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Applicant: SPECIAL METALS CORPORATION, Middle Settlement Road, New Hartford New York 13413 (US)

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- Inventor: Maurer, Gernant E., 23, Sherman Circle, Utica New York 13501 (US) Inventor: Boesch, William J., 16, Lin Road, Utica New York 13501 (US)
- Ø Designated Contracting States: CH DE FR GB IT LI SE
- (74) Representative: Sheader, Brian N. et al, ERIC POTTER & **CLARKSON 5 Market Way Broad Street, Reading** Berkshire, RG1 2BN (GB)

- Castable nickel base alloy.
- (5) A castable nickel base alloy is hot corrosion and oxidation resistant and has high temperature strength, including stress rupture strength at 760°C (1400°F) and 982°C (1800°F). The alloy contains, by weight: from 12 to 22% chromium, from 3 to 12% of at least one of up to 5% molybdenum, up to 10% tungsten and up to 2% vanadium, up to 6% tantalum, up to 2% columbium, from 2 to 6% aluminium, from 1 to 6% titanium, up to 5% cobalt, up to 2% iron, from 0.015 to 0.15% carbon, from 0.03 to 0.3% boron, up to 0.1% zirconium and balance nickel.

CASTABLE NICKEL BASE ALLOY

The present invention relates to nickel base alloys and, more particularly, to castable alloys characterised by their high temperature corrosion and strength properties and stable morphology.

Nickel base superalloys are particularly useful in high temperature applications such as gas turbines where high corrosion resistance and strength are 'required. alloying element is selected to obtain a balance of the required properties, including, e.g., hot corrosion resistance, oxidation resistance, mechanical strength, and ductility including rupture ductility at intermediate temperatures of 649° C to 816° C(1200 $^{\circ}$ F to 1500 $^{\circ}$ F) (the "ductility trough") as well as at high temperatures. On the other hand, the alloying elements must not contain excessively large amounts of any element or any combination of elements which will result in deleterious phase instabalities, substantial lattice mismatches or grain boundary weaknesses. Many of the alloying elements are continually in short supply and occasionally are unavailable. After the 1978 cobalt supply crisis, the art actively sought alloys

containing little, if any, cobalt. Cobalt has been added to superalloys for many purposes, including solid solution strengthening, phase stability, improved ductility and, possibly, hot corrosion resistance. Although superalloys containing no or small amounts of cobalt are available, generally speaking these alloys are unsatisfactory either because one property or another can not meet the high performance requirements for which superalloys are designed or because they form deleterious phases.

The alloys of the present invention contain small amounts, and preferably no, cobalt and other so-called strategic elements such as tantalum, columbium and the like. These improved alloys have high temperature properties such as high hot corrosion and oxidation resistance and high strength and ductility (including stress rupture) without the presence of deleterious phase stabilities. They are particularly useful for cast articles, such as turbine blades, vanes and the like, which must achieve their high strength by matrix solid solutioning, gamma prime precipitation and grain boundary strengthening mechanisms.

Broadly considered, the alloys of the present invention contain, by weight, from 12 to 22: chromium; from 3 to 12% of at least one of up to 5% molybdenum, up to 10% tungsten and up to 2% vanadium; up to 6% tantalum; up to 2% columbium; from 2 to 6% aluminum; from 1 to 6% titanium; up to 5% cobalt; up to 2% iron; from 0.015 to 0.15% carbon; from 0.03 to 0.3% boron; up to 0.1% zirconium; and balance nickel.

The invention also provides a castable corrosion resistant nickel base alloy having high hot strength wherein the

alloy consists of, by weight; from 15 to 22% chromium; from 5 to 10% of at least one of up to 3% molybdenum, 3 to 8% tungstenn and up to 1% Vanadium; up to 2% tantalum; up to 2% columbium; from 4 to 8% of at least one of from 2 to 5% aluminum and from 2 to 5% titanium; up to 5% cobalt; up to 2% iron; from 0.015 to 0.12% carbon; from 0.03% to 0.3% boron; up to 0.1% zirconium; and balance nickel.

The invention further provides a castable hot corrosion resistant nickel base alloy having high hot strength wherein the alloy consists of, by weight: from 14 to 20% chromium; from 5 to 10% of at least one of up to 5% molybdenum and 3 to 8% tungsten; from 4 to 8% of at least one of from 2 to 5% aluminum and from 2 to 5% titanium; up to 0.12 carbon; from 0.03 to 0.3% boron; up to 0.1% zirconium; and balance nickel.

