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(54) **HIGH CREEP RESISTANT REFRACTORY STEELS**

(57) Refractory steels comprising Iron, Nickel, Chrome, Silicon, Manganese, Carbon, Molybdenum, and optionally Tungsten and Niobium; in certain proportions, having improved creep resistance and crack growth rate, and a process of preparation thereof. The steels may be used to manufacture pieces of industrial equipment, such as radiation tubes, especially for heat

treatment furnaces; buckets, especially to contain parts in heat treatment furnaces used in the steel and aluminium flat product; beams; rolls for parts transport in hot stamping sector; trays and rails in the investment casting and ceramic sector; and entrance and outside segments in the mining and cement roasting furnaces.

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Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention is encompassed within the ferrous metals processing industry. Particularly, it relates to a new family of refractory stainless steels, particularly ferrous refractory steels, which present advantageous values of creep resistance and crack growth rate, when compared with standard refractory stainless steels, such as 1.4848 refractory steel. The refractory steels according to the present invention have modified chemical composition ranges of main chemical elements that appear in these standard steels (C, Si, Mn, Cr and Ni), incorporate new combined chemical elements such as Mo, Nb and W, and preferably are submitted to an ageing heat treatment for optimum carbides precipitation. These features allow achieving a combined effect that renders significant changes in high temperature properties of these refractory steels.

BACKGROUND OF THE INVENTION

15 **[0002]** Refractory stainless steels are commonly used in industrial equipment which is going to be in use in environments at high temperatures and in corrosion environments, supporting significant loads and wear. Their application is common in industrial machinery, working at high temperature ranges (400-1100°C) supporting loads, wear and corrosive conditions. Examples of the use of these steels can be found in structural components, radiation tubes and buckets to contain parts in heat treatment furnaces used in the steel and aluminium flat product and foundry sectors, beams for parts transport in hot stamping sector, trays and rails in the investment casting and ceramic sector and entrance and outside segments in the mining and cement roasting furnaces. The use of these steels is highly conditioned by two main factors; their in-service life and the cost of the raw materials used to manufacture them.

20 **[0003]** Refractory steels are used in applications in mild corrosive environments, where transporting or containing loads, sliding or rolling over different surfaces is required. These steels, used to manufacture components located in high demanding areas of industrial equipment (mainly furnaces), are responsible of the correct routine performance of the equipment. Their bad functioning leads to production stops (with consequent economical losses) and significant energy losses. Main failure modes of these components are linked, in order of importance, with long time deformation (creep), crack propagation, thermal fatigue, wear and corrosion. The achievement of materials with higher creep properties, crack growth rate, thermal fatigue and wear resistance, simultaneously maintaining a good level of corrosion resistance, is thus critical to avoid component prompt degradation, leading to a higher consumption of spare parts.

25 **[0004]** The in-service life of such components is critical because their substitution in an equipment working in a continuous way, requires the complete stop of the manufacturing process, representing significant energy and productivity losses for the company. In all cases, the fast degradation of components supposes also significant resources consumption of valuable and scarce elements contained therein.

30 **[0005]** Refractory stainless steels are reported in standard norm EN-101295 "Heat resistant stainless steels", including steels containing as main chemical alloying elements, C, Si, Mn, Cr, Ni, Mo, Nb or W. These steels are manufactured using casting processes, comprising chemically bonded sand molds and open air induction furnaces, or in steel making processes, using arc furnaces, ladle furnaces and a vacuum degassing step, prior to continuous casting or ingot manufacturing.

35 **[0006]** These refractory steels are characterized by a carbon (C) content up to 0.7 wt. %, which increases yield strength and tensile strength, but reduces ductility; by a silicon (Si) content in the range of 1 wt. % to 2,5 wt. %, which increases mechanical properties, such as tensile strength and yield strength, but reduces ductility and elongation, and increases brittle temperature transition; by a manganese (Mn) content, in most cases below 2 wt.%, which increases hardenability, yield strength and tensile strength.

40 **[0007]** On the other hand, the chromium (Cr) content in known refractory steels can be in a wide range from 6 to 30 wt.%, and it provides corrosion resistance, hardenability and increases yield strength and tensile strength, reducing the elongation values. Nickel content in such refractory steels moves from 5 to 50 wt. % and is mainly added to increase high temperature properties, such as creep. Nb increases high temperature properties by the precipitation of NbC and Z phase (Nb(C,N)) and W by needle shaped Laves formation.

45 **[0008]** The common practice to increase high temperature properties of creep is achieved by significantly increasing the wt. % of the nickel content; however this is a significant challenge, requiring additional nickel quantities, for example for 1.4848 refractory steels, with a Ni content around 20 wt.%, it is incremented by an additional 15 -20 wt.%, to obtain a significant effect in creep resistance and with the following drawbacks: negative effect on other properties such as thermal fatigue performance, due to the thermal conductivity reduction of the steel and an increased cost of the steel.

