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(54) **HIGH TEMPERATURE RESISTANT ALLOYS**
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ALLIAGES HAUTE TEMPERATURE

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- **PATENT ABSTRACTS OF JAPAN vol. 017, no. 259 (C-1061), 21 May 1993 (1993-05-21) -& JP 05 001355 A (KUBOTA CORP), 8 January 1993 (1993-01-08)**
- **DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US; LETZIG DIETMAR ET AL: "Screening of NiAl-base Ni-Fe-Al alloys for structural high temperature applications and development of a new Ni-30Fe-10Al-Cr alloy" XP002269246 Database accession no. EIX99484847650 -& Z METALLKD;ZEITSCHRIFT FUER METALLKUNDE/MATERIALS RESEARCH AND ADVANCED TECHNIQUES 1999 CARL HANSER VERLAG, MUNICH, GERMANY, vol. 90, no. 9, 1999, pages 712-721, XP009025297**
- **DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US; MITCHELL D R G ET AL: "Kinetic and morphological study of the coking of some heat-resistant steels" XP002269247 Database accession no. EIX94122070345 -& J MATER SCI; JOURNAL OF MATERIALS SCIENCE AUG 15 1994 PUBL BY CHAPMAN & HALL LTD, LONDON, ENGL, vol. 29, no. 16, 15 August 1994 (1994-08-15), pages 4357-4370, XP009025377**

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Description

[0001] This invention relates to high temperature alloys, and more particularly to oxide dispersion strengthened alloys having improved creep resistance and carburisation resistance at high temperatures.

[0002] Frequently high temperature alloys used, for example, in the manufacture of alloy tubes for steam methane reforming, suffer from insufficient creep resistance. In other applications of high temperature alloys, for example, alloy tubes used in ethylene pyrolysis, the alloys suffer from insufficient carburisation resistance and, in consequence, insufficient creep resistance.

[0003] The petrochemical industry continues to look for improved materials and other technologies capable of withstanding increasingly demanding process conditions to enable more efficient production and achieve enhanced yields. In the case of steam methane reforming, these conditions involve higher temperatures and higher gas pressures. In the case of ethylene pyrolysis, the conditions involve increasingly severe pyrolysis/cracking conditions (higher temperatures, shorter residence times, and lower partial pressures of product). Currently available alloys have specific deficiencies that cause relatively early failure under these process conditions. This is the case presently for both castable alloy tubes and wrought alloy tubes.

[0004] An example of a known alloy material is INCOZOY® alloy 803 (UNS S 35045), which is an iron-nickel-chromium alloy specifically designed for use in petrochemical, chemical and thermal processing applications. The composition of INCOLOY 803, by weight, is 25%Cr, 35%Ni, 1%Mn, 0.6%Ti, 0.5%Al, 0.7%Si, 0.07%C and balance Fe. Relatively unsuccessful efforts have been made to improve the properties of this alloy by the addition of further alloying components and also by cladding.

[0005] It has been known for about thirty years that alloy creep resistance can be considerably improved by adding a fine dispersion of oxide particles into a metallic matrix, yielding a so-called oxide dispersion strengthened (ODS) alloy. Such alloys exhibit a creep threshold, that is to say, below a certain stress their creep rate is very low. This behaviour is commonly explained by interfacial pinning of the moving dislocations at the oxide particle; Bartsch, M., A. Wasilkowska, A. Czyrska-Filemonowicz and U. Messerschmidt Materials Science & Engineering A 272, 152-162 (1999*).* It has recently been proposed to provide oxide dispersion strengthened clad tubes based on INCOLOY 803, but to date no entirely successful commercial product is available

(www.oit.doe.gov/imf/factsheets/mtu tubes).

[0006] The nickel-chromium-iron alloys in the ethylene pyrolysis market which have been produced to have good corrosion resistance and acceptable creep resistance mainly develop an oxide coating layer based on chromium oxide (with in some cases admixed silica). This layer under excessively carburising service conditions (high temperature, high carbon activity, low oxygen pressure) can become destabilised and is then no longer a functional carbon diffusion barrier. Alumina is known to be a very stable oxide and ideally it would be desirable to create an alumina layer on the surface of the nickel-chromium-iron alloy, for example, by adding aluminium to the melt. However, aluminium has two highly detrimental effects on the mechanical properties of such alloys and especially on the creep resistance. Firstly, addition of aluminium to the melt can produce a dispersion of alumina in the alloy that can drastically reduce the creep resistance properties. Secondly, aluminium can form brittle Ni-Al phases in the alloy.

[0007] EP-A-0050408 describes iron-chromium-nickel alloys having aluminium and an optional hafnium addition.

[0008] US 6409847 describes nickel-chromium-iron alloys having 0.1 to 1.5% of hafnium.

[0009] JP-A-05001355 describes a heat resistant cast steel containing Nb and Hf for improved creep fracture strenght.

[0010] EP-A-0391381 describes nickel-chromium-iron alloys having an optional addition of hafnium.

[0011] US 5851318 describes nickel-chromium-iron alloys containing from 0.05 to 0.2% hafnium.

[0012] It will be apparent that there is a need for new high temperature alloys with improved properties for a variety of high temperature applications.

[0013] According to the present invention there is provided a method of making a new class of improved nickel-chromium-iron alloys comprising hafnium.

[0014] The invention provides a method of making an improved creep resistant nickel-chromium-iron alloy comprising up to about 5% by weight of hafnium-containing particles.

[0015] The invention provides an improved oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.

[0016] The invention provides a corrosion resistant nickel-chromium-iron-aluminium alloy comprising up to about 15%, preferably up to about 10%, by weight of aluminium and up to about 5% by weight of hafnium-containing particles.

[0017] The alloys of the invention are castable and can be formed into tubes and coils.

[0018] According to the present invention there is provided a method of making a nickel-chromium-iron alloy having a dispersion of finely divided hafnium oxide particles to deliver a dispersion strengthening effect, the alloy having a composition comprising, by weight:

Carbon	0.01 - 0.7%
Silicon	0.1 - 3.0%
Manganese	0 - 3.0%
Nickel	15 - 90%
Chromium	5 - 40%
Molybdenum	0 - 3.0%
Niobium	0 - 2.0%
Tantalum	0 - 2.0%
Titanium	0 - 2.0%
Zirconium	0 - 2.0%
Cobalt	0 - 2.0%
Tungsten	0 - 4.0%
Hafnium	0.01 - 4.5%
Aluminium	0 - 15%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities, the alloy composition having the proviso, that at least one carbide forming element whose carbide is more stable than chromium carbide selected from niobium, tungsten, tantalum and zirconium is present, the method comprising the steps of:

preparing a charge of metal having a required composition;

melting said charge of metal except for the hafnium content and the aluminium and/or titanium and/or zirconium content, if Al and/or Ti and/or Zr present; bringing the melt to a temperature in the range from 1500 to 1700°C;

adding finely divided hafnium metal particles in an amount of 0.01 to 4.5 weight% and having a size of less than 5mm to the melt shortly before pouring to react with free oxygen;

adding the aluminium and/or titanium and/or zirconium addition, if present, after the hafnium addition; and pouring the molten metal into a mould to form a solidified cast alloy having a dispersion of finely divided hafnium oxide particles therein, the particles having an average particle size of less than 50 microns in the solidified metal.

[0019] A preferred embodiment of the method of making an oxide dispersion strengthened nickel-chromium-iron castable alloy according to the invention comprises a composition, by weight:

Carbon	0.01	-	0.5%
Silicon	0.01	-	2.5%
Manganese	0	-	2.5%
Nickel	15	-	50%
Chromium	20	-	40%
Molybdenum	0	-	1.0%
Niobium	0	-	1.7%
Titanium	0	-	0.5%
Zirconium	0	-	0.5%
Cobalt	0	-	2.0%
Tungsten	0	-	1.0%
Hafnium	0.01	-	4.5%
Aluminium	0	-	15%

Balance iron and incidental impurities.

[0020] Preferred alloy compositions according to the method of the present invention include the following compositions:

Carbon	0.3 to 0.7%
Silicon	0.1 to 2.5%
Manganese	2.5% max
Nickel	30 to 40%
Chromium	20 to 30%
Molybdenum	3.0% max
Niobium	2.0% max
Hafnium	0.01% to 4.5%
Titanium	0.5% max
Zirconium	0.5% max
Cobalt	2.0% max
Tungsten	1.0% max
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

Balance iron and incidental impurities.

Carbon	0.03 to 0.2%
Silicon	0.1 to 0.25%
Manganese	2.5% max.
Nickel	30 to 40%
Chromium	20 to 30%
Molybdenum	3.0% max.
Niobium	1.7% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.05% max.
Tungsten	1.0% max.
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities.

Carbon	0.3 to 0.7%
Silicon	0.01 to 2.5%
Manganese	2.5% max.
Nickel	40 to 60%
Chromium	3.0 to 40%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	1.0% max.
Zirconium	1.0% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities.

Carbon	0.03 to 0.2%
Silicon	0.1 to 2.5%
Manganese	2.5% max.
Nickel	40 to 50%
Chromium	30 to 40%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities.

Carbon	0.3 to 0.7%
Silicon	0.01 to 2.5%
Manganese	2.5% max.
Nickel	19 to 22%
Chromium	24 to 27%
Molybdenum	3.0% max.
Niobium	2.0% max
Hafnium	0.01 to 4.5%
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities.

Carbon	0.03 to 0.2%
Silicon	0.1 to 2.5%
Manganese	2.5% max
Nickel	30 to 45%
Chromium	19 to 22%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities.

[0021] Other preferred nickel-chromium-iron castable alloys according to the invention include the following compositions, where all percentages are given by weight:

	Carbon	Silicon	Manganese	Nickel	Chromium	Molybdenum
A	0.3-0.5	0.1-2.5	2.5 max	30-40	20-30	1.0max
B	0.03-0.2	0.1-2.5	2.5 max	30-40	20-30	1.0 max
C	0.3-0.6	0.1-2.5	2.5 max	40-60	30-40	1.0 max
D	0.03-0.2	0.1- 2.5	2.5 max	40-60	30-40	1.0 max
E	0.30-0.5	0.1-2.5	2.5 max	19-22	24-27	1.0 max
F	0.03-0.2	0.1-2.5	2.5 max	30-45	19-22	1.0 max

	Niobium	Hafnium	Optional Aluminium	Titanium	Zirconium	Cobalt	Tungste
A	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
B	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
C	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
D	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
E	2 max	0.025 - 4.5	6.0 max			2.0 max	1.0 max
F	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
balance iron and incidental impurities.							

