



(86) Date de dépôt PCT/PCT Filing Date: 2003/11/04
(87) Date publication PCT/PCT Publication Date: 2004/05/21
(85) Entrée phase nationale/National Entry: 2005/05/04
(86) N° demande PCT/PCT Application No.: GB 2003/004754
(87) N° publication PCT/PCT Publication No.: 2004/042101
(30) Priorité/Priority: 2002/11/04 (0225648.5) GB

(51) Cl.Int.⁷/Int.Cl.⁷ C22C 30/00, C22C 19/05, C22C 32/00

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(54) Titre : ALLIAGES HAUTE TEMPERATURE
(54) Title: HIGH TEMPERATURE ALLOYS

(57) **Abrégé/Abstract:**

An improved nickel-chromium-iron alloy is provided, which comprises up to about 5 % of hafnium-containing particles. In one embodiment, an improved creep resistant castable oxide dispersion strengthened nickel-chromium-iron alloy comprises up to about 5 % of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles. Further embodiments of the improved alloy can comprise additionally up to about 15 % by weight aluminium. The alloy is particularly useful in the production of creep resistant tubes and castings, for example, for the petrochemical market.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
21 May 2004 (21.05.2004)

PCT

(10) International Publication Number
WO 2004/042101 A3

(51) International Patent Classification⁷: **C22C 30/00**,
32/00, 19/05

(21) International Application Number:
PCT/GB2003/004754

(22) International Filing Date:
4 November 2003 (04.11.2003)

(25) Filing Language: English

(26) Publication Language: English

GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:
0225648.5 4 November 2002 (04.11.2002) GB

Published:
— with international search report
— with amended claims

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(88) Date of publication of the international search report:
12 August 2004

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Street East, Sheffield S4 7UQ (GB).

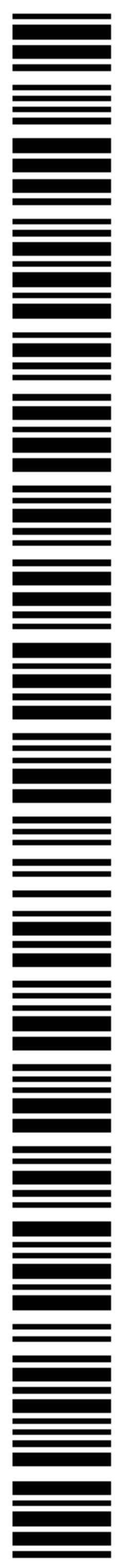
Date of publication of the amended claims:
30 September 2004

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: HIGH TEMPERATURE ALLOYS

(57) Abstract: An improved nickel-chromium-iron alloy is provided, which comprises up to about 5 % of hafnium-containing parti-
cles. In one embodiment, an improved creep resistant castable oxide dispersion strengthened nickel-chromium-iron alloy comprises
up to about 5 % of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles. Further embod-
iments of the improved alloy can comprise additionally up to about 15 % by weight aluminium. The alloy is particularly useful in
the production of creep resistant tubes and castings, for example, for the petrochemical market.



WO 2004/042101 A3

High temperature Alloys

Field of the Invention

The present invention relates to to high temperature alloys, and more
5 particularly to oxide dispersion strengthened alloys having improved creep
resistance and carburisation resistance at high temperatures.

Background to the Invention

10 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
15 resistance.

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
20 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
25 that cause relatively early failure under these process conditions. This is the
case presently for both castable alloy tubes and wrought alloy tubes.

An example of a known alloy material is INCOLOY® alloy 803 (UNS S
35045), which is an iron-nickel-chromium alloy specifically designed for use in
30 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.

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](http://www.oit.doe.gov/imf/factsheets/mtu_tubes)).

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.

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

Summary of the Invention

According to the present invention there is provided a new class of improved nickel-chromium-iron alloys comprising hafnium and methods for
5 their production.

In a first aspect, the invention provides an improved creep resistant nickel-chromium-iron alloy comprising up to about 5% by weight of hafnium-containing particles.
10

In a second aspect, 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.
15

In a third aspect, 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.
20

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

In a further aspect, the present invention provides an oxide dispersion
25 strengthened castable alloy comprising, by weight:

Carbon	0.01 – 0.7%
Silicon	0.1 – 3.0%
Manganese	0 – 3.0%
30 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%
5	Tungsten	0 – 4.0%
	Hafnium	0.01 – 4.5%
	Aluminium	0 – 15%
	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%
10	balance	iron and incidental impurities,

with 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 and that at least part of the hafnium is present as finely divided oxide particles.

A preferred embodiment of an oxide dispersion strengthened nickel-chromium-iron castable alloy according to the invention comprises, by weight:

20	Carbon	0.01 – 0.5%
	Silicon	0.01 – 2.5%
	Manganese	0 – 2.5%
	Nickel	15 – 50%
	Chromium	20 – 40%
25	Molybdenum	0 – 1.0%
	Niobium	0 – 1.7%
	Titanium	0 – 0.5%
	Zirconium	0 – 0.5%
	Cobalt	0 – 2.0%
30	Tungsten	0 – 1.0%
	Hafnium	0.01 – 4.5%
	Aluminium	0 – 15%
	balance	iron and incidental impurities,

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

5

Preferred alloy compositions according to the invention include the following:

	Carbon	0.3 to 0.7%
10	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	30 to 40%
	Chromium	20 to 30%
	Molybdenum	3.0% max.
15	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
20	Tungsten	1.0% max.
	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%
	Balance	iron and incidental impurities,

25 with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

	Carbon	0.03 to 0.2%
30	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.
5	Zirconium	0.5% max.
	Cobalt	2.05% max.
	Tungsten	1.0% max.
	Aluminium	0 – 15.0%
	Nitrogen	0.001 – 0.5%
10	Oxygen	0.001 – 0.7%
	balance iron and incidental impurities,	

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

	Carbon	0.3 to 0.7%
	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
20	Nickel	40 to 60%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
25	Titanium	1.0% max.
	Zirconium	1.0% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 – 15.0%
30	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%
	balance iron and incidental impurities,	

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

5	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 50%
	Chromium	30 to 40%
10	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
15	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 – 15.0%
	Nitrogen	0.001 – 0.5%
	Oxygen	0.001 – 0.7%
20	balance iron and incidental impurities,	

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

25	Carbon	0.3 to 0.7%
	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
	Nickel	19 to 22%
30	Chromium	24 to 27%
	Molybdenum	3.0% max.
	Niobium	2.0% max
	Hafnium	0.01 to 4.5%

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,

10 with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

15 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%
20 Titanium 0.5% max.
Zirconium 0.5% max.
Cobalt 2.0% max.
Tungsten 1.0% max.,
Aluminium 0 – 15.0%
25 Nitrogen 0.001 – 0.5%
Oxygen 0.001 – 0.7%
balance iron and incidental impurities,

30 with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

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	1.0 max
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	Tungsten
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.

