloy Microstructure

No microstructural differences between alloys J and L were observed. In alloy J, neither electron probe micro-analysis or optical examination were able to detect any intermetallics containing platinum. Alloy K (containing 0.3 Hf — 0.9 Pt) had a grain size smaller than alloy L and similar to that in Hf-containing alloys with no platinum (alloys M and N). Again, no platinum-containing intermetallics could be detected in alloy K and it would appear that the hafnium and platinum additions were both completely soluble in the alloy, at least at the concentrations used here. On oxidation of the samples of alloy K, the hafnium usually oxidised internally, but there was no apparent segregation of the platinum.

#### Oxidation Kinetics

Figures 1 and 2 of the accompanying drawings show the effect of Pt and Pt + Hf additions on the rate of weight gain of the basic Co-10Cr-11Al alloy L under isothermal oxidising conditions at 1100°C. Figure 1 shows that the addition of 1% Pt (alloy J) results in a slight decrease in the isothermal oxidation rate. Figure 2 is a plot of wt gain versus time each on a logarithmic scale. When measured over the period 10 to 100 h to avoid the initial transient stages of oxidation, the slope of the curve for alloy L has a value of 0.5, corresponding almost exactly to a parabolic rate law. The slope is reduced to 0.4 for the Co-10Cr-11Al-1Pt alloy J.

For the alloys containing 0.3 wt% Hf (alloys K and N) the situation was rather different. Neither conformed to a parabolic rate law, the Co-10Cr-11Al-0.3Hf alloy N had a slope of 0.28 whilst for the alloy containing 0.9 Pt (alloy K) the slope was 0.18. In addition, Figure 1 shows that the initial stages of oxidation of alloy K were terminated more rapidly than in alloy N, and that with both these Hf-containing alloys the transient stage was shorter than with the Hf-free alloys J and L. As indicated previously, it is difficult to define precisely the end of the transient stage, but typically it lasted for  $\frac{1}{2}$ —1 h. Table 5 compares with weight gains of the four alloys after this period (1 h) and after 120 h exposure. Also included for comparison are the data for an alloy R known to the Applicants to have a particularly low overall weight gain under these conditions. This alloy R is Co-10Cr-11Al-0.3Hf internally oxidized for 300 h at 1200°C.

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TABLE 5

## Weight Gain Data at 1100°C: Isothermal Exposure

5	Alloy	Weight Gain mg/cm <sup>2</sup>	
		1 h	120 h
	L : Co-10Cr-11Al	0.15	0.9
10	J : Co-10Cr-11Al-1Pt	0.16	0.72
	N : Co-10Cr-11Al-0.3Hf	0.2	0.53
15	K : Co-10Cr-11Al-0.3Hf-0.9Pt	0.1	0.2
	R : Co-10Cr-11Al-0.3Hf	0.09	0.18
20	(internally oxidized 300 h at 1200°C).		

## Scale Morphology

The Al<sub>2</sub>O<sub>3</sub> scale which formed on the alloy Co-10Cr-11Al-1Pt (alloy J) after 265 h oxidation at 1200°C was not adherent and spalled from the alloy on cooling. The oxide was multi-layered in many locations, particularly at the corners of the sample, and the outer layer of oxide at the gas/scale interface was heavily wrinkled. Similar features were observed with the ternary Co-Cr-Al alloy (alloy L) oxidized under similar conditions.

Surface examinations of the alloy Co-10Cr-11Al-0.3Hf-0.9Pt (alloy K) after oxidation at 1200°C revealed features similar to those of the alloy Co-10Cr-11Al-0.3Hf (alloy N). The Al<sub>2</sub>O<sub>3</sub> scale was tightly adherent to the substrate and spalled during cooling only from small discrete areas. The major difference between the two alloys was that, with the Pt-free alloy N, the substrate surface appeared to be more heavily convoluted than with the Pt-containing alloy K.