[0022] The amount of hafnium in the alloy, by weight, is preferably from 0.05 to 3.0%, more preferably from 0.1% to 1.0% and most preferably from 0.2 to 0.5% for the high carbon alloy (0.3 - 0.6% carbon), and more than 1% for the low carbon alloy (0.03 - 0.2% carbon), preferably from 1% to 4.5%. Hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of less than 50 microns in the solidified metal.

[0023] Examples of particularly preferred alloy compositions according to the method of invention consist essentially of the following components, by weight:

Carbon	0.45%
Silicon	1.3%
Manganese	0.9%
Nickel	33.8%
Chromium	25.7%
Molybdenum	0.03%
Niobium	0.85%
Hafnium	0.25%
Titanium	0.1%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.01%
Nitrogen	0.1%
Iron	balance.

Carbon	0.07%
Silicon	1.0%
Manganese	0.98%
Nickel	32.5%

(continued)

Chromium	25.8%
Molybdenum	0.20%
Niobium	0.04%
Hafnium	1.1%
Titanium	0.12%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.08%
Nitrogen	0.1%
Iron	balance.

Carbon	0.34%
Silicon	1.68%
Manganese	1.10%
Nickel	32.0%
Chromium	21.3%
Molybdenum	0.01%
Niobium	0.80%
Hafnium	0.25%
Titanium	0.12%
Zirconium	0.01%
Aluminium	3.28%
Cobalt	0.04%
Tungsten	0.01%
Iron	balance,

Carbon	0.42%
Silicon	1.79%
Manganese	1.17%
Nickel	33.2%
Chromium	23.3%
Molybdenum	0.02%
Niobium	0.77%
Hafnium	0.24%
Titanium	0.10%
Zirconium	0.01%
Aluminium	1.64%
Cobalt	0.04%
Tungsten	0.08%
Iron	balance.

[0024] Incidental impurities in the alloys of the invention can comprise, for example, phosphorus, sulphur, vanadium, zinc, arsenic, tin, lead, copper and cerium, up to a total amount of about 1.0%.

The invention provides a method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

To manufacture the alloys of the invention, it is important to provide conditions in the melt which permit oxidation of the hafnium particles without allowing detrimental reactions which would result in the hafnium (with or without aluminium) being taken up in the slag. The correct oxidising conditions can be achieved by appropriate adjustment or additions of the components, for example, silicon and/or manganese, and by ensuring that unwanted contaminants are absent or kept to a minimum. If the slag is able to react with the oxidised hafnium particles this of course removes them detrimentally from the melt. The level of oxygen in the melt can be varied by additions of, for example, one or more of silicon, niobium, titanium, zirconium, chromium, manganese, calcium and the optimum free oxygen level necessary to react with the hafnium particles can readily be found by routine experimentation.

[0025] In the manufacture of the castable nickel-chromium-iron alloys of the invention, it is often desirable to introduce micro-additions of certain components to obtain the desired alloy properties. Such components can be very reactive with oxygen, but in general less reactive than hafnium. Formation of oxides by these micro-additions should be avoided, and preferably the added components should form carbides, carbonitrides, or nitrides, or stay in solid solution. Preferably any such micro-additions are made after the addition of hafnium. For example, after the reaction of the hafnium particles with free oxygen, alloying amounts of titanium and/or zirconium may be added, up to the specified limits of 0.5% by weight in each case. The substantial removal of available free oxygen from the melt helps to ensure that any such titanium and/or zirconium additions do not form oxides, which could react detrimentally with the hafnium particles and reduce the yields of titanium, zirconium and hafnium present in the alloy.

[0026] It is important that the hafnium is added to the melt as finely divided particles and that it is oxidised in situ.

[0027] We have discovered that hafnium added to nickel/chromium alloys in non-particulate form does not disperse, or reacts only with the carbon/nitrogen present resulting in a decrease of the alloy properties. Attempts to add large pieces of hafnium to nickel/chromium micro-alloys have revealed that the hafnium does not disperse, but settles to the bottom of the alloy melt, and so is not present in the final casting. Surprisingly, we have also found that the addition of hafnia (hafnium oxide) particles directly to the melt does not provide the desired dispersion strengthening either. Hafnia added in this way simply goes into the slag. According to the invention it has been found that it is necessary to carry out the oxidation of the hafnium particles in the melt in order to obtain the desired improvements.

[0028] The charge make up can be a virgin charge (pure metals), a mixture of virgin charge and reverts, a mixture of virgin charge and ingots, or a mixture of virgin charge and reverts and ingots. The ingots can be made from argon/oxygen decarburisation (AOD) revert alloy treatment or from in-house reverts treated, for example, by argon purging. In each case the chemical composition of the melt should be carefully monitored to avoid contaminants and the formation of unwanted slag.

Special care should be taken to deslag the bath, and the maximum amount of slag is preferably removed from the surface of the bath. It is possible to improve slag removal by the use of a neutral deslag powder. If desired the melt can be maintained in an argon atmosphere, but this is not essential.

The melt temperature is in the range of from 1500°C to 1700 °C, preferably from 1610 °C to 1670 °C for nickel-chromium-iron, and 1630°C to 1690C for nickel-chromium-iron-aluminium.

[0029] Hafnium particles are preferably added to the melt just before pouring the molten alloy into the mould. If a ladle is used, the hafnium is preferably added in the ladle. To improve the hafnium dispersion, the molten alloy is preferably stirred before pouring.

Any type of hafnium can be used, but electrolytic hafnium is preferred. The hafnium particles are preferably reduced in size as much as possible, for example, by grinding to a fine powder in a suitable mill. The hafnium particles have a particle size of less than 5 mm, preferably less than 4 mm, with an average particle size of from 1 to 2 mm. When dispersed in the melt, the hafnium particles are further reduced in size.

The high carbon alloys of the invention (0.3 - 0.6% carbon) have a primary carbide network similar to the corresponding alloys without the oxide dispersion. The primary carbides are mainly composed of chromium and/or iron carbo-nitrides, optionally with niobium, titanium and/or zirconium carbo-nitrides also present. The invention also provides the possibility of obtaining a dispersion of secondary carbides after the alloy has been brought to a high temperature. These secondary carbides are mainly chromium (or other elements such as iron) carbo-nitrides and optionally niobium, titanium (and/or zirconium) carbo-nitrides.

The low carbon alloys of the invention (0.03 - 0.2% carbon) can contain a dispersion of carbides, carbo-nitrides, or nitrides, for example, titanium nitrides, titanium carbo-nitrides, niobium carbides, niobium carbo-nitrides, niobium nitrides, zirconium nitrides, zirconium carbo-nitrides, zirconium carbides, tantalum carbides, tantalum carbo-nitrides, tantalum nitrides, tungsten carbides, tungsten nitrides, and/or tungsten carbo-nitrides.

[0030] In additions to these precipitates, the invention provides for the formation of a hafnia / hafnium oxide dispersion (the hafnium can be oxidised to form HfO_2 but it can be expected that there will also be formed an oxide HfO_x with x as a variable). Furthermore, in alloys containing more than a trace of niobium and titanium, for example, high carbon nickel-chromium-iron alloys, hafnium/niobium/titanium carbo-nitrides and (rarely) oxides mixtures (wherein the quantities of niobium and titanium are variable as well as the quantities of nitrogen and oxygen) can be expected to be present. Also, more numerous titanium nitride (and/or carbide) dispersions may be observed in the alloy, some of which may also contain hafnia particles. It is also possible that some hafnium carbo-nitrides may be formed.

[0031] According to another aspect of the invention, there is provided an oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles, the alloy having a carbon content of from 0.3% to 0.5% by weight and having improved high temperature creep resistance, leading to an improved service life expectancy. Without wishing to be confined to any particular theory, it is believed that the creep resistance of such high carbon alloys, in the substantial absence of aluminium, derives from the ability of the particle dispersion to delay the motion of the dislocations in the alloy lattice. In the case of a micro-alloy, without the oxide dispersion, the motion of dislocations can be delayed by the presence of carbide (and/or nitride) precipitates, but the presence of the oxide dispersion provides a substantial unexpected extra improvement. An example of a high carbon oxide dispersion strengthened alloy is alloy A in Table 1 (wherein aluminium is absent).

[0032] In a still further aspect, the invention provides an oxide dispersion strengthened nickel-chromium-iron alloy, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles, the alloy having a carbon content of from 0.03% - 0.2%, preferably 0.03% - 0.1%, more preferably 0.03% - 0.08%, for example, about 0.05% - 0.07%, and a significantly increased service temperature, preferably greater than 1150°C. Without wishing to be confined to any particular theory, it is believed that the improved high temperature performance of the new low carbon alloys of this further aspect of the invention is due to the replacement of the strengthening carbide dispersion by a hafnia dispersion which is more stable than the carbide at high temperature. An example of a low carbon oxide dispersion strengthened alloy is alloy B in Table 1 (wherein aluminium is absent).

[0033] Where the nickel-chromium-iron alloy of the invention also comprises aluminium, the aluminium is preferably present in an amount of from 0.1% to 10% by weight, more preferably from 0.5% to 6% by weight and most preferably from.1.0 to 5% by weight.

[0034] In a still further aspect of the invention, there is provided a method of manufacturing a carburisation resistant nickel-chromium-iron alloy which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.

[0035] Preferably the aluminium is added to the melt immediately before pouring the molten alloy into the mould.

[0036] Without wishing to be confined by any particular theory, it is believed that the addition of hafnium limits the amount of available oxygen in the alloy able to react with the aluminium and minimises or eliminates the formation of a detrimental dispersion of alumina particles.

[0037] The alloys of the invention can be formed into tubes, for example, by rotational moulding, and such rotationally moulded tubes are a further aspect of the invention. The rotational moulding process can provide a non-uniform particle distribution in the tube wall, with the greater concentration of particles being towards the outer surface of the tube wall, and this can be beneficial in some cases. For example, in certain applications the internal bore of the tube is machined, removing 4-5 mm of material; this gradient of concentration ensures that the hafnium/hafnia reinforcement is kept in the useful part of the tube. Other components that can be manufactured from the new alloys include fittings, fully fabricated ethylene furnace assemblies, reformer tubes and manifolds.

[0038] For high chromium content (more than 10%) alloys, a further advantage of the hafnium addition is that it can tend to improve the oxide layer adherence at the surface of an alloy tube. For example, where nickel-chromium-iron alloys are used in ethylene furnaces, they are able to develop an oxide layer on the surface that protects the alloy against corrosion by carburisation. This protective oxide layer is formed ideally of chromium/manganese/silicon oxides, but can also include iron and nickel oxides. The oxide layer has a tendency to spall during the tube service life (because of differences of coefficients of expansion with the alloy, compressive stresses in the oxide, etc). Spalling leaves the alloy unprotected against corrosion from the gaseous and particulate reactants of the ethylene cracking process. It has surprisingly been found that the addition of hafnium as described herein can tend to delay the spalling of the protective oxide layer.

