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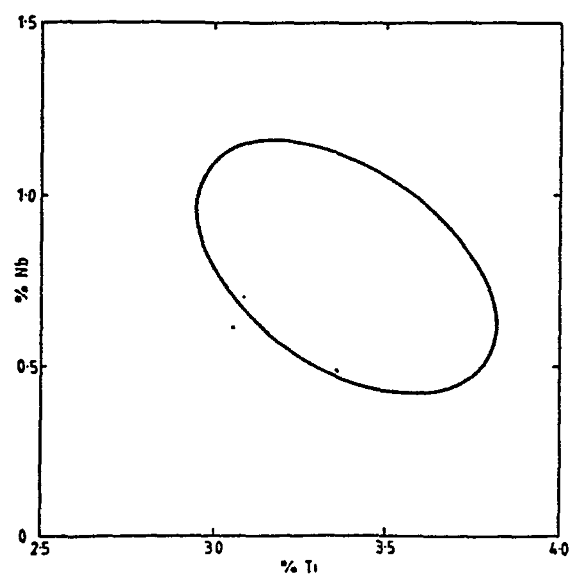
(54) **Nickel-chromium-cobalt base alloys and castings thereof.**

(57) Nickel-chromium-cobalt base casting alloys having compositions within the range (in percent by weight) Cr 20-23%, Co 17-23%, W 1-2.5%, Mo 0-0.5%, Nb 0.4-1.2%, Ta 0.6-1.4%, Ti 2.95-3.85%, Al 1.6-2.8%, Hf 0.3-1.3%, Zr 0.005-1%, B 0.001-1%, C 0.01-0.25%, balance Ni and impurities, wherein the contents of Nb, Hf, Ti and Al are further specifically correlated, exhibit at high temperatures a combination of good resistance to corrosion and very high creep-rupture lives, particularly when directionally solidified. The alloys are useful as materials for cast blades and vanes for gas turbines for marine and land-based service.



EP 0 053 948 A1

Nickel-Chromium-Cobalt Base alloys and Castings Thereof

This invention relates to improved castable nickel-chromium-cobalt base alloys and castings of these alloys.

Nickel-chromium and nickel-chromium-cobalt base alloys containing titanium and aluminium develop, on suitable heat-treatment, a high level of creep-rupture strength at high temperatures and are widely used in applications giving rise to high stress at elevated temperatures, such as gas turbine engine rotor blades and vanes. However, the need to use impure fuels such as diesel oil in land-based and marine propulsion turbines gives rise to sulphidation attack. Operation in marine and other chloride-containing environments also results in severe corrosion problems.

Many gas turbine and other components, particularly those of complex design, are best produced by precision casting, and there is thus a need for an alloy that can be cast to shape and possesses, in the cast form, a high level of strength at elevated temperatures in conjunction with good resistance to corrosion in sulphur- and chloride-containing environments and structural stability, i.e. freedom from sigma-phase formation, after extended service at elevated temperatures.

In our UK specification No. 1 367 661 we have described and claimed alloys that exhibit this combination of properties and contain from 0.02 to 0.25% carbon, from 20 to 25% chromium, from 5 to 25% cobalt, one or both of molybdenum (up to 3.5%) and tungsten (up to 5%) in such amounts that the value of %W+ 0.5 (%Mo) is from 0.5 to 5%, from 1.7 to 5% titanium and from 1 to 4% aluminium, with the provisos that the sum of the aluminium and titanium contents is from 4 to 7% and the ratio of titanium to aluminium is from 0.75 : 1 to 4:1, from 0.5 to 3% tantalum, from 0 to 3% niobium, from 0.005 to 1.0%

zirconium and from 0 to 1.99% hafnium, with the proviso that the value of %Zr + 0.5 (%Hf) is from 0.01 to 1%, from 0.001 to 0.05% boron, and from 0 to 0.2% in total of yttrium or lanthanum or both, the balance, apart from impurities, being nickel in an amount of at least 30%. All the percentages and ratios in this composition range, and elsewhere in the present specification and claims, are by weight.