The alloy of the present invention may additionally consist of, by weight: up to 5% copper; up to 5% manganese; up to 6% of at least one of up to 3% rhenium and up to 3% ruthenium; up to 0.17% of at least one of cerium, lanthanum and yttrium; and up to 0.15% of at least one of up to 0.05% magnesium, up to 0.05% calcium, up to 0.05% strontium and up to 0.05% barium. Chromium is added to the alloy in amounts sufficient to achieve hot corrosion resistance and oxidation resistance. However, more than 22% chromium may result in undesirable topologically close packed phases. Molybdenum and tungsten are added for solid solution strengthening and also precipitation strengthening (as gamma prime phases) and grain boundary strengthening (by partitioning to carbides and borides). The addition of molybdenum and tungsten must be carefully controlled to prevent phase instabilities or lattice

mismatches. Also, only minimum amounts of tungsten are used in rotating parts because of its high density. Vanadium may be added as a solid solution strengthener and to obtain a decrease in density, but vanadium impairs oxidation resistance and should not exceed 2% by weight of the alloy. Preferably the alloy contains no vanadium and from 5 to 10% total of molybdenum and tungsten.

Aluminum and titanium produce the gamma prime phase which precipitates to strengthen the alloy. In addition aluminum increases the oxidation resistance of the alloy. Also titanium forms MC carbides which strengthen the alloy at the expense of ductility properties. Gamma prime phases are largely coherent with the matrix, although the nickel, chromium, molybdenum and tungsten on the one hand and the aluminum and titanium on the other must be balanced to minimise the mismatch in the lattice while, preferably, effecting a slight triaxial compression upon the gamma prime compounds. Preferably, the alloy contains from 4 to 8% of aluminum and titanium. Excessive additions of aluminum or titanium will result in the presence of additional phases. The addition of more than about 6% aluminum to the alloy may result in "j" body centred phases. The aluminum to titanium ratio at least partially determines the gamma prime morphology, i.e., substituting titanium for aluminum changes the phase from cubic to spheroidal. Also excessive amounts of titanium will result in a hexagonal Ni₂Ti phase. Columbium and tantalum may be added in small amounts to precipitate as an additional body centred tetrahedronal phase; preferably, however, the alloy contains no more than 2% of either one

Carbon forms various types of carbides which either strengthen the matrix or grain boundaries. Boron forms borides with molybdenum, tungsten and chromium which appear to reduce grain boundary tearing and improve high temperature strength. It also appears that the presence of borides and carbides leads to a more stable grain boundary network which results in improved castability and retards the penetration of oxygen. The alloy preferably contains from 0.03 to 0.2% boron. Excessive amounts of carbon lead to embrittling phases and excessive amounts of boron lead to the formation of incipient melting compounds. The addition of small amounts of zirconium also strengthens the grain boundary, although the addition of excessive amounts causes incipient melting at the grain boundaries.

The alloy may contain up to 2% iron, although iron is usually considered to be a contaminant because it tends to decrease oxidation resistance and strength. Preferably, iron is present in lower amounts although larger amounts may be added where chromium is added as ferrochromium, a composition normally containing 70% chromium and 30% iron, and the design requirements are less exacting. In these applications, iron is also desirable because it provides some structural stability. Iron may also be added separately for the same reason where high performance is not required.

Although the alloy is designed to contain no cobalt, up to 5% may be added to increase gamma prime volume fraction, solid solution strengthen the matrix, and decrease gamma prime solvus.

Nickel constitutes the balance of the composition 0068628 Commercially available nickel will also contain incidental amounts of sulfur, arsenic, lead, phosphorus, manganese, copper, magnesium and calcium.

Optionally, surface active elements, including lanthanum, yttrium, calcium, barium, strontium, magnesium and cerium may be added to control grain boundary phases for increasing the tolerance for lead, sulfur, and other contaminants. Up to 5% manganese and copper may be added to control the gamma prime solvus. In high temperature strength applications up to 10% of at least one of ruthenium and rhenium may be added for phase solvus control.

The following example is illustrative of the invention. Five heats were melted and stress rupture tested. The nominal chemistry of the heats are tabulated in Table I. Heat A represents a commercially available cobalt free alloy known as 713. Heats B to E are representative of the presently claimed invention and are arranged according to their increasing chromium content. Heats A, B and C were stress rupture tested in the as cast condition. Heats D and E were cast and heat treated before being tested.

TABLE I
COMPOSITION, WEIGHT PER CENT

Heat	A	<u>B</u>	<u>C</u>	<u>D</u>	E
Element					
Cr	12	12	14	16	16
Mo	4.5	5	5	1	1
W	_	-	2	6	10
Ti	0.6	2	4	3.5	3.5
Al	5.9	4.5	4	3.5	3.5
С	.05	.03	•03	.03	.03
В	.OI	•09	•09	.09	.09
Zr	.10	-	-	•05	.05
Nb	2	2	-	-	~

<u>A</u>	<u>B</u>	<u>c</u>	<u>D</u>	0068628
-	2	-	_	_
Bal	Bal	Bal	Bal	Bal
4.5	5	7	7	1
6.5	6.5	8	7	7
	- Bal 4.5	- 2 Bal Bal 4.5 5	<u>A</u> <u>B</u> <u>C</u> - 2 - Bal Bal Bal 4.5 5 7	<u>A</u> <u>B</u> <u>C</u> <u>D</u> - 2 Bal Bal Bal Bal 4.5 5 7 7

The compositions of Heats A to E were stress rupture tested at $760^{\circ}\text{C}(1400^{\circ}\text{F})$ (at the "ductility trough") and at $982^{\circ}\text{C}(1800^{\circ}\text{F})$. The results are tabulated in Table 2.