## Claims

1. An alloy consisting of at least 5 wt% of chromium, from 0 to 3 wt% C, a component X, a component Z, and a balance of one or more of nickel, cobalt and iron together with incidental elements and impurities if any, wherein component X is one or more of:

- (i) at least 2 wt% in total of one or more of aluminium, titanium, tantalum and niobium;
- (ii) at least 5 wt% in total of one or both of tungsten and molybdenum; and
- (iii) at least 60 wt% of nickel;

and having a strengthening phase selected from either a transition metal carbide or an intermetallic transition metal compound, and component Z comprises m<sub>p</sub> wt% of one or more platinum-group metals (as herein defined) together with m<sub>c</sub> wt% of one or more platinum-complementing metals (as herein defined), where the limits for m<sub>p</sub> and m<sub>c</sub> are set by the expressions

$$0.1 \leq m_p + m_c \leq 5$$

$$0.3 \leq m_p/m_c \leq 20$$

the weight percentages being expressed in terms of the total alloy weight.

2. An alloy according to claim 1 wherein said one or more platinum-group metals and said one or more platinum-complementing metals are present in substantial stoichiometric association.

3. An alloy according to claim 1 or claim 2 having up to 3 wt% C, and wherein the carbon is present throughout the microstructure as a dispersed transition metal carbide phase.

4. An alloy according to claim 1 or claim 2 without carbon and having an intermetallic transition metal compound dispersed throughout the microstructure.

5. An alloy according to any of claims 1 to 4 wherein component Z comprises from 50 wt% to 93 wt% of one or more of the platinum-group metals expressed as a percentage of component Z.

6. A method of modifying the oxidation resistance and corrosion resistance of a nickel-based, cobalt-based or iron-based alloy having a strengthening phase selected from either a transition metal carbide or an intermetallic transition metal compound which comprises including in the alloy composition an amount m<sub>p</sub> wt% of one or more platinum-group metals (as herein defined) and an amount m<sub>c</sub> wt% of one or more platinum-complementing metals (as herein defined), where the limits for m<sub>p</sub> and m<sub>c</sub> are set by the expressions

$$0.1 \leq m_p + m_c \leq 5$$

$$0.3 \leq m_p/m_c \leq 20$$

5 the weight percentages being expressed in terms of the total weight of the modified alloy.

7. A method according to claim 6 wherein said one or more platinum-group metals and said one or more platinum-complementing metals are present in substantial stoichiometric association.

8. A method according to claim 6 or claim 7 wherein the strengthening phase is a transition metal carbide.

10 9. A method according to claim 6 or claim 7 wherein the strengthening phase is an intermetallic transition metal compound.

10. A method according to any of claims 6 to 9 wherein said included metals comprise from 50 wt% to 93 wt% of one or more of the platinum-group metals expressed as a percentage of the included metals.

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### Revendications

1. Alliage composé d'au moins 5% en poids de chrome, 0 à 3% en poids de C, un composant X et un composant Z, le reste se composant de nickel et/ou de cobalt et/ou de fer avec des éléments

20 d'accompagnement et des impuretés, le cas échéant, le composant (X) étant constitué de  
(i) au moins 2% en poids au total d'aluminium et/ou de titane et/ou de tantale et/ou de niobium,  
(ii) au moins 5% en poids au total de tungstène et/ou de molybdène et  
(iii) au moins 60% en poids de nickel

comprenant une phase de renforcement choisie parmi les carbures de métaux de transition ou parmi les  
25 composés intermétalliques de métaux de transition, le composant (Z) contenant  $m_p$  % en poids d'un ou plusieurs métaux du groupe du platine comme définis ensemble avec  $m_c$  % en poids d'un ou plusieurs métaux complémentaires du platine comme définis, les limites étant définies par les expressions

$$0,1 \leq m_p + m_c \leq 5 \text{ et}$$

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$$0,3 \leq m_p/m_c \leq 20,$$

et les pourcentages en poids se référant toujours au poids total de l'alliage.

2. Alliage selon la revendication 1, caractérisé en ce que le ou bien les métaux du groupe du platine  
35 et le ou bien les métaux complémentaires du platine étant présents en quantités nettement stoechiométriques.

3. Alliage selon la revendication 1 ou 2 contenant jusqu'au 3% en poids de C, caractérisé en ce que le carbone est présent à travers la microstructure en tant qu'une phase dispersée de carbure de métal de transition.

40 4. Alliage selon la revendication 1 ou 2 sans carbone, caractérisé par un composé intermétallique d'un métal de transition dispersé à travers la microstructure.

5. Alliage selon l'une des revendications 1 à 4, caractérisé en ce que le composant Z contient 50 à 93% en poids d'un ou plusieurs métaux du groupe du platine exprimé en pourcentage du composant Z.