One alloy according to this specification is available commercially under the designation IN-939, with the nominal composition:

C 0.15%, Cr 22.5%, Co 19%, W 2%, Ti 3.7%,
Al 1.9%, Ta 1.4%, Nb 1.0%, Zr 0.1%,
B 0.01%, Ni balance.

After heat-treatment consisting of solution-heating for 4 hours at 1150°C, air-cooling and then ageing for 16 hours at 850°C, equiaxed castings of Alloy IN-939 (made by vacuum melting followed by remelting and casting under vacuum) typically have a creep-rupture life at 870°C under a stress of 185 N/mm^2 (19 kgf/mm^2) of about 1250 hours, which corresponds to about 850 hours at the same temperature under the higher stress of 200 N/mm^2. When the alloys are directionally-solidified to produce a columnar crystal structure the creep-rupture life, when stressed along the major crystal axis, is increased to about 1170 hours at 870°C and 200 N/mm^2.

In UK specification No. 1 367 661 creep-rupture test results are also given for two alloy compositions with and without additions of hafnium. Comparison of the results for the hafnium-containing and hafnium-free alloys shows that the presence of 0.75% hafnium had little or no effect on the creep-rupture life, though it produced some increase in the elongation at rupture.

The present invention is based on the discovery that by means of a special correlation of the contents of titanium, aluminium, niobium and hafnium in a range of alloy compositions that also contain nickel, chromium, cobalt, tungsten (with or without molybdenum), tantalum, carbon, boron and zirconium, the creep-rupture life of castings of the alloys, particularly in the directionally-solidified form, can be further substantially increased.

According to the invention, nickel-chromium-cobalt alloys contain from 20 to 23% chromium, from 17 to 23% cobalt, from 1 to 2.5% tungsten, from 0 to 0.5% molybdenum, from 0.4 to 1.2% niobium, from 0.6 to 1.4% tantalum, from 2.95 to 3.85% titanium, from 1.6 to 2.8% aluminium, from 0.3 to 1.3% hafnium, from 0.005 to 1% zirconium, from 0.001 to 1% boron, and from 0.01 to 0.25% carbon, the balance apart from impurities, being nickel, with the proviso that the contents of niobium, hafnium, titanium and aluminium (in wt. % of the alloy) are so correlated that they satisfy the expression:

$$28327\,Nb + 804\,Hf + 36956\,Ti + 115057\,Al - 6676\,Nb^2 - 564\,Hf^2 - 4847\,Ti^2 - 54349\,Al^2 + 8392\,Al^3 - 5255\,(Nb \times Ti) \geqslant 153123.$$

The value of this expression is referred to herein as the Correlation Factor, and advantageously it is at least 153223.

In general the contents of zirconium, boron and carbon preferably lie within the narrower ranges 0.005 - 0.15% zirconium, 0.002 - 0.02% boron and 0.05 to 0.20% carbon though smaller amounts of carbon and boron may be present in single-crystal castings where their contribution to grain-boundary strengthening is not required.

Within the preferred composition range the alloys of the invention, in the directionally-solidified form and after solution-heating and ageing, may exhibit creep-rupture lives in excess of 1600 hours, at 200 N/mm^2 and 870°C.

The effect of the required correlation with hafnium and aluminium in restricting the contents of titanium and niobium is shown for alloys that contain 0.7% hafnium and 2% aluminium in the accompanying drawing, in which the alloys having compositions corresponding to points in the area defined by the ellipse have a Correlation Factor of at least 153 223.

Apart from the constituents set forth above, impurities that may be present include small amounts of silicon, manganese and iron, though these should be kept as low as possible. The silicon content should not exceed 1%, and preferably is less than 0.5%, most preferably not more than 0.2%, as it impairs the corrosion resistance. Manganese should be less than 1%, and is preferably not more than 0.2%. The iron content may be as much as 3%, but is preferably not more than 0.5%. Traces of nitrogen and sulphur may also be present, but preferably not more than 0.005% each.

A preferred alloy according to the invention has the nominal composition:

Cr 22%, Co 19%. W 2%, Ta 1.1%, Ti 3.4%, Nb 0.8%, Hf 0.7%, Al 2%, C 0.15%, Zr 0.1%, B 0.01%, balance Ni and impurities.