[0039] Embodiments of alloys according to the invention are illustrated in the accompanying Drawings, by way of example only, in which:

Figure 1 is a photomicrograph of a first alloy according to the invention with its composition by weight;
Figure 2 is a photomicrograph of a second alloy according to the invention with its composition by weight;
Figure 3 is a photomicrograph of a third alloy according to the invention with its composition by weight;
Figure 4 is a photomicrograph of a fourth alloy according to the invention with its composition by weight;
Figure 5 is a photomicrograph of a fifth alloy according to the invention; and
Figure 6 is a photomicrograph of a sixth alloy according to the invention.

[0040] The invention is further illustrated by the following Examples, in which all percentages are by weight:

Example 1

[0041] The following melt composition is produced in a clean furnace:

Nickel	35%
Chromium	25%
Carbon	0.4%
Niobium	0.8 - 0.9%
Silicon	1.6 - 1.8%
Manganese	1.1 - 1.3%
Iron	balance.

[0042] The temperature of the melt is raised to a tap temperature of from 1640°C to 1650°C and the silicon content checked to obtain the correct oxidising conditions. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped into a ladle and 0.35% hafnium particles of particle size maximum 5 mm, average 1 to 2 mm, are added to the tap stream. After the hafnium addition, 0.18% titanium, in the form of FeTi is added to the ladle.

[0043] The alloy in the ladle is stirred and immediately poured into a tube mould.

[0044] The creep resistance properties of the alloy thus produced were compared with the properties of an otherwise identical commercial alloy without hafnium.

[0045] The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a typical figure of 16.7 MPa at a temperature of 1100°C (Figure 7). The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 275 hours. The alloy according to the invention had a minimum failure time of rupture of 370 hours and a mean value failure of 430 hours. The creep strength comparison is shown in Figure 8.

[0046] The results of a 100,000 hour creep rupture stress test for the alloy of Example 1 are given in Table 1:

Table 1

CREEP RUPTURE STRESS 100,000H LIFE FOR ALLOY EXAMPLE 1: N/mm2 (psi)

	900	950	1000	1050	1100
MEAN	**33.86** **(4929)**	**23.15** **(3374)**	**14.70** **(2148)**	**8.67** **(1273)**	**4.75** **(704)**
Minimum	**31.37** **(456.7)**	**21.44** **(3126)**	**13.62** **(1991)**	**8.03** **(1180)**	**4.40** **(653)**

Example 2

[0047] The procedure of Example 1 is repeated using the same melt composition except that the titanium addition is omitted.

[0048] The creep resistance properties of the alloy thus produced were compared with the properties of an otherwise identical commercial alloy from which the hafnium addition was omitted.

[0049] The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a typical figure of 16.2 MPa at a temperature of 1100°C. The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 202 hours. The alloy according to the invention had a minimum failure time of rupture of 396 hours, a mean value failure of 430 hours and a maximum failure time of rupture of 629 hours.

[0050] The results of Examples 1 and 2 show the dramatic improvement in creep properties that can be obtained using the alloys and method of the invention.

Example 3

[0051] This example describes the production of a low carbon oxide dispersion strengthened alloy according to the invention.

[0052] The following melt composition is produced in a clean furnace:

Nickel	33% - 35%
Chromium	24% - 26%
Carbon	0.04% - 0.08%

(continued)

Silicon	1.0% - 1.2%
Manganese	1.0% - 1.2%
Molybdenum	0.14% - 0.3%
Iron	balance.

[0053] The temperature of the melt is raised to a tap temperature of from 1640°C to 1650°C and the silicon content checked. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped into a ladle and 0.75% hafnium particles of particle size maximum 5 mm, average 1 - 2 mm, are added to the tap stream. After the hafnium addition, 0.25% titanium, in the form of FeTi is added to the ladle.

[0054] The alloy in the ladle is stirred and immediately poured into a tube mould. The chemical composition of the tube alloy by spectrometer analysis is:

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti
0.07	1.0	0.91	32.9	25.5	0.20	0.03	0.30	0.17

Zr	Co	W
0.01	0.03	0.06

Traces (P+ S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.24

[0055] A photomicrograph of the alloy is shown in Figure 5. The dispersed oxidised particles can clearly be seen.

Example 4

[0056] The procedure of Example 3 is repeated using the same melt composition except that the hafnium addition is 0.5%. The chemical composition of the tube alloy by spectrometer analysis is:

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti
0.07	1.00	0.98	32.5	25.8	0.02	0.04	0.50	0.12

Zr	Co	W
0.01	0.04	0.08

Traces (P+ S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.23

[0057] A photomicrograph of the alloy is shown in Figure 6. The dispersed oxidised particles can clearly be seen.

[0058] Examples 3 and 4 show a higher solidus than the high carbon alloys of Examples 1 and 2, indeed their solidus is 1344°C instead of 1260°C for the high carbon alloys.

Example 5

[0059] This Example describes the production of an oxide dispersion strengthened nickel-chromium-iron alloy according to the invention comprising both hafnium and aluminium.

[0060] A nickel-chromium-iron alloy melt having the following constituents by weight is formed in a clean furnace and brought to tapping temperature.

Nickel	35%
Chromium	25%
Carbon	0.4%
Niobium	0.8 - 0.9%
Silicon	1.6 - 1.8%
Manganese	1.1 - 1.3%
Iron	balance.

[0061] Once the appropriate oxidising conditions have been obtained, 100kg of the melt is tapped into a ladle, whilst at the same time adding hafnium particles to the tap stream to give a hafnium level of 0.15% to 0.30% by weight in the alloy. Immediately before pouring aluminium is added to the melt to give an aluminium level of 1.5% to 1.8%.

[0062] The alloy of Example 5 has been tested to confirm that aluminium can improve the carburisation resistance of a hafnium-containing alloy according to the invention. A very severe pack-carburisation test was performed, the results of which are shown in Figure 9. The creep resistance of the alloy was found to be substantially maintained compared to an identical alloy without hafnia and aluminium additions. Indeed only a decrease of maximum 20% in creep resistance was observed compared to an identical alloy without hafnium and aluminium additions. On the other hand, an identical alloy with an aluminium addition, but without hafnium, showed a decrease in creep resistance of 80%.

[0063] The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

[0064] All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

[0065] Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

[0066] The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

1. A method of making a nickel-chromium-iron alloy having a dispersion of finely divided hafnium oxide particles to deliver a dispersion strengthening effect, the alloy having a composition comprising, by weight:

Carbon	0.01 - 0.7%
Silicon	0.1 - 3.0%
Manganese	0 - 3.0%
Nickel	15 - 90%
Chromium	5 - 40%
Molybdenum	0 - 3.0%
Niobium	0 - 2.0%
Tantalum	0 - 2.0%
Titanium	0 - 2.0%
Zirconium	0 - 2.0%
Cobalt	0 - 2.0%
Tungsten	0 - 4.0%
Hafnium	0.01 - 4.5%
Aluminium	0 - 15%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities, the alloy composition having the proviso, that at least one carbide forming element whose carbide is more stable than chromium carbide selected from niobium, titanium, tungsten, tantalum and zirconium is present, the method comprising the steps of:

preparing a charge of metal having a required composition;
melting said charge of metal except for the hafnium content and the aluminium and/or titanium and/or zirconium content, if Al and/or Ti and/or Zr present;
bringing the melt to a temperature in the range from 1500 to 1700°C;
adding finely divided hafnium metal particles in an amount of 0.01 to 4.5 weight% and having a size of less than 5mm to the melt shortly before pouring to react with free oxygen;
adding the aluminium and/or titanium and/or zirconium addition, if present, after the hafnium addition; and
pouring the molten metal into a mould to form a solidified cast alloy having a dispersion of finely divided hafnium oxide particles therein, the particles having an average particle size of less than 50 microns in the solidified metal.

2. A method of making a nickel-chromium iron alloy as claimed in claim 1 wherein the hafnium is added to a tap stream from a melting furnace before pouring into a mould.

3. A method according to claim 1, in which the hafnium particles are added to the molten alloy in a ladle.

4. A method according to any one preceding claim, in which the hafnium is electrolytic hafnium.

5. A method according to any one preceding claim, wherein the level of oxygen in the melt is varied by additions of one or more of niobium, titanium and zirconium.

6. A method according to claim 5, in which titanium is added in the form of TiFe after the hafnium addition.

7. A method of manufacturing a corrosion resistant nickel-chromium-iron alloy according to any one preceding claim which comprises the additional step of adding finely divided hafnium particles prior to aluminium to a melt of the alloy before pouring.

8. A method according to claim 7, wherein the aluminium is added to the melt immediately before pouring the molten alloy into a mould.

9. A method according to any one preceding claim, in which the alloy is formed into a tube by rotational moulding.

10. A method of making an oxide dispersion strengthened nickel-chromium-iron alloy according to claim 1 comprising, by weighty :

Carbon	0.01 to 0-5%
Silicon	0.01 to 2.5%
Manganese	0 to 2.5%
Nickel	15 to 50%
Chromium	20 to 40%
Molybdenum	0 to 1.0%
Niobium	0 to 1.7%
Titanium	0 to 0.5%
Zirconium	0 to 0.5%
Cobalt	0 to 2.0%
Tungsten	0 to 1.0%
Hafnium	0.01 to 4.5%
Aluminium	0 to 15%

balance iron and incidental impurities,
with the proviso that at least one of niobium, titanium and zirconium is present.

11. A method of making an alloy according to claim 1 having the following composition, by weight:

Carbon	0.3 to 0.7%
Silicon	0.1 to 2.5%
Manganese	2.5% max.
Nickel	30 to 40%
Chromium	20 to 30%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities.

12. A method of making an alloy according to claim 1 having one of the following compositions, by weight:

Carbon	0.3 to 0.7%
Silicon	0.01 to 2.5%
Manganese	2.5% max.
Nickel	40 to 60%
Chromium	30 to 40%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	1.0% max.
Zirconium	1.0% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities; or

Carbon	0.3 to 0.7%
Silicon	0.01 to 2.5%
Manganese	2.5% max.
Nickel	19 to 22%
Chromium	24 to 27%
Molybdenum	3.0% max.
Niobium	2.0% max
Hafnium	0.01 to 4.5%
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

(continued)

balance iron and incidental impurities; or

13. A method of making an alloy according to any one of claims 1 and 10 to 12, and having a carbon content of from 0.3 to 0.5% by weight.

14. A method of making an alloy according to claim 1 or claim 10, having a carbon content of from 0.03 to 0.2% by weight.