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%.. Preferably the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less, more preferably from 5 microns to 0.25 microns or less.

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

10

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

25

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

30

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

11

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

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

15

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%.

20

In a still further aspect, the invention provides a method of manufacturing an oxide dispersion strengthened castable 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.

25

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, 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

30

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.

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 and/or 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.

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

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.

5

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
10 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
15 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.

20 The melt temperature is preferably in the range of from 1350°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.

Hafnium particles are preferably added to the melt just before pouring
25 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.
30 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

preferably 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.

5 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
10 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.

15 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
20 nitrides, tungsten carbides, tungsten nitrides, and/or tungsten carbo-nitrides.

 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
25 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
30 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.

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).

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).

30

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.

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

In a still further aspect of the invention this method allows the addition of elements that are reactive with oxygen for example titanium, zirconium or
10 aluminium, to the melt, before pouring the molten alloy into the mould.

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

15 The removal of available free oxygen from the melt, involves the reaction of the hafnium particles with oxygen, this helps to ensure that any titanium and/or zirconium and/or aluminium additions do not form oxides, which could react detrimentally with the hafnium particles and reduce the yields of titanium, zirconium and aluminium present in the alloy.

20

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.

25

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
30 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.

- 5 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
- 10 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
- 15 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.

Brief Description of the Drawings

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

5

Figure 1 is a photomicrograph of a first alloy according to the invention with its composition by weight;

10

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;

15

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

20

Figure 6 is a photomicrograph of a sixth alloy according to the invention.

25

Figure 7 is a chart showing the results of a Larson-Miller plot of stress-rupture properties of prior art alloys and an alloy according to this invention.

Figure 8 is a chart showing comparison of creep strength between a prior art alloy and an alloy according to this invention.

30

Figure 9 shows the results of a pack-carburisation test performed between a prior art alloy and an alloy according to this invention.

Detailed Description of the Best Mode for Carrying Out the Invention

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

5

Example 1

The following melt composition is produced in a clean furnace:

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

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-
20 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 in order to get oxidised, and so to transform the hafnium in hafnium oxide. After the hafnium addition, 0.18% titanium, in the form of FeTi is added to the ladle.

25

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

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

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
 5 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.

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

10

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 (4567)	21.44 (3126)	13.62 (1991)	8.03 (1180)	4.40 (653)

Example 2

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

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

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
 25 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.

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

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

The following melt composition is produced in a clean furnace:

15	Nickel	33% - 35%
	Chromium	24% - 26%
	Carbon	0.04% - 0.08%
	Silicon	1.0% – 1.2%
	Manganese	1.0% – 1.2%
20	Molybdenum	0.14% - 0.3%
	Iron	balance.

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 in order to get oxidised, and so to transform the hafnium in hafnium oxide dispersion. After the hafnium addition, 0.25% titanium, in the form of FeTi is added to the ladle.

30

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:

22

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

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

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

10 Example 4

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

15

Zr	Co	W
0.01	0.04	0.08

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

20

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

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

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

10 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%
15	Niobium	0.8 – 0.9%
	Silicon	1.6 – 1.8%
	Manganese	1.1 – 1.3%
	Iron	balance.

20 100Kg of the melted is tapped into a ladle, whilst adding hafnium particles to the tap stream to give a hafnium level of 0.15% to 0.30% by weight in the alloy and in order to get it oxidised, and so to transform the hafnium in hafnium oxide dispersion. Immediately before pouring aluminium is added to the melt to give an aluminium level of 1.5% to 1.8%.

25

 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
30 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%.

5 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.

10 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.

15 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
20 disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel
25 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.

AMENDED CLAIMS

**[Received by the International Bureau on 09 August 2004 (09.08.2004);
original claims 15-17, 22, 25, 44, 46-47, 50, 58-59 cancelled'
original claims 37 and 38 replaced by amended claims 37 and 38
(14 pages)]**

1. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

Carbon	0.01 – 0.7%
Silicon	0.1 – 3.0%
Manganese	0 – 2.5%
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,

with 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 and that at least part of the hafnium is present as finely divided oxide particles.

2. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

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%,

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

3. 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,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

4. An alloy according to claim 1 having the following composition, 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,	

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

5. An alloy according to claim 1 having the following composition, 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,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

6. An alloy according to claim 1 having the following composition, by weight:

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,	

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

7. An alloy according to claim 1 having the following composition, by weight:

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,	

with the proviso that at least one of niobium, titanium and zirconium is

present and that at least part of the hafnium is present as finely divided oxide particles.

8. An alloy according to claim 1 having the following composition, by weight:

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,	

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

9. An alloy according to any one of claims 1, 2, 3, 5, or 7, having a carbon content of from 0.3 to 0.5% by weight.

10. An alloy according to claim 1 or 2, having a carbon content of from 0.03 to 0.2% by weight.

11. 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%.

12. An alloy according to claim 11, 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 0.1% to 1.0%.

13. An alloy according to claim 11 or 12, 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 0.2 to 0.5%.

14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.

18. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.

19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 5 microns to 0.25 microns, or less.

20. An alloy 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	balance,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

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

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

Carbon 0.34%

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

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

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

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

21. An alloy according to any one of the preceding claims substantially as described in Examples 1 to 4.

23. A nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

24. 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 divided oxidised particles.

26. 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.

27. A method according to claim 26, in which the alloy is an alloy as claimed in any of claims 1 to 25.

28. A method according to claim 26 or 27, wherein the hafnium particles have a particle size of less than 50 microns.

29. A method according to any one of claims 26 to 28, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.

30. A method according to any one of claims 26 to 29, wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.

31. A method according to claim 30, in which the hafnium particles are

added to the molten alloy in a ladle.