The Correlation Factor calculated for this composition is 153 855.

The alloys should be prepared by vacuum melting and then subjected to vacuum refining, e.g. by holding under vacuum for from 15 minutes to 1 hour. In the production of castings by remelting the alloys, the cast stick or other initial form should be remelted and cast under vacuum.

The alloys have good castability and are particularly suitable for the production of cast shaped articles and parts. To obtain the best properties, in particular creep-rupture life, resistance to thermal fatigue, and ductility, the castings are preferably directionally solidified to obtain a columnar crystal structure, but the invention specifically includes shaped castings made from the alloys both with substantially equiaxed and with columnar crystal structures. Such castings include parts of gas turbine enginess, for example gas turbine rotor or stator blades, both with and without cooling passages, and integrally bladed turbine rotor discs. Directional solidification may be effected in any manner conventionally employed for high-temperature alloys.

To develop the desired creep-rupture properties, the castings must be subjected to a heat-treatment comprising solution-heating and ageing. The solution-heating preferably consists in heating for from 2 to 24 hours at from 1120 to 1200°C, and is followed by ageing in the temperature range from 1020 to 650°C for from 2 to 24 hours. The ageing may be effected in a single stage, or in two stages, e.g. from 2 to 12 hours at 1020-870°C and then from 6 to 48 hours at 860-650°C. Suitable heat treatments are:

(i) 4 hours/1160°C + 16 hours/843°C (single ageing)

(ii) 8 hours/1160°C + 4 hours/900°C + 16 hours/760°C (double ageing).

Between each stage of heat-treatment the alloy may be air-cooled.

The importance of maintaining the alloy composition and Correlation Factor within the range according to the invention is shown by tests performed on a series of alloys having the compositions set forth in Table I below. Of these, Alloys 1 to 3 are in accordance with the invention, while Alloys A to E are not. All the alloys were melted and cast in vacuum and cast using a hot refractory or exothermic mould with a chill base to produce castings having a columnar crystal structure. The castings were heat treated as indicated in Table II, and standard creep-rupture test pieces were machined from them so that the whole of the test piece had a columnar crystal structure extending axially of the test piece.

The test pieces were then subjected to creep-rupture tests under a stress of 200 N/mm^2 at 870°C, with the results set out in Table II, which also includes the Correlation Factor calculated from the alloy compositions.

The test results show that the creep-rupture lives of Alloys 1 to 3 according to the invention are substantially better than those of Alloys A to E, of which Alloy E is IN-939.

TABLE I

Composition (weight %)

Alloy No.	C	Cr	Co	W	Nb	Ta	Hf	Ti	Al	Zr	B
1	0.14	22.2	19.0	2.0	0.8	1.1	0.7	3.5	2.3	0.09	0.007
2	0.16	22.0	18.9	2.0	0.8	1.1	0.8	3.5	2.0	0.09	0.006
3	0.15	22.3	18.9	2.1	0.9	1.1	0.7	3.5	1.9	0.11	0.009
A	0.16	22.1	18.7	1.8	1.3	1.1	1.0	3.0	2.2	0.11	0.009
B	0.15	21.9	18.8	1.8	0.3	1.2	1.0	3.4	2.1	0.11	0.008
C	0.15	22.1	18.6	1.9	1.3	1.1	0.9	3.3	2.1	0.10	0.010
D	0.15	22.4	18.9	1.9	0.5	1.1	0.6	3.8	2.4	0.10	0.010
E	0.11	22.6	18.6	2.0	1.0	1.4	-	3.7	2.1	0.10	0.020

TABLE II

Alloy No.	Heat-treatment	Creep-rupture properties at 200 N/mm^2 /870°C		Correlation Factor
		Life (h)	Elong. (%)	
1	(a)	2414	21.0	153 162
2	(a)	1807	26.3	153 781
3	(b)	2007	21.0	153 759
A	(a)	1306	30.2	151 967
B	(a)	1284	15.8	152 055
C	(a)	1408	26.6	152 095
D	(a)	1691	26.3	152 329
E	(c)	1164	30.6	-

(a) 8 h/1160°C AC* + 4 h. 900°C AC + 16 h./760°C AC.