15. A method of making an alloy according to claim 1, having one of the following compositions, by weight:

Carbon	0.03 to 0.2%
Silicon	0.1 to 0.25%
Manganese	2.5% max.
Nickel	30 to 40%
Chromium	20 to 30%
Molybdenum	3.0% max.
Niobium	1.7% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.05% max.
Tungsten	1.0% max.
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
oxygen	0.001 - 0.7%

balance iron and incidental impurities; or

Carbon	0.03 to 0.2%
Silicon	0.1 to 2.5%
Manganese	2.5% max.
Nickel	40 to 50%
Chromium	30 to 40%
Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.,
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%

balance iron and incidental impurities; or

Carbon	0.03 to 0.2%
Silicon	0.1 to 2.5%
Manganese	2.5% max
Nickel	30 to 45%
Chromium	19 to 22%

(continued)

Molybdenum	3.0% max.
Niobium	2.0% max.
Hafnium	0.01 to 4.5%
Titanium	0.5% max.
Zirconium	0.5% max.
Cobalt	2.0% max.
Tungsten	1.0% max.
Aluminium	0 - 15.0%
Nitrogen	0.001 - 0.5%
Oxygen	0.001 - 0.7%
balance iron and incidental impurities.	

16. A method of making an alloy according to claim 1, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.

17. A method of making an alloy according to claim 16, in which the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

18. A method of making an alloy according to claim 17, in which the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

19. A method of making an alloy according to any one of claims 1, 12 and 15 to 18, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 10% and the amount of hafnium by weight is from 0.01% to 4.5%.

20. A method of making an alloy according to claim 19, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 6% and the amount of hafnium by weight is from 0.1% to 1.0%.

21. A method of making an alloy according to claim 19 or 20, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 4.5% and the amount of hafnium by weight is from 0.2% to 0.5%.

22. A method of making an alloy according to claim 1 having any one of the following compositions, by weight:

Carbon	0.45%
Silicon	1.3%
Manganese	0.9%
Nickel	33.8%
Chromium	25.7%
Molybdenum	0.03%
Niobium	0.85%
Hafnium	0.25%
Titanium	0.1%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.01%
Nitrogen	0.1%
Iron and incidental impurities balance; or	

Carbon	0.07%
Silicon	1.0%
Manganese	0.98%
Nickel	32.5%

(continued)

Chromium	25.8%
Molybdenum	0.20%
Niobium	0.04%
Hafnium	1.1%
Titanium	0.12%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.08%
Nitrogen	0.1%

Iron and incidental impurities balance; or

Carbon	0.34%
Silicon	1.68%
Manganese	1.10%
Nickel	32.0%
Chromium	21.3%
Molybdenum	0.01%
Niobium	0.80%
Hafnium	0.25%
Titanium	0.12%
Zirconium	0.01%
Aluminium	3.28%
Cobalt	0.04%
Tungsten	0.01%

Iron and incidental impurities balance; or

Carbon	0.42%
Silicon	1.79%
Manganese	1.17%
Nickel	33.2%
Chromium	23.3%
Molybdenum	0.02%
Niobium	0.77%

Patentansprüche

1. Verfahren zur Herstellung einer Nickel-Chrom-Eisen-Legierung mit einer Dispersion von fein verteilten Hafniumoxidpartikeln, um einen Dispersions-verstärkenden Effekt zu ergeben, wobei die Legierung eine Zusammensetzung aufweist, die auf das Gewicht bezogen umfaßt:

Kohlenstoff	0,01 - 0,7%,
Silicium	0,1 - 3,0%,
Mangan	0 - 3,0%,
Nickel	15 - 90%,
Chrom	5 - 40%,
Molybdän	0 - 3,0%,
Niob	0 - 2,0%,

(fortgesetzt)

Tantal	0 - 2,0%,
Titan	0 - 2,0%,
Zirkonium	0 - 2,0%,
Kobalt	0 - 2,0%,
Wolfram	0 - 4,0%,
Hafnium	0,01 - 4,5%,
Aluminium	0 - 15%,
Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen, wobei die Legierungszusammensetzung der Maßgabe unterliegt, daß mindestens ein Carbid-bildendes Element, dessen Carbid stabiler als Chromcarbid ist, ausgewählt unter Niob, Titan, Wolfram, Tantal und Zirkonium, vorhanden ist, wobei das Verfahren die Schritte umfaßt:

Herstellen einer Metallcharge mit einer erforderlichen Zusammensetzung;
Schmelzen der Metallcharge, bis auf den Hafniumanteil und den Aluminium- und/oder Titan-und/oder Zirkoniumanteil, sofern Al und/oder Ti und/oder Zr vorhanden sind;
Einstellen der Temperatur der Schmelze im Bereich von 1500 bis 1700°C;
Zugeben fein verteilter Hafnium-Metallpartikel in einer Menge von 0,01 bis 4,5 Gew.-% und mit einer Größe von weniger als 5 mm zu der Schmelze kurz vor dem Gießen, zur Reaktion mit freiem Sauerstoff;
Zugeben des Aluminium- und/oder Titan- und/oder Zirkoniumzuschlags, falls vorhanden, nach der Hafnium-Zugabe, und
Gießen des geschmolzenen Metalls in eine Form, um eine verfestigte Gußlegierung zu bilden, die eine Dispersion von fein verteilten Hafniumoxidpartikeln darin aufweist, wobei die Partikel eine mittlere Teilchengröße von weniger als 50 Mikron in dem verfestigten Material aufweisen.

2. Verfahren zur Herstellung einer Nickel-Chrom-Eisen-Legierung nach Anspruch 1, wobei das Hafnium einem Strom aus einem Schmelzofen vor dem Gießen in eine Form zugegeben wird.

3. Verfahren nach Anspruch 1, wobei die Hafniumpartikel der geschmolzenen Legierung in einer Gußform zugegeben werden.

4. Verfahren nach einem vorhergehenden Anspruch, wobei das Hafnium elektrolytisches Hafnium ist.

5. Verfahren nach einem vorhergehenden Anspruch, wobei die Sauerstoffmenge in der Schmelze durch Zugabe von Niob und/oder Titan und/oder Zirkonium variiert wird.

6. Verfahren nach Anspruch 5, wobei Titan in Form von TiFe nach der Hafnium-Zugabe zugegeben wird.

7. Verfahren zur Herstellung einer korrosionsbeständigen Nickel-Chrom-Eisen-Legierung nach einem vorhergehenden Anspruch, das den zusätzlichen Schritt der Zugabe fein verteilter Hafniumpartikel vor dem Aluminium zu einer Schmelze der Legierung vor dem Gießen umfaßt.

8. Verfahren nach Anspruch 7, wobei das Aluminium der Schmelze unmittelbar vor dem Gießen der geschmolzenen Legierung in eine Form zugegeben wird.

9. Verfahren nach einem vorhergehenden Anspruch, wobei die Legierung durch Drehgießen zu einem Rohr geformt wird.

10. Verfahren zur Herstellung einer Oxiddispersions-verstärkten Nickel-Chrom-Eisen-Legierung nach Anspruch 1, die auf das Gewicht bezogen umfaßt:

Kohlenstoff	0,01-0,5%,
Silicium	0,01-2,5%,

(fortgesetzt)

Mangan	0-2,5%,
Nickel	15-50%,
Chrom	20 - 40%,
Molybdän	0-1,0%,
Niob	0-1,7%,
Titan	0-0,5%,
Zirkonium	0-0,5%,
Kobalt	0-2,0%,
Wolfram	0-1,0%,
Hafnium	0,01-4,5%,
Aluminium	0-15%,

als Rest Eisen und unvermeidbare Verunreinigungen,
mit der Maßgabe, daß Niob und/oder Titan und/oder Zirkonium vorhanden sind.

11. Verfahren zur Herstellung einer Legierung nach Anspruch 1, wobei die Legierung, bezogen auf das Gewicht, folgende Zusammensetzung aufweist:

Kohlenstoff	0,3-0,7%,
Silicium	0,1-2,5%,
Mangan	max.2,5%,
Nickel	30 - 40%,
Chrom	20 - 30%,
Molybdän	max. 3,0%,
Niob	max. 2,0%,
Hafnium	0,01 bis 4,5%,
Titan	max. 0,5%,
Zirkonium	max. 0,5%,
Kobalt	max. 2,0%,
Wolfram	max. 1,0%,
Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen.

12. Verfahren zur Herstellung einer Legierung nach Anspruch 1, wobei die Legierung, bezogen auf das Gewicht, eine der folgenden Zusammensetzungen aufweist:

Kohlenstoff	0,3-0,7%,
Silicium	0,01-2,5%,
Mangan	max.2,5%,
Nickel	40-60%,
Chrom	30 - 40%,
Molybdän	max. 3,0%,
Niob	max. 2,0%,
Hafnium	0,01-4,5%,
Titan	max. 1,0%,
Zirkonium	max. 1,0%,
Kobalt	max. 2,0%,
Wolfram	max. 1,0%,
Aluminium	0-15,0%,

(fortgesetzt)

Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen, oder

Kohlenstoff	0,3-0,7%,
Silicium	0,01-2,5%,
Mangan	max. 2,5%,
Nickel	19-22%,
Chrom	24 - 27%,
Molybdän	max. 3,0%,
Niob	max. 2,0%,
Hafnium	0,01-4,5%,
Kobalt	max. 2,0%,
Wolfram	max. 1,0%,
Aluminium	0-15,0%,
Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen.

13. Verfahren zur Herstellung einer Legierung nach einem der Ansprüche 1 und 10 bis 12 und mit einem Kohlenstoffgehalt von 0,3 bis 0,5 Gew.-%.

14. Verfahren zur Herstellung einer Legierung nach Anspruch 1 oder Anspruch 10, mit einem Kohlenstoffgehalt von 0,03 bis 0,2 Gew.-%.

15. Verfahren zur Herstellung einer Legierung nach Anspruch 1, wobei die Legierung, bezogen auf das Gewicht, eine der folgenden Zusammensetzungen aufweist:

Kohlenstoff	0,03-0,2%,
Silicium	0,1-0,25%,
Mangan	max. 2,5%,
Nickel	30 - 40%,
Chrom	20 - 30%,
Molybdän	max. 3,0%,
Niob	max. 1,7%,
Hafnium	0,01-4,5%,
Titan	max. 0,5%,
Zirkonium	max. 0,5%,
Kobalt	max. 2,05%,
Wolfram	max. 1,0%,
Aluminium	0-15,0%,
Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen, oder

Kohlenstoff	0,03-0,2%,
Silicium	0,1-2,5%,
Mangan	max. 2,5%,

(fortgesetzt)

Nickel	40 - 50%,
Chrom	30 - 40%,
Molybdän	max. 3,0%,
Niob	max. 2,0%,
Hafnium	0,01-4,5%,
Titan	max. 0,5%,
Zirkonium	max. 0,5%,
Kobalt	max. 2,0%,
Wolfram	max. 1,0%,
Aluminium	0-15,0%,
Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen, oder

Kohlenstoff	0,03-0,2%,
Silicium	0,1-2,5%,
Mangan	max. 2,5%,
Nickel	30 - 45%,
Chrom	19-22%,
Molybdän	max. 3,0%,
Niob	max. 2,0%,
Hafnium	0,01-4,5%,
Titan	max. 0,5%,
Zirkonium	max. 0,5%,
Kobalt	max. 2,0%,
Wolfram	max.1,0%,
Aluminium	0-15,0%,
Stickstoff	0,001 - 0,5%,
Sauerstoff	0,001 - 0,7%,

als Rest Eisen und unvermeidbare Verunreinigungen.