32. A method according to claim 30, in which the hafnium particles are added to the molten alloy in the furnace

33. A method according to anyone of claims 26 to 32, in which the hafnium is electrolytic hafnium.

34. A method according to any one of claims 26 to 33, wherein the level of oxygen in the melt is varied by the addition of one or more substance selected from the group:

- silicon,
- chromium,
- manganese,
- calcium,
- CaSi,
- CaSiMn,
- niobium,
- titanium,
- zirconium.

35. 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 and varying the level of oxygen in the melt by, the addition of at least one substance chosen from the group:

- silicon,
- chromium,
- manganese,
- calcium,
- CaSi,
- CaSiMn,
- niobium,
- titanium,

zirconium.

36. 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 the formation of detrimental oxide from the reactive elements titanium, zirconium, aluminium is reduced.

37. A method according to any one of claims 26 to 36 wherein any one of the elements titanium or zirconium are added after hafnium into the melt.

38. A method as claimed in claim 37 wherein any one of the elements titanium or zirconium are added after the hafnium in the melt, and just before pouring in the mould.

39. 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 and which controls the partial pressure of oxygen to permit the oxidation of the hafnium in situ.

40. 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 and which controls the free oxygen content to permit the oxidation of the hafnium in situ.

41. 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 and which controls the partial pressure of at least one element selected from the following group:

oxygen,
carbon,
nitrogen,

hydrogen;

to permit the oxidation of the hafnium in situ.

42. 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 and which permits the oxidation in situ of beneficial oxide dispersion as hafnium oxide, avoiding the formation of detrimental precipitates.

43. A method as claimed in claim 42 which limits in situ oxidation to beneficial oxide dispersion of hafnium oxides and avoid its reaction with slag.

45. A method according to any of claims 26 to 44, in which the melt temperature is in the range of from 1350°C to 1700°C.

48. A method according to any one of claims 26 to 47, in which the alloy is formed into a tube by rotational moulding.

49. A method according to any one of claims 26 to 48 substantially as described in Examples 1 to 4.

51. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium particles to the melt before pouring.

52. A creep resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

53. A tube according to claim 52, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.

54. A nickel-chromium-iron alloy tube comprising up to about 5% of

hafnium-containing particles substantially as herein before described.

55. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.

56. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.

57. A nickel-chromium-iron alloy having a structure substantially as described and illustrated in Figures 5 or 6 of the accompanying Drawings.

60. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.

61. An alloy according to any one of claims 1 to 25, 56 and 57 produced by a method according to any one of claims 26 to 51.