6. Procédé pour modifier la résistance à l'oxydation et à la corrosion d'alliages à base de nickel,  
45 cobalt ou fer comprenant une phase de renforcement choisie parmi les carbures de métaux de transition ou bien parmi les composés intermétalliques de métaux de transition, comprenant l'introduction de  $m_p$  % en poids d'un ou plusieurs métaux du groupe du platine comme définis et de  $m_c$  % en poids d'un ou plusieurs métaux complémentaires du platine comme définis dans la composition de l'alliage, les limites étant définies par les expressions

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$$0,1 \leq m_p + m_c \leq 5 \text{ et}$$

$$0,3 \leq m_p/m_c \leq 20,$$

55 et les pourcentages en poids se référant toujours au poids total de l'alliage modifié.

7. Procédé selon la revendication 6, caractérisé en ce qu'un ou plusieurs métaux du groupe du platine et un ou plusieurs métaux complémentaires du platine se présentent en quantités nettement stoechiométriques.

8. Procédé selon la revendication 6 ou 7, caractérisé en ce que la phase de renforcement est  
60 constituée d'un carbure d'un métal de transition.

9. Procédé selon la revendication 6 ou 7, caractérisé en ce que la phase de renforcement est constituée d'un composé intermétallique d'un métal de transition.

10. Procédé selon l'une des revendications 6 à 9, caractérisé en ce que les métaux contenus  
65 contiennent 50 à 93% en poids d'un ou plusieurs métaux du groupe du platine, exprimé en pourcentage des métaux contenus.

## Patentansprüche

1. Legierung aus mindestens 5 Gew.-% Chrom, 0 bis 3 Gew.-% C, einer Komponente X und einer Komponente Z, wobei der Rest aus Nickel und/oder Kobalt und/oder Eisen gegebenenfalls zusammen mit Begleitelementen und Verunreinigungen besteht, wobei die Komponente (X) aus
- (i) insgesamt mindestens 2 Gew.-% Aluminium und/oder Titan und/oder Tantal und/oder Niob,
  - (ii) insgesamt mindestens 5 Gew.-% Wolfram und/oder Molybdän und
  - (iii) mindestens 60 Gew.-% Nickel

besteht, mit einer Verstärkungsphase die unter de Übergangsmetallcarbiden oder intermetallischen Übergangsmetallverbindungen ausgewählt ist, wobei die Komponente Z  $m_p$  Gew.-% eines oder mehrerer Metalle der Platingruppe wie definiert zusammen mit  $m_c$  Gew.-% eines oder mehrerer Platin-Ergänzungsmetalle wie definiert enthält, die Grenzwerte für  $m_p$  und  $m_c$  durch die Ausdrücke

$$0,1 \leq m_p + m_c \leq 5 \text{ und}$$

$$0,3 \leq m_p/m_c \leq 20$$

gegeben und die Gew.-%-Angaben jeweils auf das Gesamtgewicht der Legierung bezogen sind.

2. Legierung nach Anspruch 1, dadurch gekennzeichnet, daß das bzw die Metalle der Platingruppe und das bzw die Platin-Ergänzungsmetalle in im wesentlichen stöchiometrischen Mengen vorliegen.

3. Legierung nach Anspruch 1 oder 2 mit bis zu 3 Gew.-% C, dadurch gekennzeichnet, daß der Kohlenstoff über die ganze Mikrostruktur als disperse Übergangsmetallcarbidgephase vorliegt.

4. Legierung nach Anspruch 1 oder 2 ohne Kohlenstoff, gekennzeichnet durch eine intermetallische Übergangsmetallverbindung, die über die gesamte Mikrostruktur dispers verteilt ist.

5. Legierung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Komponente Z 50 bis 93 Gew.-% eines oder mehrerer Metalle der Platingruppe, ausgedrückt als Prozentsatz der Komponente Z, enthält.