50 **[0009]** The above mentioned 1.4848 refractory steel is an austenitic stainless steel formulated for casting, is known to be a heat resistant stainless steel, and is widely used in applications such as the automotive industry (e.g. turbochargers, manifolds, parts for hot gas ranges - 950°C...), mechanical engineering (flow elements, parts for stable hot gas ranges

900-1100°C) and plant engineering (for oil and gas, valve bodies...). 1.4848 is the EN numeric designation for this material; besides iron, it contains Carbon, Chrome, Manganese, Molybdenum, Nickel, Phosphorus, Silicon and Sulfur, in the following ranges:

5	Chrome:	24.0-27.0 wt. %
	Nickel:	19.0-22.0 wt. %
	Silicon:	1-2.5 wt. %
	Carbon:	0.30-0.50 wt. %
10	Manganese:	<2.5 wt. %
	Molybdenum:	<0.5 wt. %
	Phosphorus:	<0.03 wt. %
	Sulfur:	<0.03 wt. %

15 **[0010]** There remains a need for new refractory steels with superior properties that will extend the in-use life on components at an affordable price.

BRIEF DESCRIPTION OF THE FIGURES

20 **[0011]** **Figure 1.** Microstructure of Steel 3 according to the invention, showing Tungsten and Niobium eutectic carbides.

Figure 2: Visual comparison of carbides precipitation before (Figure 2a) and after ageing heat treatment (Figure 2b) of Steel 3 according to the invention.

25 **Figure 3:** Scheme of keelblock test sample. The area of extraction of the samples is indicated. The measurements are provided in millimetres:

Measurements (mm)	u	v	x	y	Z
	25	55	40	140	140

30 **Figure 4:** Scheme of test specimens for long term creep testing, with detailed measurements, provided in mm. Ø refers to diameter. R2 refers to a radius of 2 mm. M12 refers to thread type M12.

Figure 5: Scheme of test specimens for creep crack growth rate testing, with detailed measurements, provided in mm. Ø refers to diameter.

35 **Figure 6:** Scheme of test sample for thermal fatigue, with detailed measurements, provided in mm. Ø refers to diameter. R3 refers to a radius of 3 mm.

Figure 7: Microstructure of samples of Steels 1, 2, 3, 4 and 5 according to the invention.

40 **[0012]** The microstructure images were taken with a field emission scanning electron microscope (FE-SEM); Ultra Plus by Zeiss (DE).

DESCRIPTION OF THE INVENTION

45 **[0013]** Refractory stainless steels are well-known by their balance of high temperature mechanical properties in a corrosive environment supporting significant loads, at an affordable price and are used in mass production of industrial components.

[0014] The present invention provides new refractory steels, to achieve higher values of deformation resistance to constant loads at high temperature even when a crack has been initiated (creep and crack growth rate), in comparison with reference steels such as 1.4848 refractory steel.

50 **[0015]** In a first aspect, the present invention refers to a refractory steel, comprising, in weight percentages based on the total weight of the steel:

18.0 - 26.0 wt. % Nickel (Ni);

55 16.0 - 26.0 wt. % Chrome (Cr);

1.0 - 2.0 wt. % Silicon (Si);

0.5 - 1.5 wt. % Manganese (Mn);

0.4 - 0.7 wt. % Carbon (C);

5 0.2 - 1.0 wt. % Molybdenum (Mo);

0.1 - 2.0 wt. % Tungsten (W);

10 0.1 - 1.0 wt. % Niobium (Nb)

≤ 0.1 wt. % impurities;

the balance being iron;

15 with the proviso that the sum of weight percentages of Molybdenum, Tungsten and Niobium is between 0.5 - 4.0 wt. %.

[0016] As impurities in the refractory steel of the invention, which are unavoidable, especially phosphorus (P) and sulphur (S) may be mentioned. Phosphorus and sulphur are generally each comprised in an amount of 0.03 wt. % or less.

[0017] The condition that the sum of weight percentages of Molybdenum, Tungsten and Niobium is between 0.5 - 4.0 wt. % means that, if e.g. Tungsten and Niobium are absent or at extremely low concentrations, e.g. below 0.05 wt. %, Molybdenum is necessarily present at an amount of between 0.5 and 4.0 wt. %.

[0018] It is noted that in the ranges of weight percentages indicated in the present document the end values of the ranges, i.e. both the inferior and superior values defining the range, are intended to be expressly included in said ranges. As a way of example, a range of 0.5 - 1.0 wt. % (or expressed as between 0.5 and 1.0 wt. %, intended herein to have the same meaning), will include the end values, i.e. the exemplified range includes the value 0.5 wt.% and the value 1.0 wt. %.