1/9

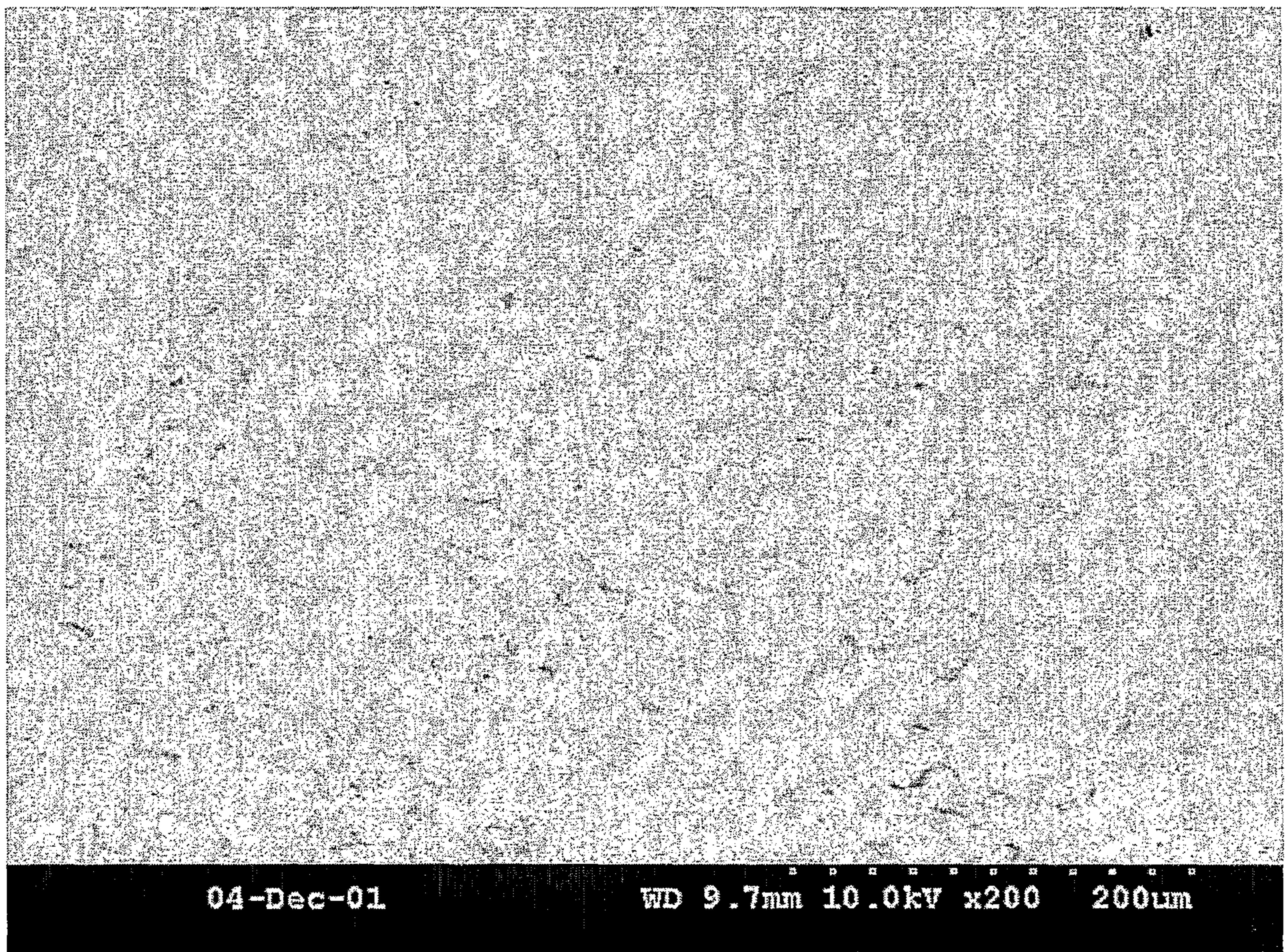


Figure 1

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. 1

2/9

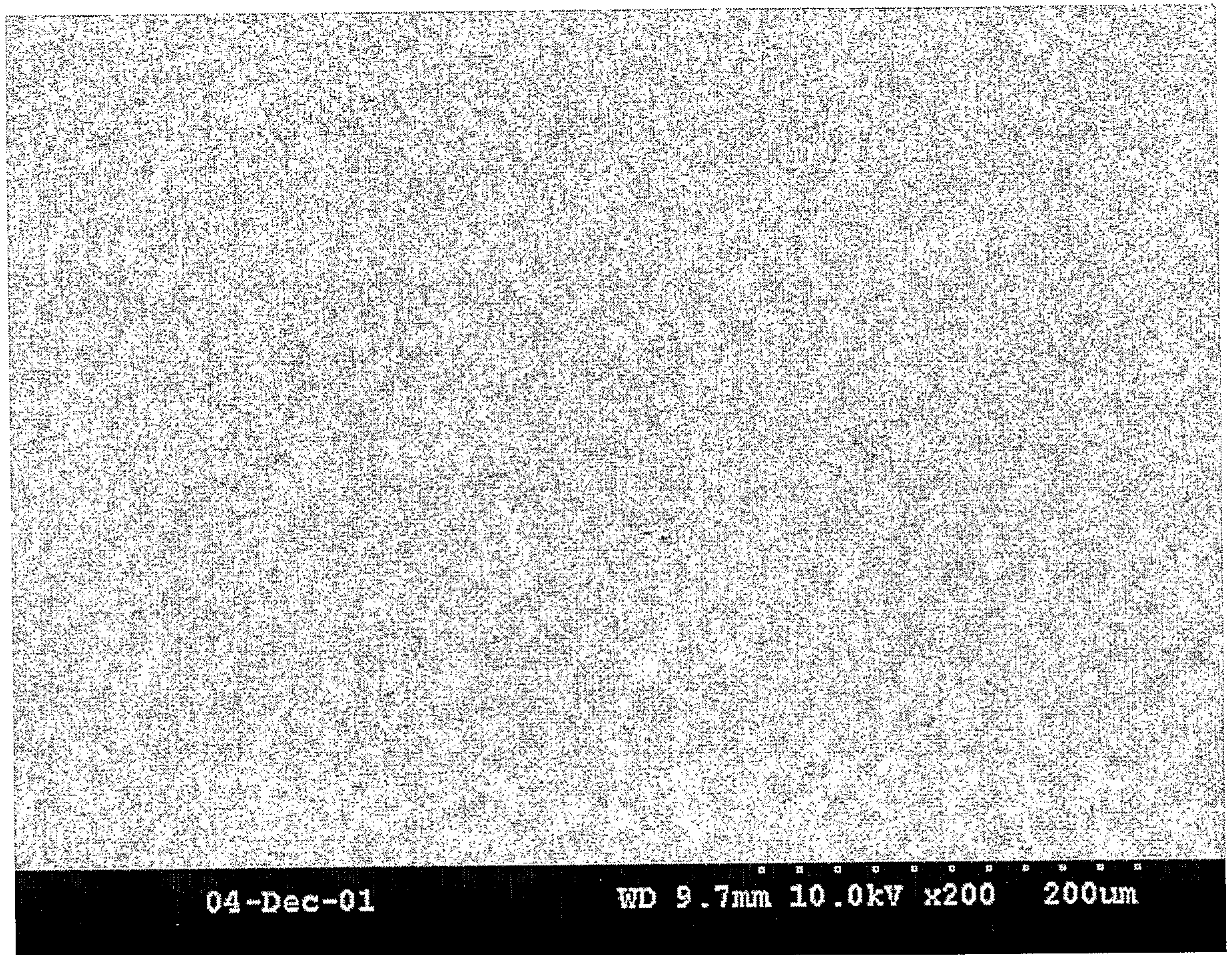