6. Verfahren zur Modifizierung der Oxidationsbeständigkeit und Korrosionsfestigkeit von Legierungen auf Nickel-, Kobalt- oder Eisenbasis mit einer unter den Übergangsmetallcarbiden oder intermetallischen Übergangsmetallverbindungen ausgewählten Verstärkungsphase, wobei  $m_p$  Gew.-% eines oder mehrerer Metalle der Platingruppe wie definiert und  $m_c$  Gew.-% eines oder mehrerer Platin-Ergänzungsmetalle wie definiert in die Legierungszusammensetzung eingebracht werden und die Grenzwerte für  $m_p$  und  $m_c$  durch die Ausdrücke

$$0,1 \leq m_p + m_c \leq 5 \text{ und}$$

$$0,3 \leq m_p/m_c \leq 20$$

gegeben und die Gew.-%-Angaben jeweils auf das Gesamtgewicht der modifizierten Legierung bezogen sind.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß eines oder mehrere Metalle der Platingruppe und eines oder mehrere Platin-Ergänzungsmetalle in im wesentlichen stöchiometrischen Mengen eingesetzt werden.

8. Verfahren nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß die Verstärkungsphase aus einem Übergangsmetallcarbidge besteht.

9. Verfahren nach einem der Ansprüche 6 oder 7, dadurch gekennzeichnet, daß die Verstärkungsphase aus einer intermetallischen Übergangsmetallverbindung besteht.

10. Verfahren nach einem der Ansprüche 6 bis 9, dadurch gekennzeichnet, daß die enthaltenen Metalle 50 bis 93 Gew.-% eines oder mehrerer Metalle der Platingruppe enthalten, ausgedrückt als Prozentsatz der enthaltenen Metalle.

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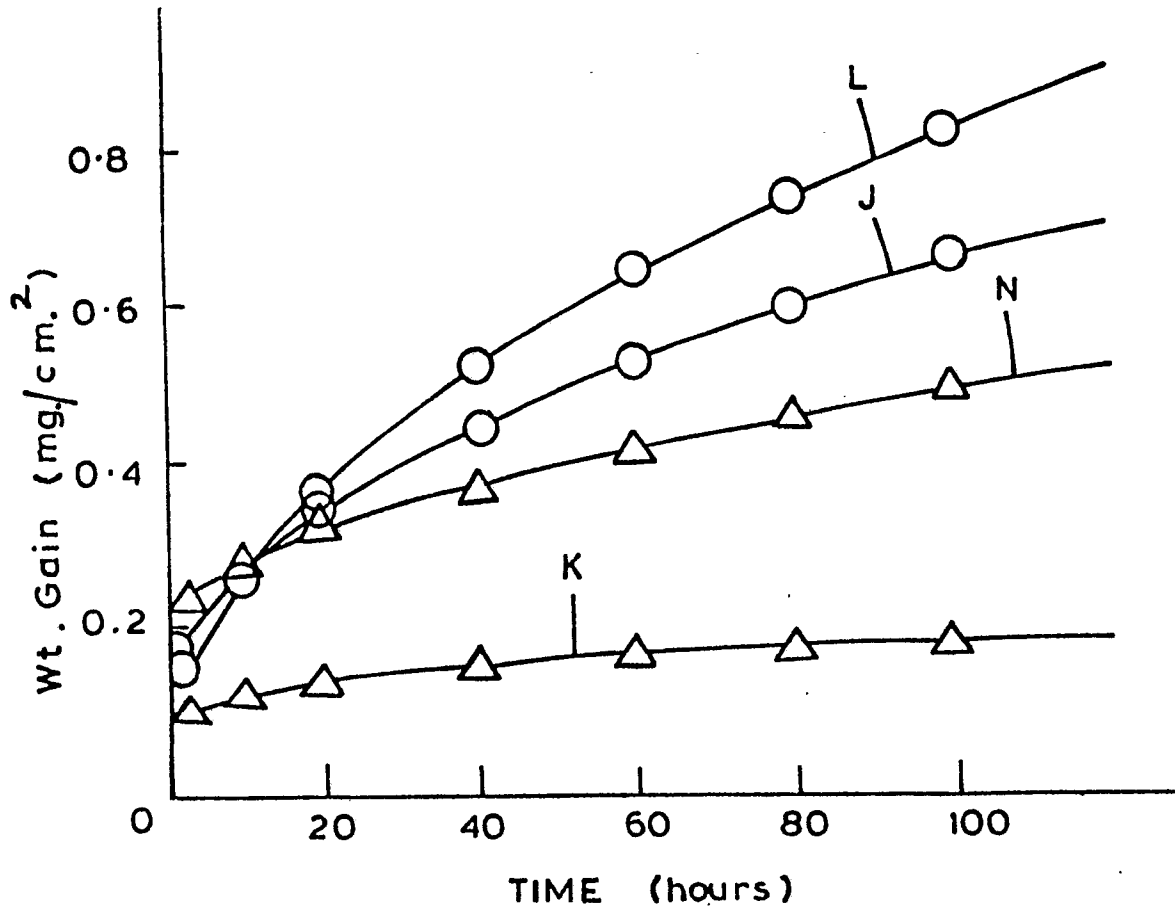


FIG.1.