16. Verfahren zur Herstellung einer Legierung nach Anspruch 1, wobei die Menge an Kohlenstoff in der Legierung 0,3 bis 0,6 Gew.-% und die Menge an Hafnium in der Legierung 0,01 bis 3,0 Gew.-% beträgt.

17. Verfahren zur Herstellung einer Legierung nach Anspruch 16, wobei die Menge an Hafnium in der Legierung 0,1 bis 1,0 Gew.-% beträgt.

18. Verfahren zur Herstellung einer Legierung nach Anspruch 17, wobei die Menge an Hafnium in der Legierung 0,2 bis 0,5 Gew.-% beträgt.

19. Verfahren zur Herstellung einer Legierung nach einem der Ansprüche 1, 12 und 15 bis 18, wobei die Menge an Aluminium in der Legierung 0,1 bis 10 Gew.-% und die Menge an Hafnium 0,01 bis 4,5 Gew.-% beträgt.

20. Verfahren zur Herstellung einer Legierung nach Anspruch 19, wobei die Menge an Aluminium in der Legierung 0,1 bis 6 Gew.-% und die Menge an Hafnium 0,1 bis 1,0 Gew.-% beträgt.

21. Verfahren zur Herstellung einer Legierung nach Anspruch 19 oder 20, wobei die Menge an Aluminium in der Legierung 0,1 bis 4,5 Gew.-% und die Menge an Hafnium 0,2 bis 0,5 Gew.-% beträgt.

22. Verfahren zur Herstellung einer Legierung nach Anspruch 1, wobei die Legierung, bezogen auf das Gewicht, eine der folgenden Zusammensetzungen aufweist:

Kohlenstoff	0,45%,
Silicium	1,3%,
Mangan	0,9%,
Nickel	33,8%,
Chrom	25,7%,
Molybdän	0,03%,
Niob	0,85%,
Hafnium	0,25%,
Titan	0,1%,
Zirkonium	0,01%,
Kobalt	0,04%,
Wolfram	0,01%,
Stickstoff	0,1%,

als Rest Eisen und unvermeidbare Verunreinigungen, oder

Kohlenstoff	0,07%,
Silicium	1,0%,
Mangan	0,98%,
Nickel	32,5%,
Chrom	25,8%,
Molybdän	0,20%,
Niob	0,04%,
Hafnium	1,1 %,
Titan	0,12%,
Zirkonium	0,01%,
Kobalt	0,04%,
Wolfram	0,08%,
Stickstoff	0,1%,

als Rest Eisen und unvermeidbare Verunreinigungen, oder

Kohlenstoff	0,34%,
Silicium	1,68%,
Mangan	1,10%,
Nickel	32,0%,
Chrom	21,3%,
Molybdän	0,01%,
Niob	0,80%,
Hafnium	0,25%,
Titan	0,12%,
Zirkonium	0,01%,
Aluminium	3,28%,
Kobalt	0,04%,
Wolfram	0,01%,

als Rest Eisen und unvermeidbare Verunreinigungen, oder

Kohlenstoff	0,42%,
Silicium	1,79%,

(fortgesetzt)

Mangan	1,17%,
Nickel	33,2%,
Chrom	23,3%,
Molybdän	0,02%,
Niob	0,77%.

Revendications

1. Procédé pour réaliser un alliage nickel-chrome-fer, ayant une dispersion de particules oxyde Hf divisées finement, pour réaliser un effet de renforcement de dispersion, l'alliage ayant une composition comprenant, en poids :

Carbone	0.01 - 0.7%
Silicium	0.1 - 3.0%
Mn	0-3.0%
Nickel	15-90%
Chrome	5-40%
Mo	0-3.0%
Nb	0-2.0%
Tantale	0-2.0%
Titanium	0-2.0%
Zr	0-2.0%
Co	0-2.0%
Tungstène	0-4.0%
Hf	0.01-4.5%
Aluminium	0-15%
Azote	0.001 - 0.5%
Oxygène	0.001 - 0.7%

le reste de fer et d'impuretés incidentes,
la composition d'alliage étant telle qu'au moins un élément, formant un carbure dont le carbure est plus stable que le carbure de chrome, et choisi parmi Nb, titanium, tungstène, tantale, et Zr, est présent,
le procédé comprenant les étapes de :

- préparer une charge de métal ayant une composition requise ;
- mélanger ladite charge de métal excepté pour la teneur en l'Hf et l'aluminium et/ou titane et/ou Zr, si de l'aluminium et/ou du titane et/ou du Zr est présent ;
- porter le mélange à une température dans la gamme de 1500 à 1700°C ;
- ajouter des particules de métal Hf finement divisées dans une quantité de 0,01 à 4,5 % en poids et ayant une taille inférieure à 5 mm, au mélange fondu, peu de temps avant le versement pour réagir avec l'oxygène libre ;
- ajouter l'aluminium et/ou le titane et/ou le Zr, si présent, après l'addition de Hf ; et
- verser le métal fondu dans un moule pour former un alliage découlée solidifié ayant une dispersion de particules oxyde Hf finement divisées, les particules ayant une de taille de particules moyenne inférieure à 50 microns dans le métal solidifié.

2. Procédé selon la revendication 1, **caractérisé en ce que** le Hf est ajouté à un courant de piquée à partir d'un fourneau de fusion avant le versement dans un moule.

3. Procédé selon la revendication 1, **caractérisé en ce que** les particules de Hf sont ajoutées à l'alliage fondu dans une poche de coulée.

4. Procédé selon l'une des revendications précédentes, **caractérisé en ce que** le Hf est du Hf électrolytique.

5. Procédé selon l'une des revendications précédentes, **caractérisé en ce que** le niveau d'oxygène dans le la partie fondue varie en fonction des additions de l'un ou plusieurs de Nb, titane et Zr.

6. Procédé selon revendications 5, **caractérisé en ce que** le titane est ajouté sous la forme de TiFe après l'addition de Hf.

7. Procédé fabrication d'un alliage résistants à la corrosion nickelchrome -- fer, selon l'une des revendications précédentes, **caractérisé en ce qu'**il comporte l'étape additionnelle d'ajouter des particules de Hf finement divisées avant l'aluminium à l'ensemble fondu de l'alliage avant le versement.

8. Procédé selon la revendication 7, **caractérisé en ce que** le l'aluminium est ajouté au mélange fondue immédiatement avant versement de l'alliage fondu dans un moule.

9. Procédé selon l'une des revendications précédentes, **caractérisé en ce que** l'alliage est formé dans un tube par moulage rotatif.

10. Procédé de réalisation d'un alliage à dispersion renforcée oxyde nickel-Cr-fer selon la revendication 1, comprenant en poids :

Carbone	0.01 à 0.05%
Silicium	0.01 à 2.5%
Mn	0 à 2.5%
Nickel	15 à 50%
Chrome	20 à 40%
Mo	0 à 1.0%
Nb	0 à 1.7%
Titane	0 à 0.5%
Zr	0 à 0.5%
Co	0 à 2.0%
Tungstène	0 à 1.0%
Hf	0.01 à 4.5%
Aluminium	0 à 15%

le reste étant du fer et des impuretés incidentes, et l'alliage étant tel qu'au moins un l'un parmi Nb, titane et Zr est présent.

11. Procédé de réalisation d'un alliage selon la revendication 1, ayant la composition suivante en poids :

Carbone	0.3 à 0.7%
Silicium	0.1 à 2.5%
Mn	2.5% max.
Nickel	30 à 40%
Chrome	20 à 30%
Mo	3.0% max.
Nb	2.0% max.
Hf	0.01 à 4.5%
Titane	0.5% max.
Zr	0.5% max.
Co	2.0% max.
Tungstène	1.0% max.
Azote	0.001- 0.5%
Oxygène	0.001 - 0.7%

le reste étant du fer et des impuretés incidentes.

12. Procédé de fabrication d'alliage selon la revendication 1, ayant l'une des compositions suivantes, en poids :

Carbone	0.3 à 0.7%
Silicium	0.01 à 2.5%
Mn	2.5% max.
Nickel	40 à 60%
Chrome	30 à 40%
Mo	3.0% max.
Nb	2.0% max.
Hf	0.01 à 4.5%
Titane	1.0% max.
Zr	1.0% max.
Co	2.0% max.
Tungstène	1.0% max
Al	0-15.0%
Azote	0.001 - 0.5%
Oxygène	0.001 - 0.7%

le reste étant du fer et des impuretés incidentes, ou

Carbone	0.3 à 0.7%
Silicium	0.01 à 2.5%
Mn	2.5% max.
Nickel	19 à 22%
Chrome	24 à 27%
Mo	3.0% max.
Nb	2.0% max.
Hf	0.01 à 4.5%
Co	2.0% max.
Tungstène	1.0% max.
Al	0 - 15.0%
Azote	0.001 - 0.5%
Oxygène	0.001 - 0.7%

le reste étant du fer et des impuretés incidentes.

13. Procédé pour fabriquer un alliage selon l'une des revendications 1 et 10 à 12, et ayant une teneur en carbone de 0,3 jusqu'à 0,5 % en poids.

14. Procédé pour fabriquer un alliage selon l'une des revendications 1 ou 10, ayant une teneur en carbone de 0,03 jusqu'à 0,2 % en poids.

15. Procédé de fabrication d'un alliage selon la revendication 1, ayant l'une des compositions suivantes, en poids :

Carbone	0.03 à 0.2%
Silicium	0.1 à 0.25%
Mn	2.5% max.
Nickel	30 à 40%
Chrome	20 à 30%
Mo	3.0% max.
Nb	1.7% max.
Hf	0.01 à 4.5%
Titane	0.5% max.