Figure 2

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. 2

3/9

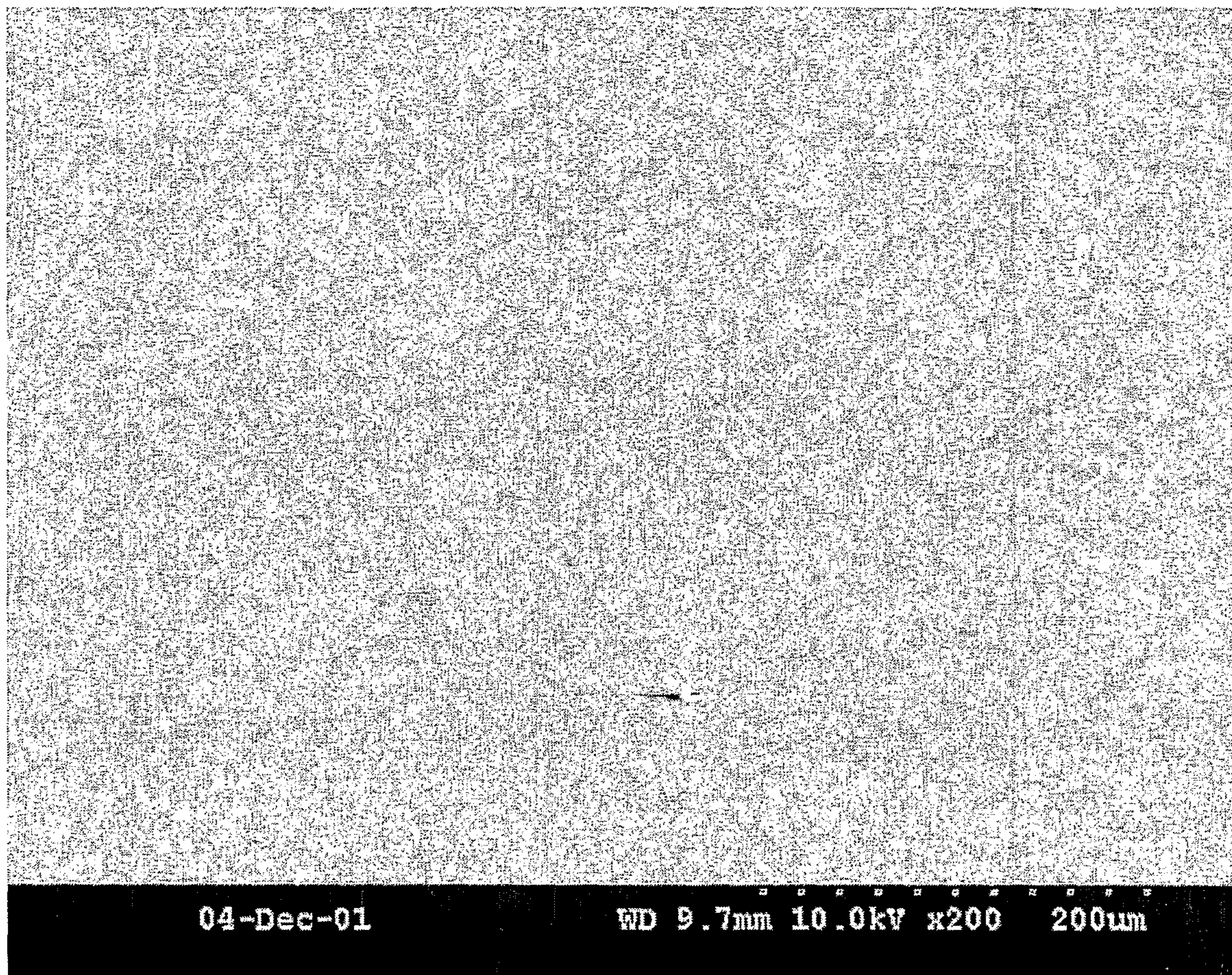


Figure 3