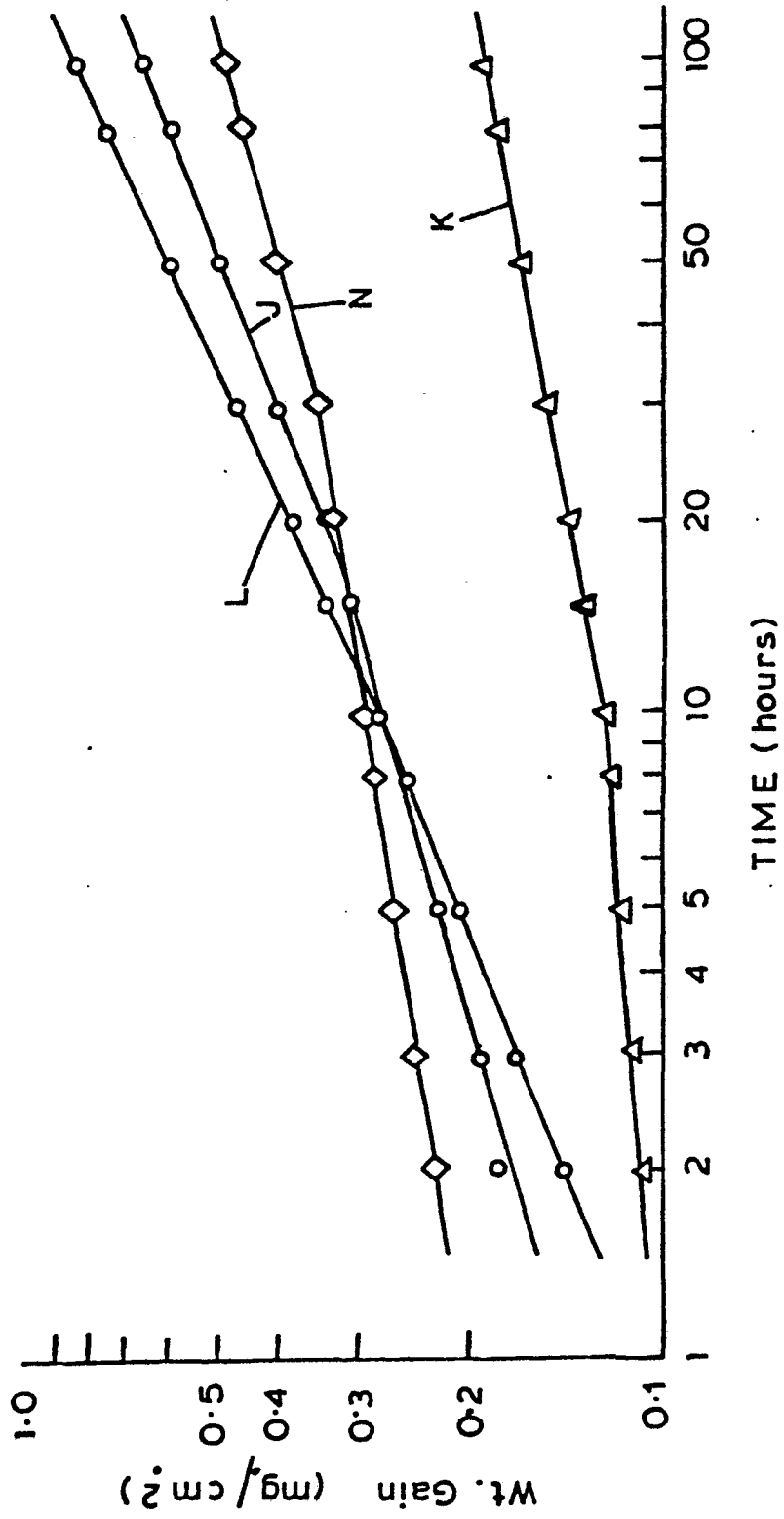


FIG.2.