(suite)

Zr	0.5% max.
Co	2.05% max.
Tungstène	1.0% max.
Al	0-15.0%
Azote	0.001-0.5%
Oxygène	0.001-0.7%

le reste étant du fer et des impuretés incidentes, ou

Carbone	0.03 à 0.2%
Silicium	0.1 à 2.5%
Mn	2.5% max.
Nickel	30 à 45%
Chrome	30 à 40%
Mo	3.0% max.
Nb	2.0% max.
Hf	0.01 à 4.5%
Co	2.0% max.
Tungstène	1.0%
Al	0-15.0%
Azote	0.001 - 0.5%
Oxygène	0.001 - 0.7%

le reste étant du fer et des impuretés incidentes, ou

Carbone	0.03 à 0.2%
Silicium	0.1 à 2.5%
Mn	2.5% max.
Nickel	30 à 45%
Chrome	19 à 22%
Mo	3.0% max.
Nb	2.0% max.
Hf	0.01 à 4.5%
Titane	0.5% max.
Zr	0.5% max.
Co	2.0% max.
Tungstène	1.0% max.
Al	0-15.0%
Azote	0.001 - 0.5%
Oxygène	0.001 - 0.7%

le reste étant du fer et des impuretés incidentes.

16. Procédé de fabrication d’un alliage selon la revendication 1, dans lequel la quantité de carbone dans l’alliage, en poids, est de 0,3 à 0,6 % et la quantité de Hf en poids est de 0,01 jusqu’à 3,0 %.

17. Procédé pour réaliser un alliage selon la revendication 16, dans lequel la quantité de Hf est en poids de 0,1 % à 1,0 %.

18. Procédé pour réaliser un alliage selon revendications 17, dans lequel la quantité de Hf est en poids de 0,2 jusqu’à 0,5 % en poids.

19. Procédé pour réaliser un alliage selon l’une des revendications 1,12 et 15 à 18, dans lequel la quantité d’aluminium en poids est de 0,1 % à 10 %, la quantité de Hf en poids est de 0,01 % à 4,5 %.

20. Procédé de réalisation d'un alliage selon la revendication 19, dans lequel la quantité d'aluminium en poids est de 0,1 à 6 % et la quantité de Hf en poids est de 0,1 % à 1,0 %.

21. Procédé de réalisation d'un alliage selon la revendication 19 août 20, dans lequel la quantité d'aluminium est en poids de 0,1 % à 4,5 % et la quantité de Hf en poids est de 0,2 % à 0,5 %.

22. Procédé de régression un alliage selon la revendication 1, ayant l'une des compositions suivantes, en poids :

Carbone	0.45%
Silicium	1.3%
Mn	0.9%
Nickel	33.8%
Chrome	25.7%
Mo	0.03%
Nb	0.85%
Hf	0.25%
Titane	0.1%
Zr	0.01%
Co	0.04%
Tungstène	0.01%
Azote	0.1%

le reste étant du fer et des impuretés incidentes, ou

Carbone	0.07%
Silicium	1.0%
Mn	0.98%
Nickel	32.5%
Chrome	25.8%
Mo	0.20%
Nb	0.04%
Hf	1.1%
Titane	0.12%
Zr	0.01%
Co	0.04%
Tungstène	0.08%
Azote	0.1%

le reste étant du fer et des impuretés incidentes, ou

Carbone	0.34%
Silicium	1.68%
Mn	1.10%
Nickel	32.0%
Chrome	21.3%
Mo	0.01%
Nb	0.80%
Hf	0.25%
Titane	0.12%
Zr	0.01%
Al	3.28%

(suite)

Co	0.04%
Tungstène	0.01 %

le reste étant du fer et des impuretés incidentes, ou

Carbone	0.42%
Silicium	1.79%
Mn	1.17%
Nickel	33.2%
Chrome	23.3%
Mo	0.02%
Nb	0.77%

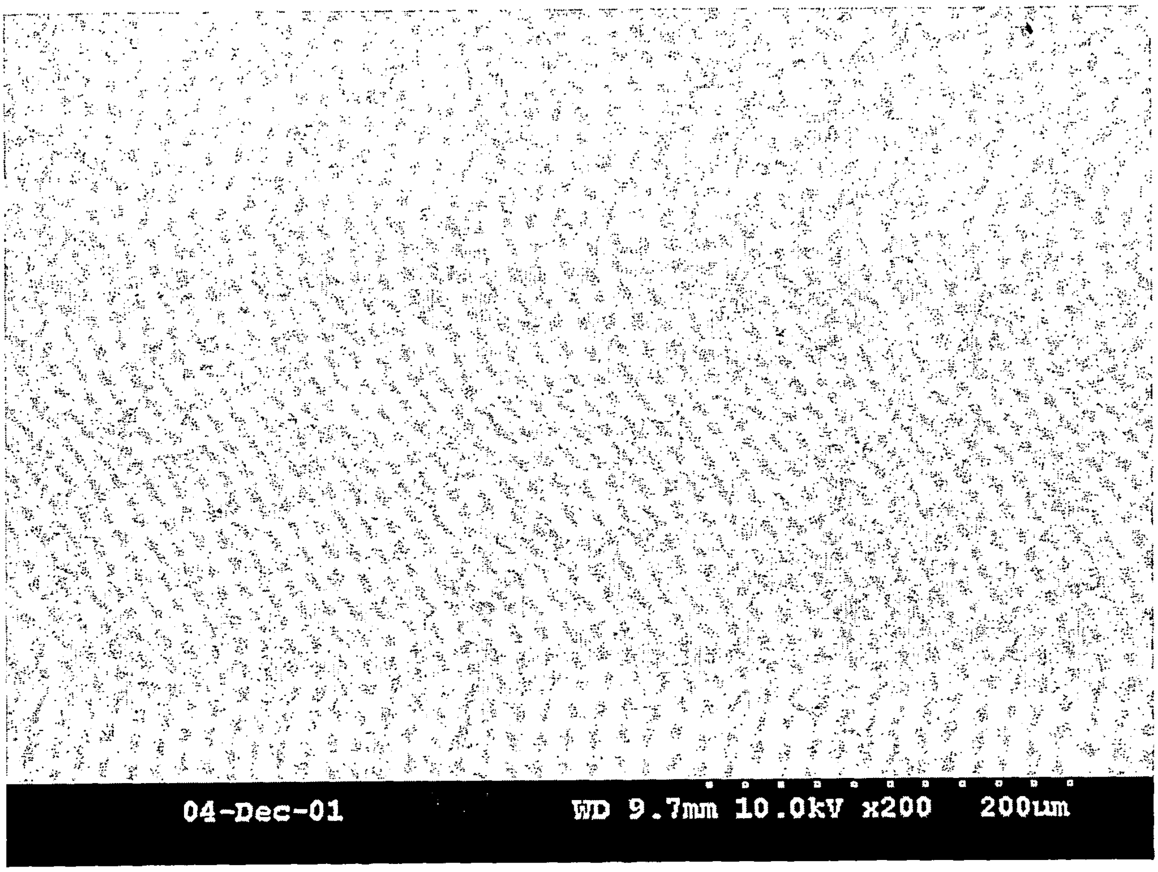

Fig. 1

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.41	1.12	0.73	34.3	25.7	0.02	0.96	0.26	0.00	0.008	0.05	0.01

Traces (Al + P + S + V +Zn + As + N + Sn + Pb + Cu + Ce) = 0.31

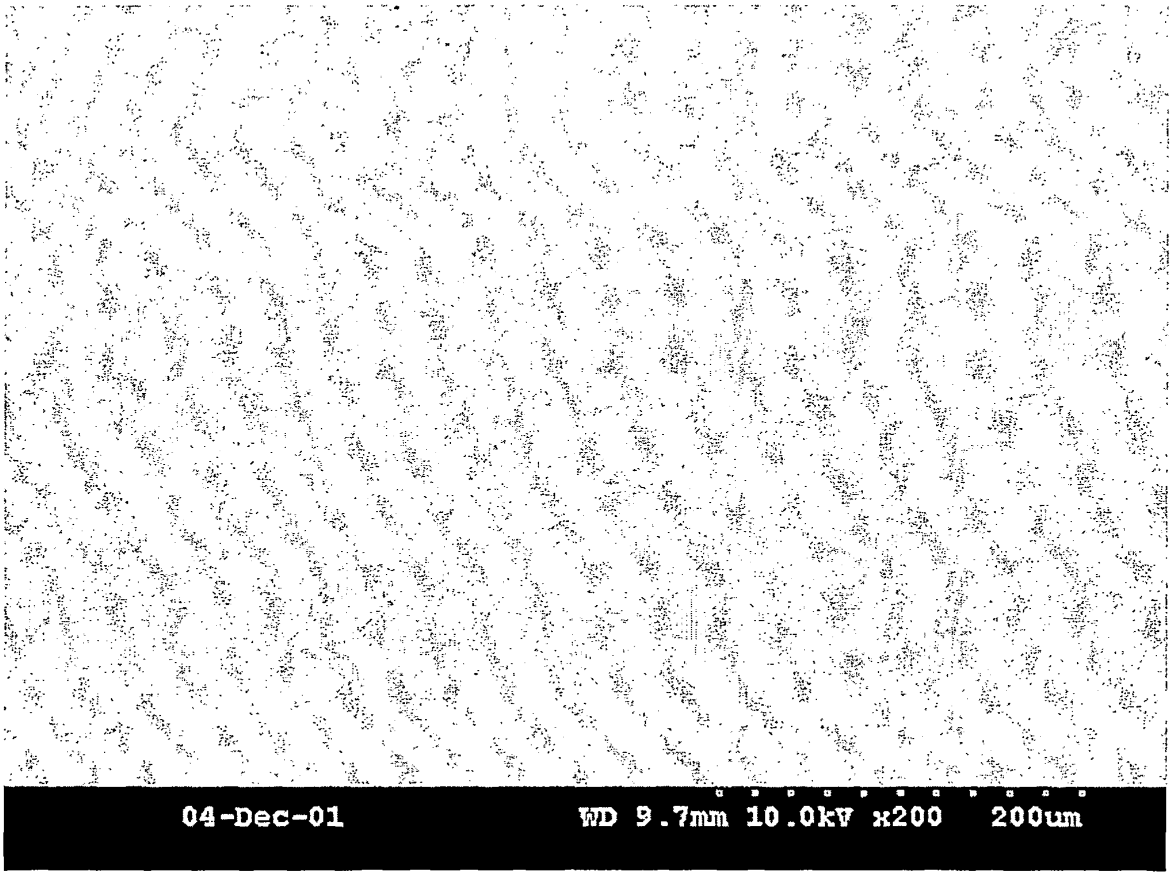

Fig. 2

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.41	1.85	1.47	34.7	24.4	0.05	0.96	0.10	0.09	0.01	0.04	0.02