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. 3

4/9

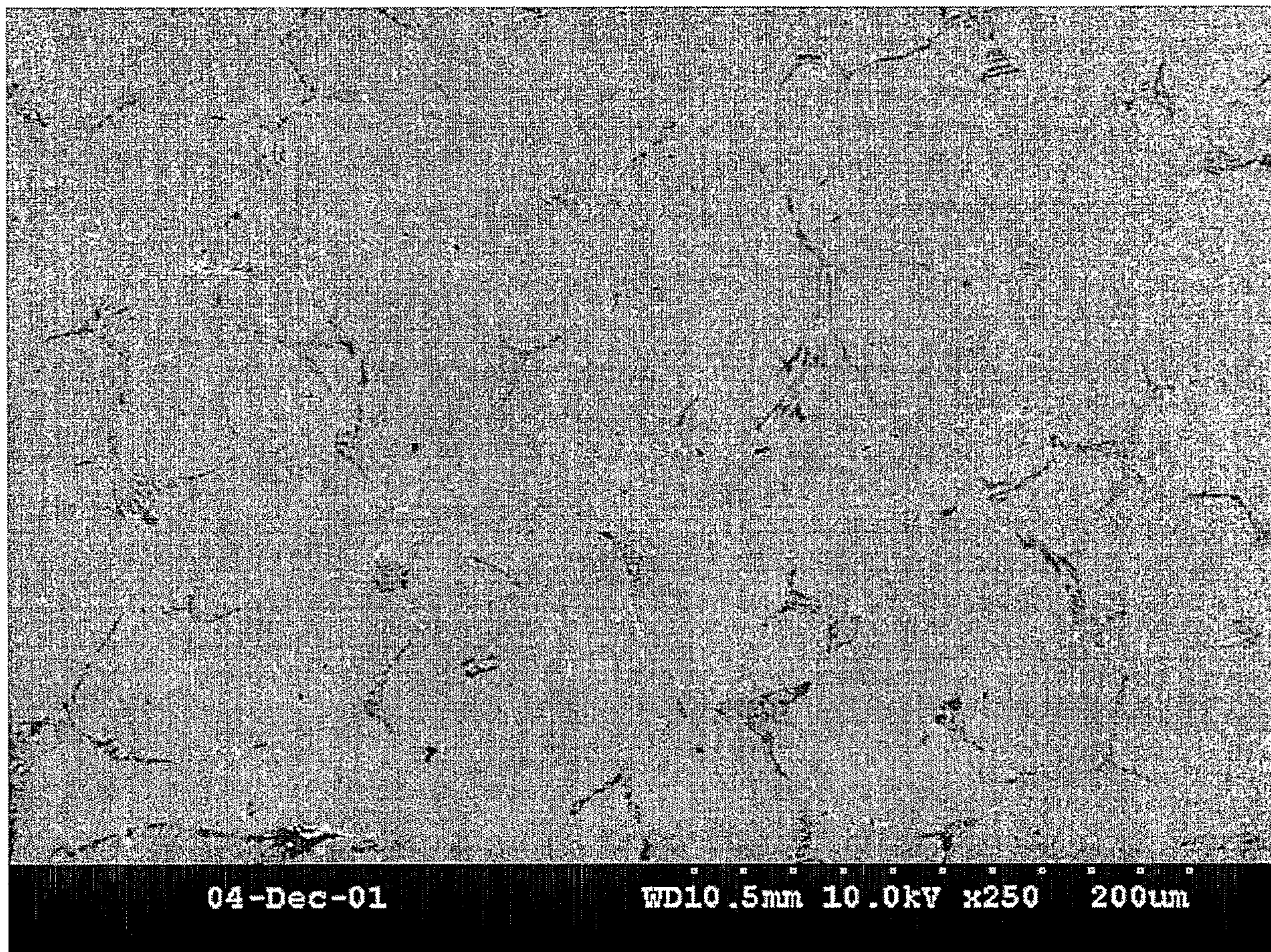


Figure 4

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. 4