(b) 8 h/1160°C AC +16 h. 760°C AC.

(c) 4 h/1160°C AC +16 h. 850°C AC.

* AC = air-cooled.

Hot-corrosion tests were carried out on an alloy according to the invention having the composition, in per cent by weight (Alloy 4)

C 0.15, Cr 22.0, Co 19.0, W 2.0, Nb 0.8, Ta 1.1, Hf 0.7, Ti 3.6, Al 2.0, Zr 0.10, B 0.01, Ni balance

and on a specimen of IN-939 (Alloy E). Cylindrical test pieces machined from heat-treated castings of the alloys were exposed for 500 hours in a rig burning marine diesel fuel, at an air: fuel ratio of 30:1. Ditertiary butyl sulphide was added to raise the sulphur content of the fuel to 3% by weight, and ASTM sea salt was added to the hot gas stream at a concentration in air of 10 ppm. The specimens were heated at 704°C and thermally cycled to room temperature using forced air cooling once every 24 hours. The depth of penetration of the corrosion from the surface of the specimens was then measured, and found to be as follows:

Alloy No.	Average penetration in micrometres
4	2.5, 7.5, 7.5, 5.0 (four specimens)
F	38

Although primarily intended for the production of castings, the alloys may also be useful in the wrought forms. They may be used to produce single crystal castings, for example single-crystal gas turbine blades or vanes. If heat-treated in vacuum, they may be rapidly quenched after each stage of heating by gas fan quenching.

Claims

1. A nickel-chromium-cobalt alloy, characterised in that it contains from 20 to 23% chromium, from 17 to 23% cobalt, from 1 to 2.5% tungsten, from 0 to 0.5% molybdenum, from 0.4 to 1.2% niobium, from 0.6 to 1.4% tantalum, from 2.95 to 3.85% titanium, from 1.6 to 2.8% aluminium, from 0.3 to 1.3% hafnium, from 0.005 to 1% zirconium, from 0.001 to 1% boron, and from 0.01 to 0.25% carbon, the balance, apart from impurities, being nickel, wherein the contents of niobium, hafnium, titanium and aluminium are so correlated that they satisfy the expression (the Correlation Factor):