Traces (Al + P + S + V +Zn + As + N + Sn + Pb + Cu + Ce) = 0.32

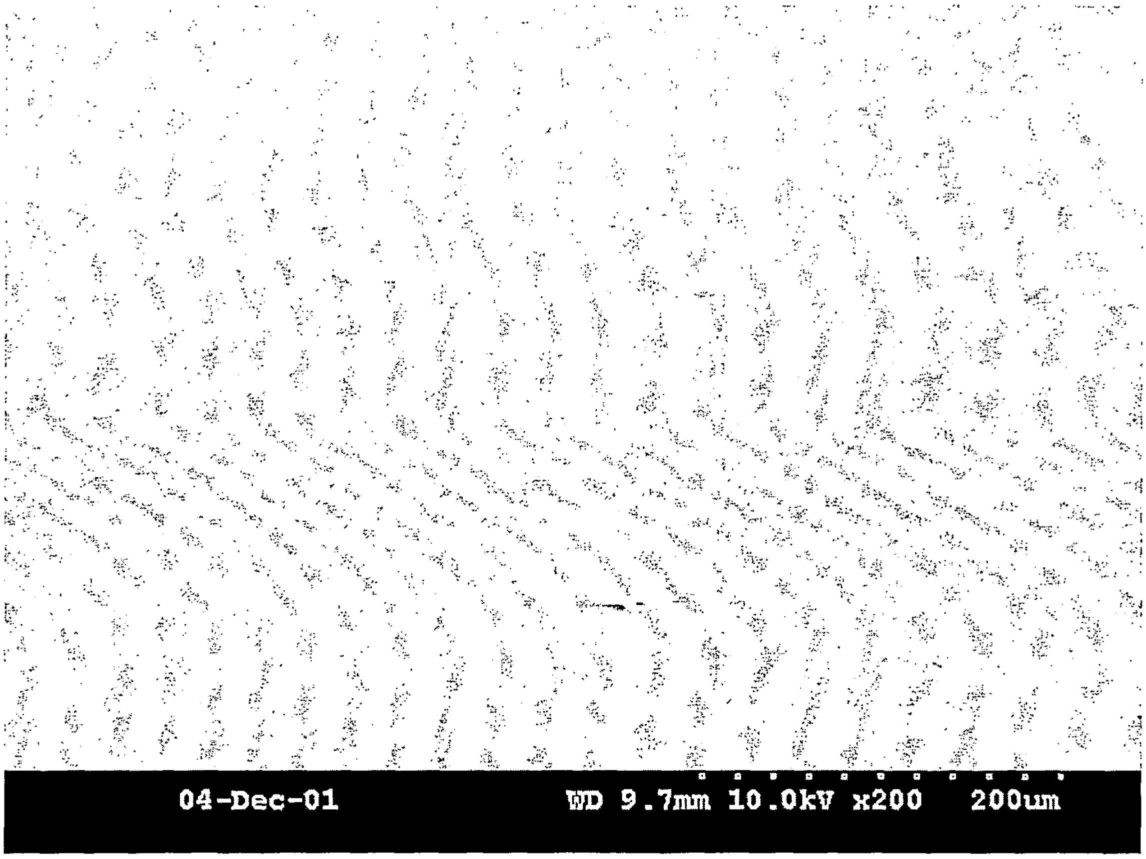

Fig. 3

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.40	1.51	0.96	33.2	24.7	0.02	0.77	0.31	0.08	0.01	0.05	0.01

Traces (Al + P + S + V +Zn + As + N + Sn + Pb + Cu + Ce) = 0.28

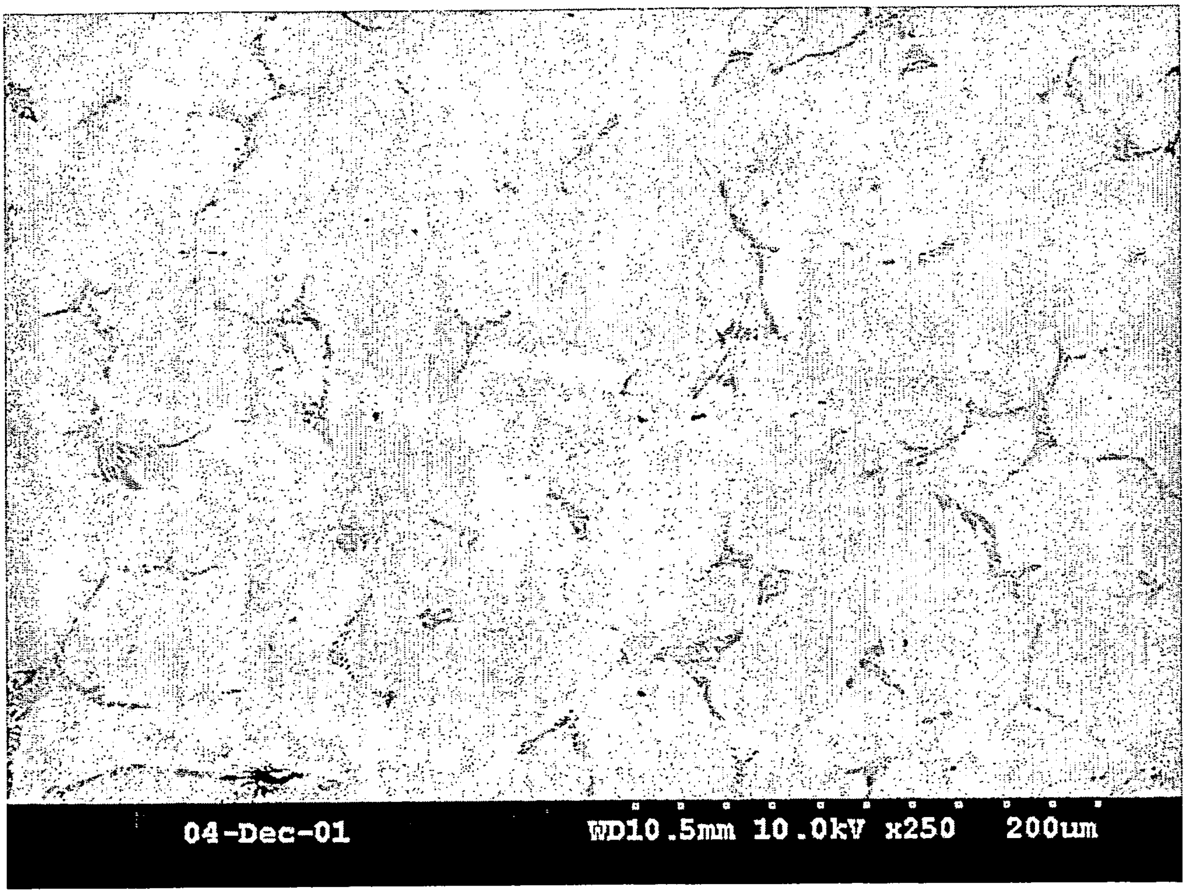

Fig. 4

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.45	1.30	0.90	33.8	25.7	0.03	0.85	0.25	0.10	0.01	0.04	0.01