5/9

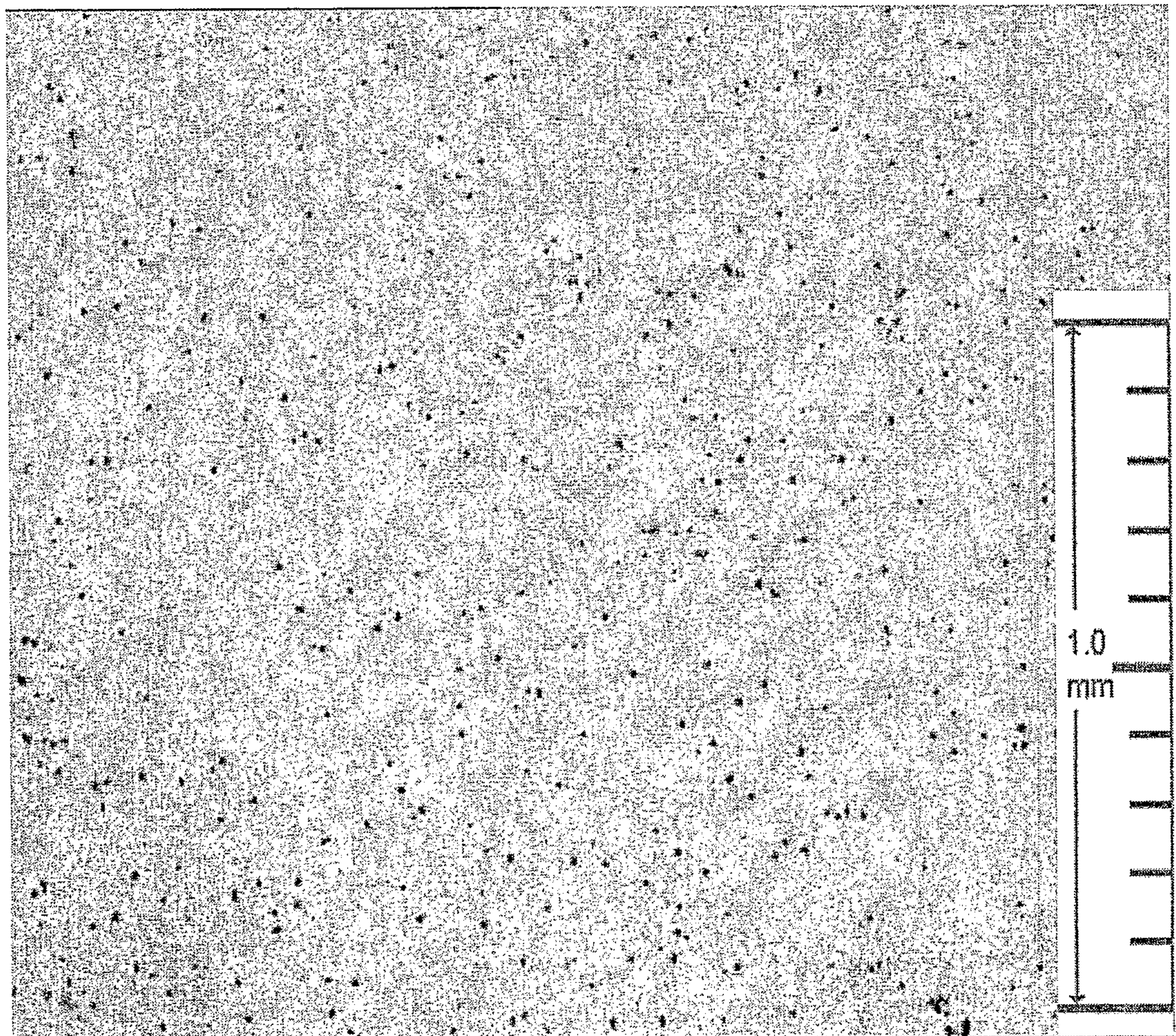


Fig. 5

6/9

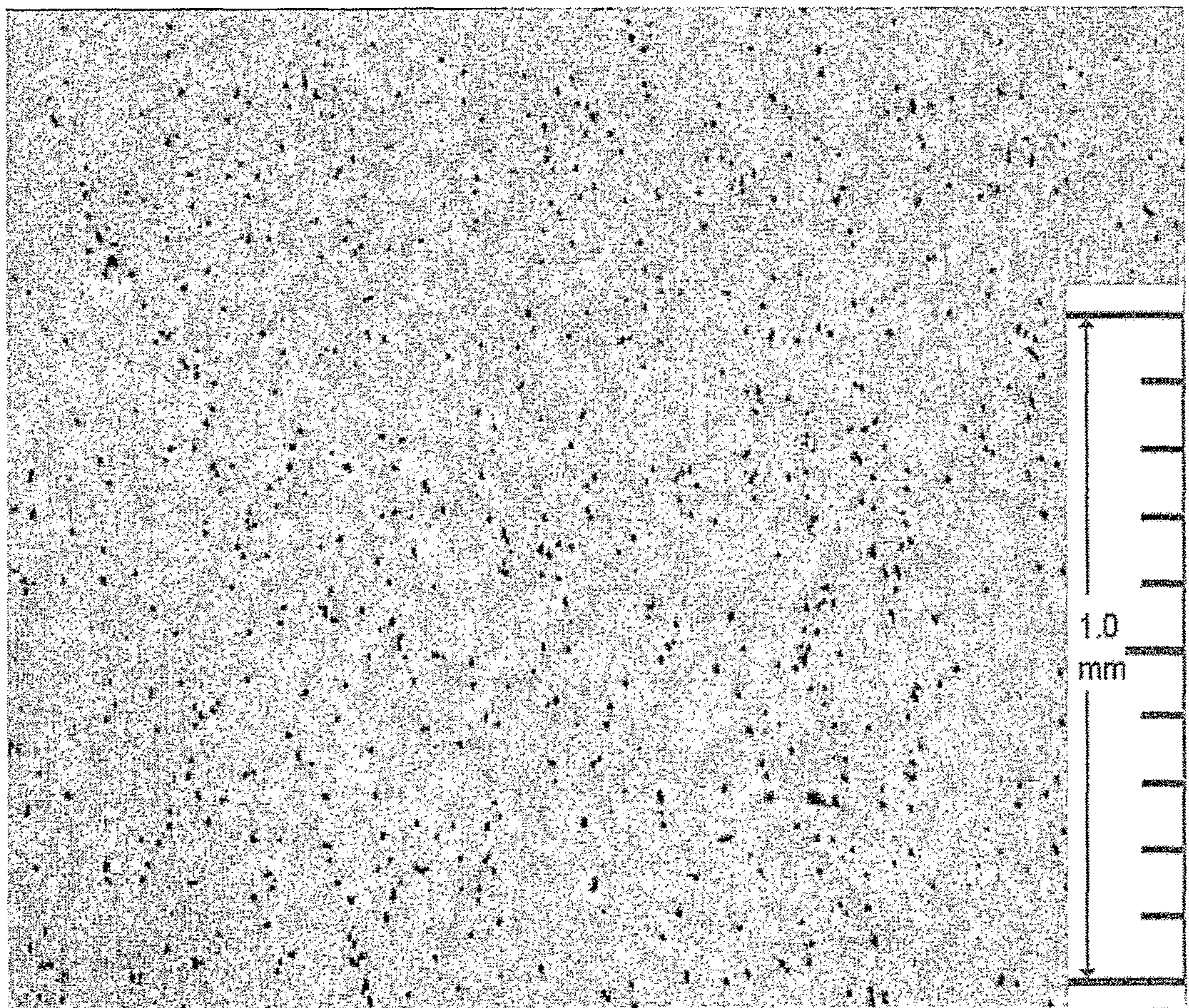


Fig. 6

7/9