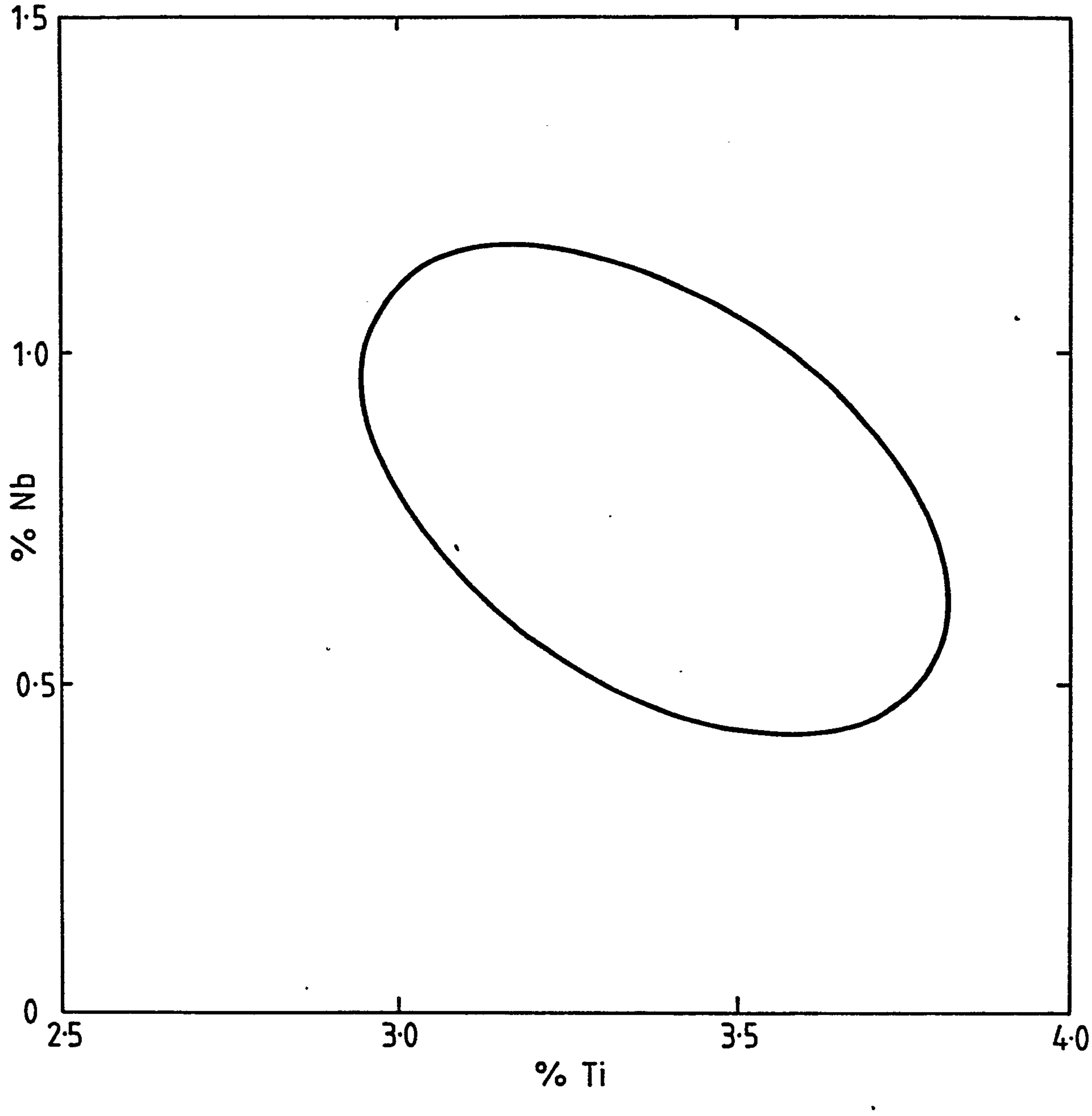
$$28327\,Nb + 804\,Hf + 36956\,Ti + 115057\,Al - 6676\,Nb^2 - 564\,Hf^2 - 4847\,Ti^2 - 54349\,Al^2 + 8392\,Al^3 - 5255\,(Nb \times Ti) \geqslant 153123.$$

2. An alloy according to claim 1 in which the carbon content is from 0.05 to 0.20%, the zirconium content is from 0.005 to 0.15% and the boron content is from 0.002 to 0.02%.

3. An alloy according to claim 1 or claim 2 in which the value of the Correlation Factor is at least 153223.

4. An alloy according to claim 1 that contains about 22% chromium, about 19% cobalt, about 2% tungsten, about 1.1% tantalum, about 3.4% titanium, about 0.8% niobium, about 0.7% hafnium, about 2% aluminium, about 0.15% carbon, about 0.1% zirconium, and about 0.01% boron, the balance, apart from impurities, being nickel.

5. A directionally-solidified casting made from an alloy according to any preceding claim.


1·5
1·0
0·5
0
% Nb
2·5
3·0
3·5
4·0
% Ti

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EUROPEAN SEARCH REPORT

Application number
EP 81 30 5828

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	FR - A - 2 136 231 (INTERNATIONAL NICKEL Ltd.)		C 22 C 19/05
	* claims 1,2,3,4 *	1	
A/D	& GB - A - 1 367 661		

A	GB - A - 607 616 (GRESHAM et al.)		
	* claims 1,3 *	1	
	---		TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
A	GB - A - 1 036 179 (HENRY WIGGIN & CY. Ltd.)		C 22 C 19/05
	* claim 1 *	1	
A	FR - A - 2 037 772 (INTERNATIONAL NICKEL Ltd.)		
	* claims 1,2 *	1	

A	FR - A - 1 071 278 (MOND NICKEL CY.)		
	* abstract 2,3,4 *	1	

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
O: non-written disclosure
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D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

λ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	17-03-1982	LIPPENS