Traces (Al + P + S + V +Zn + As + N + Sn + Pb + Cu + Ce) = 0.29

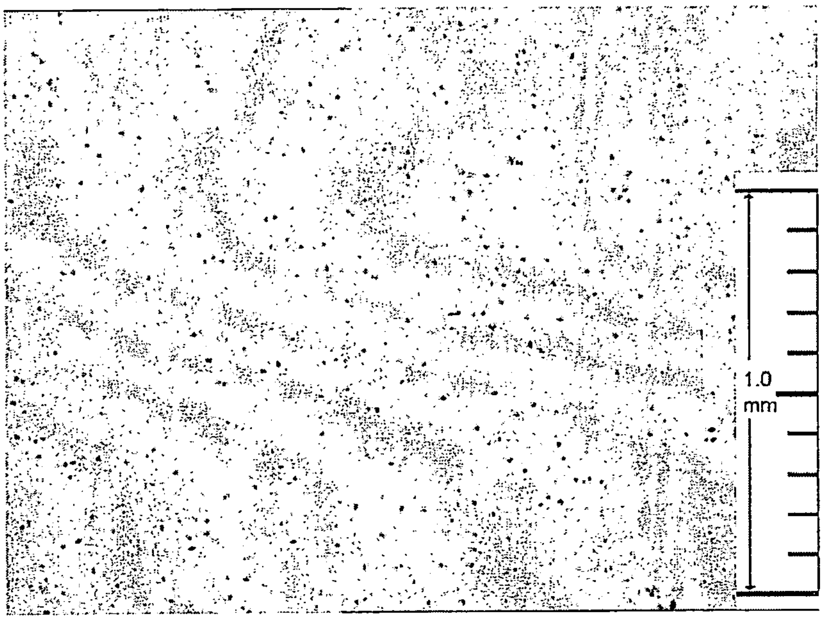

Fig. 5

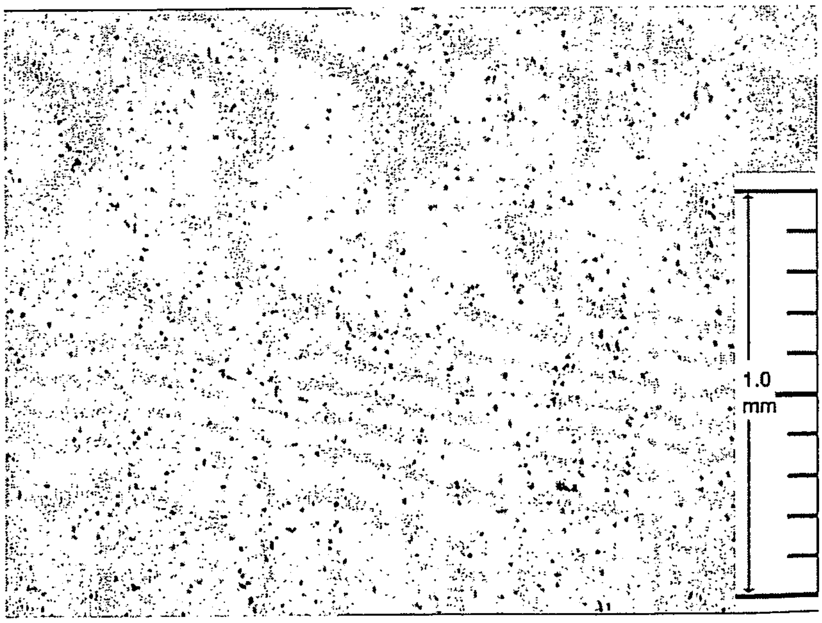

Fig. 6

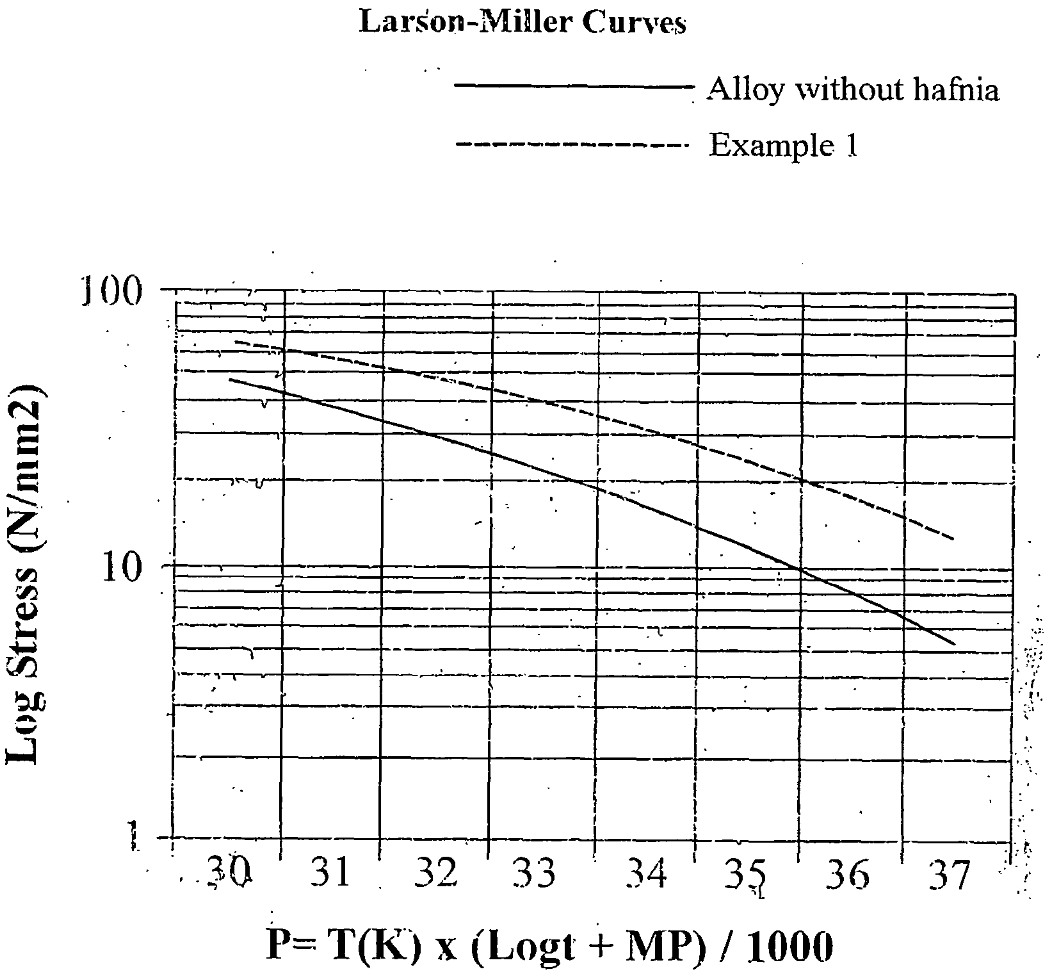
Larson-Miller Curves
Alloy without hafnia
Example 1
100
10
1
30
31
32
33
34
35
36
37
Log Stress (N/mm2)
P= T(K) x (Logt + MP) / 1000

Fig. 7

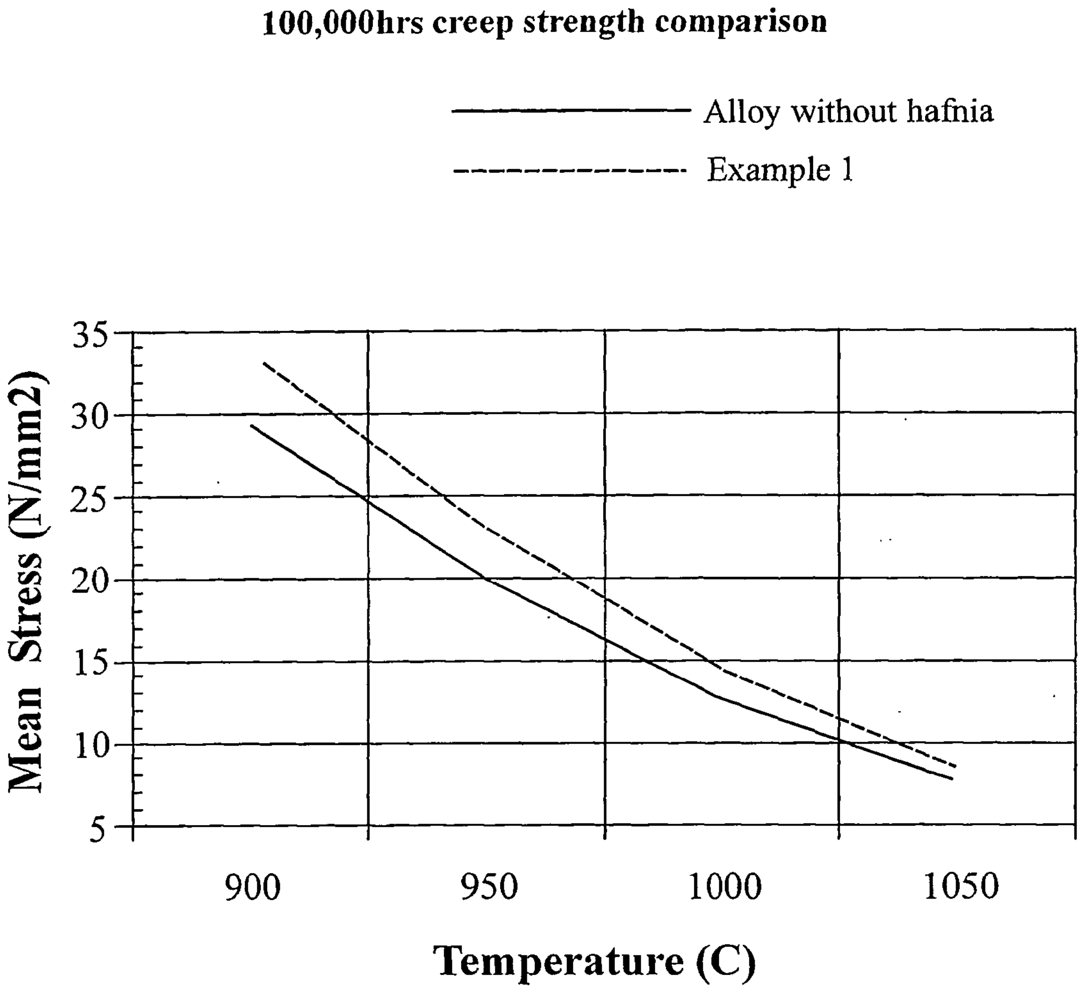
100,000hrs creep strength comparison
Alloy without hafnia
Example 1
Mean Stress (N/mm2)
35
30
25
20
15
10
5
900
950
1000
1050
Temperature (C)

Fig. 8

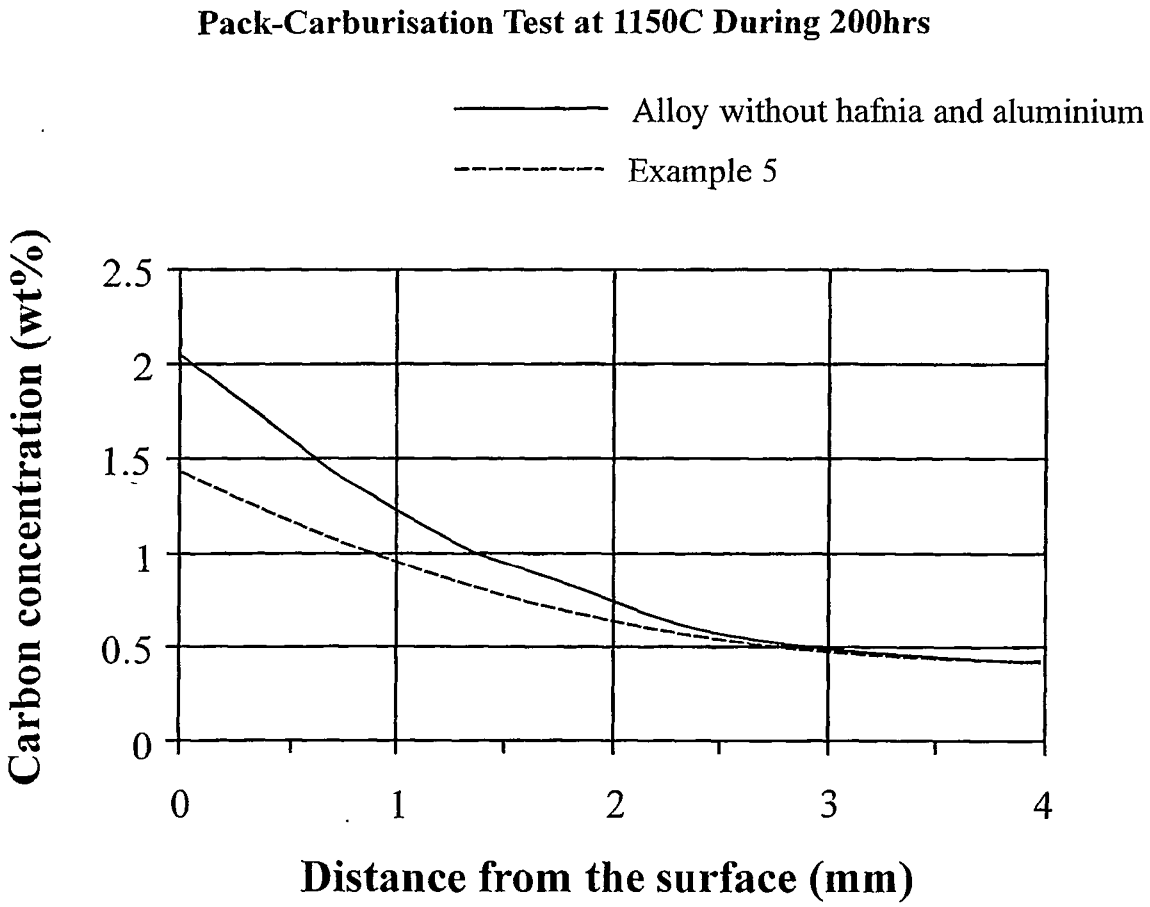
Pack-Carburisation Test at 1150C During 200hrs
Alloy without hafnia and aluminium
Example 5
Carbon concentration (wt%)
2.5
2
1.5
1
0.5
0
0
1
2
3
4
Distance from the surface (mm)

Fig. 9

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0050408 A **[0007]**
- US 6409847 B **[0008]**
- JP 05001355 A **[0009]**
- EP 0391381 A **[0010]**
- US 5851318 A **[0011]**

Non-patent literature cited in the description

- **BARTSCH, M. ; A. WASILKOWSKA ; A. CZYRSKA-FILEMONOWICZ ; U. MESSERSCHMIDT.** *Materials Science & Engineering,* 1999, vol. A 272, 152-162 **[0005]**