TABLE 2 STRESS RUPTURE

<u>Heat</u>	<u>A</u>	<u>B</u>	· <u>C</u>	D	E
760°C(1400°F)/90Ksi 982°C(1800°F)/22Ksi Heat Treatmen:	80.7 54.3 As Cast	137.1 54.3 As	114.5 67.1 As Cast	140.7 71.5 1163 (2125 F)	113.5
	Cast	Casc		927 ^O C (1700 ^O F)	- 16hrs

Heats A, B and C were tested in the as-cast condition. Heat A is representative of the prior art and represents a control. Heats B and C clearly have superior stress rupture lives at $760^{\circ}\text{C}(1400^{\circ}\text{F})$ and are at least as effective at higher temperatures. Heat C is particularly of interest to the art in view of the fact that it achieves superior stress rupture strength at $760^{\circ}\text{C}(1400^{\circ}\text{F})$ and $982^{\circ}\text{C}(1800^{\circ}\text{F})$ without the addition of columbium and tantalum and with higher chromium content.

Heats D and E were heat treated before being tested. They also have stress rupture properties which are superior to Heat A, the industry standard. Like Heat C, the alloys of Heats D and E achieve their superior properties without the addition of columbium or tantalum and despite higher

chromium content and without any phase instability.

The alloys exhibited by Heats B, C D and E which illustrate the present invention also are hot corrosion resistant and oxidation resistant yet are not susceptible to deleterious phase instabilities. Thus the improves alloys are particularly suitable in such demanding applications as turbine motors, blades, nozzles and vanes and the like. the manufacture of such articles, master alloy or remelt ingots are melted in an inert atmosphere and then investment cast into the shape of the desired article. The shaped art-: icle may then be hot isostatically pressed to improve the integrity of the cast microstructure by decreasing normal microshock. The shaped articles may be further heat treated to produce a particular microstructure that would give the desired combination of mechanical and physical properties. In general, the alloy would be used for castings with a polycrystalline grain structure, although it is possible to use the alloy in a directionally solidified structure either as a single crystal or with aligned grain boundaries. directionally solidified structure, carbon, boron and zirconium are held to minimum values.

- alloy having high hot strength characterised in that the alloy consists of, by weight from 12 to 22% chromium; from 3 to 12% of at least one of up to 5% molybdenum, up to 10% tungsten and up to 2% vanadium; up to 6% tantalum; up to 2% columbium; from 2 to 6% aluminum, from 1 to 6% titanium; up to 5% cobalt; up to 2% iron; from 0.015 to 0.15% carbon; from 0.03 to 0.3% boron; up to 0.1% zirconium; and balance nickel.
- 2. A castable corrosion resistant nickel base alloy having high hot strength characterised in that the alloy consists of, by weight: from 15 to 22% chromium; from 5 to 10% of at least one of up to 3% molybdenum, 3 to 8% tungsten and up to 1% vanadium; up to 2% tantalum; up to 2% columbium; from 4 to 8% of at least one of from 2 to 5% aluminum and from 2 to 5% titanium; up to 5% cobalt; up to 2% iron; from 0.015% to 0.12% carbon; from 0.03% to 0.3% boron; up to 0.1% zirconium; and balance nickel.
- 3. A castable hot corrosion resistant nickel base alloy having high hot strength characterised in that the alloy consists of, by weight: from 14 to 20% chromium; from 5 to 10% of at least one of up to 5% molybdenum and 3 to 8% tungsten; from 4 to 8% of at least one of from 2 to 5% aluminum and from 2 to 5% titanium; up to 0.12% carbon, from 0.03 to 0.3% boron; up to 0.1% zirconium; and the balance nickel.
- 4. A castable hot corrosion resistant alloy according to claim 1, 2 or 3, characterised in that the alloy contains from 0.03 to 0.2% boron.

- 5. A hot corrosion resistant nickel base alloy having high hot strength, characterised in that the alloy consists of, by weight: 16% chromium; 1% molybdenum; 6% tungsten; 3.5% aluminum; 3.5% titanium; 0.03% carbon; 0.09% boron, 0.05% zirconium; and balance nickel.
- 6. A castable hot corrosion resistant nickel base alloy according to claim 1, 2 or 3, characterised in that the alloy additionally consists of, by weight: up to 5% copper; up to 5% manganese; up to 6% of at least one of up to 3% rhenium and up to 3% ruthenium; up to 0.17% of at least one of cerium, lanthanum and yttrium; and up to 0.15% of at least one of up to 0.05% Magnesium, up to 0.05% calcium, up to 0.05% strontium and up to 0.05% barium.
- 7. A process for producing cast articles <u>characterised</u> in comprising the steps of melting an alloy of any one of the preceding claims, casting the alloy into a shape, and hot isostatically pressing the shape.