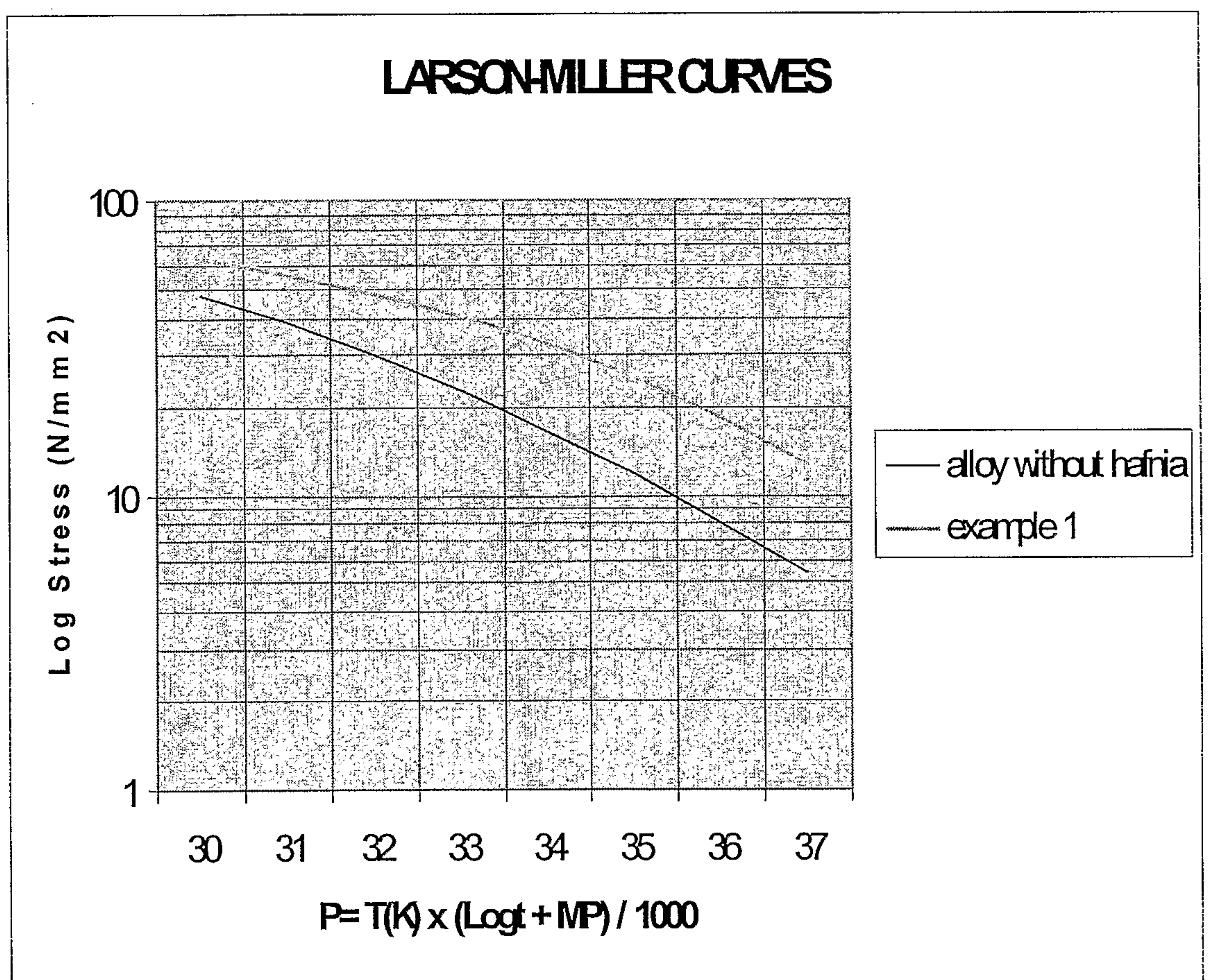


Fig. 7

8/9

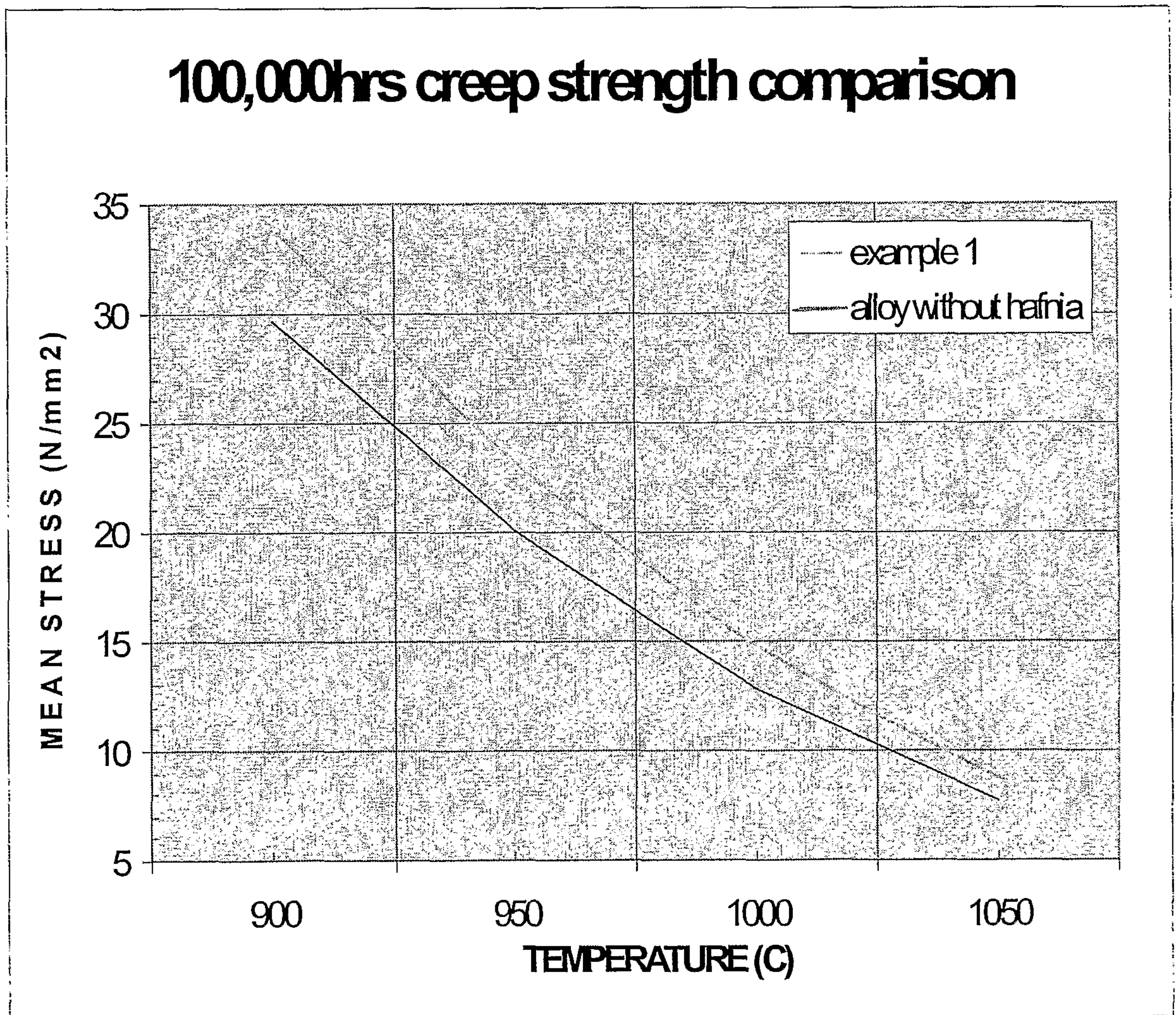


Fig. 8

9/9

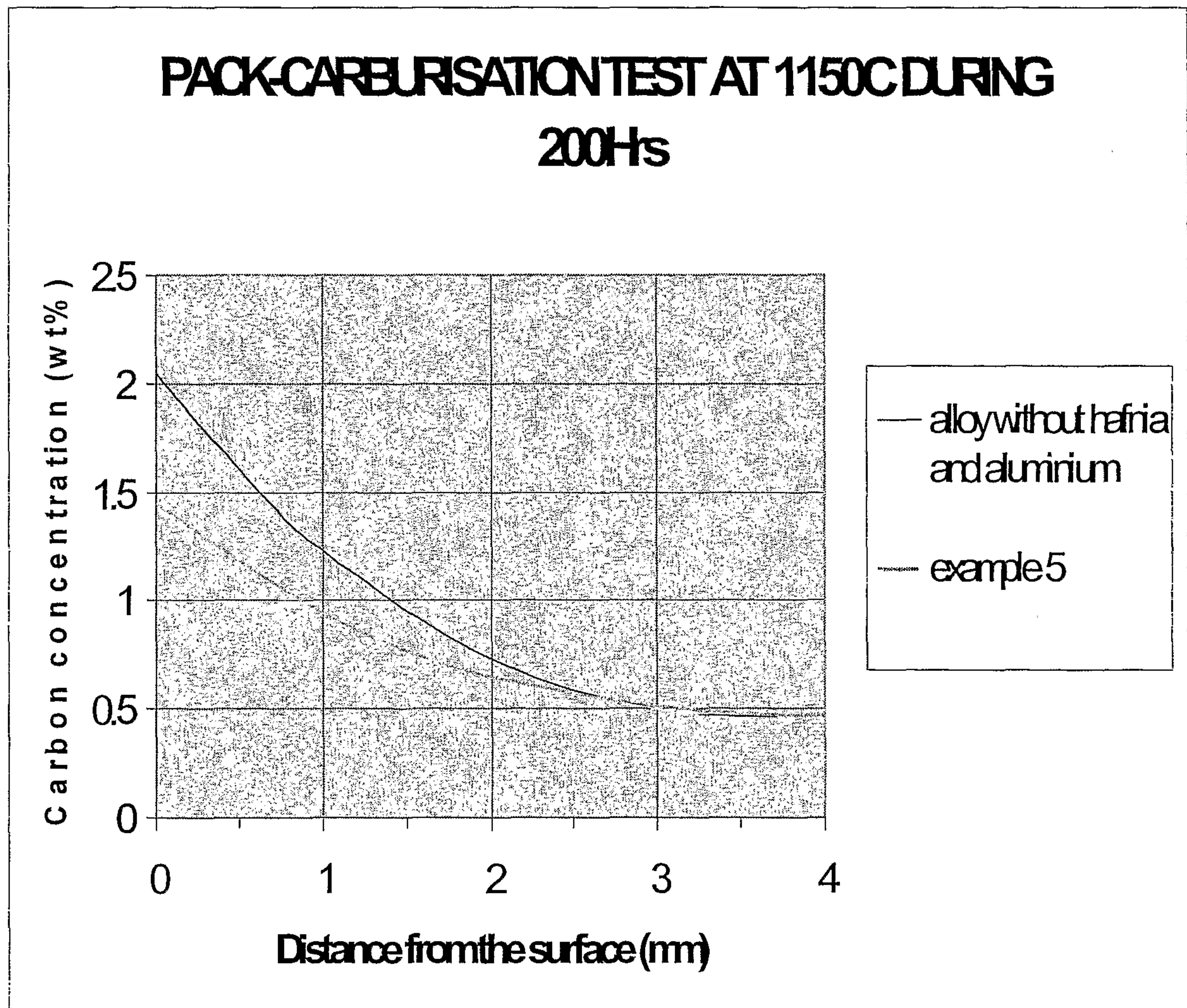


Fig. 9