[0019] According to particular embodiments, in the refractory steel of the invention the sum of weight percentages of Molybdenum, Tungsten and Niobium is between 0.6 and 4.0 wt. %, between 0.6 and 3.0 wt. %, between 0.6 and 2.8 wt. %, between 2.0 and 3.0 wt. %, between 2.5 and 3 wt. % or between 2.5 and 2.8 wt. %.

[0020] According to further particular embodiments, the Tungsten content (given in weight percentage) in the refractory steel of the invention is between 2 and 4 times the Niobium content and between 2 and 4 times the Molybdenum content, one independently from one another. That is, as way of clarification, and without limitation, if e.g. the Tungsten content in the refractory steel is 1.5 wt. %, the Niobium and Molybdenum contents will be each, independently, between 0.375 and 0.75 wt. % (between a ¼ and ½ the content of Tungsten). Further embodiments provide a Tungsten content (given in weight percentage) of between 3 and 4 times the Niobium content, or between 3 and 3.5 times the Niobium content, and of between 2 and 3 times the Molybdenum content, or of between 2.5 and 3 times the Molybdenum content.

[0021] According to particular embodiments, the Nickel content in the refractory steel of the invention is between 20 and 26 wt.%, between 20 and 25 wt.%, between 20 and 22 wt. % or between 24 and 25 wt. %.

[0022] According to additional particular embodiments, the Chrome content in the refractory steel of the invention is between 19 and 25 wt. %, between 19 and 22 wt. %, between 21 and 25 wt. %, between 21 and 23 wt. %, between 24 and 25 wt. %.

[0023] Further particular embodiments provide a refractory steel wherein the Silicon content is between 1.5 and 2 wt. %, between 1.5 and 1.8 wt. %, between 1.6 and 1.8 wt. %, between 1.6 and 1.7 wt. %, or between 1.7 and 1.8 wt. %.

[0024] According to further particular embodiments, the Manganese content in the refractory steel of the invention is between 0.5 and 1 wt. %, between 0.8 and 1 wt. %, or between 0.9 and 1 wt. %.

[0025] According to further particular embodiments, the Carbon content in the refractory steel of the invention is between 0.5 and 0.7 wt.%, between 0.4 and 0.6 wt.%, between 0.5 and 0.7 wt.%, or between 0.5 and 0.6 wt. %.

[0026] Additional particular embodiments of the present invention refer to a refractory steel wherein the Molybdenum content is between 0.5 and 0.8 wt. %, between 0.55 and 0.65 wt. %, or between 0.6 and 0.7 wt. %.

[0027] Further particular embodiments of the invention provide a refractory steel having a Tungsten content of between 1 and 2 wt. %, between 1.3 and 1.8 wt. %, between 0 and 1.7 wt. %, between 0 and 0.3 wt. %, between 0 and 0.1 wt. %, or between 1.4 and 1.7 wt. %.

[0028] According to additional particular embodiments the Niobium content in the refractory steel of the present invention is between 0 and 0.8 wt. %, between 0 and 0.6 wt. %, between 0.4 and 0.8 wt. %, between 0.4 and 0.6 wt. %, between 0.4 and 0.5 wt. %, between 0 and 0.5 wt. %, between 0 and 0.3 %, or between 0 and 0.1 wt. %.

[0029] An embodiment of the present invention is also a refractory steel consisting of the following elements, in weight percentages based on the total weight of the steel:

18.0 - 26.0 wt. % Nickel (Ni);

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16.0 - 26.0 wt. % Chrome (Cr);

1.0 - 2.0 wt. % Silicon (Si);

5 0.5 - 1.5 wt. % Manganese (Mn);

0.4 - 0.7 wt. % Carbon (C);

10 0.2 - 1.0 wt. % Molybdenum (Mo);

0.1 - 2.0 wt. % Tungsten (W);

0.1 - 1.0 wt. % Niobium (Nb)

15 \leq 0.1 wt. % impurities;

the balance being iron;

with the proviso that the sum of weight percentages of Molybdenum, Tungsten and Niobium is between 0.5 - 4.0 wt. %.

20 **[0030]** The above indicated particular ranges of the elements are also intended to apply to this refractory steel.

[0031] It is further expressly noted that the present invention is intended to encompass all possible combinations of any of the above defined particular ranges of weight percentages of the different elements with any of the other above defined particular ranges for the other elements contained therein.

[0032] For example, the present invention encompasses a refractory steel comprising:

25

a Nickel content between 20 and 22 wt. %;

a Chrome content between 19 and 22 wt. %;

30 a Silicon content between 1.7 and 1.8 wt. %;

a Manganese content between 0.9 and 1 wt. %;

a Carbon content between 0.5 and 0.6 wt.%;

35

a Molybdenum content between 0.55 and 0.65 wt. %;

a Tungsten content between 1.4 and 1.7 wt. %;

40

a Niobium content between 0.4 and 0.5 wt. %.

[0033] The present invention also encompasses a refractory steel comprising:

45

a Nickel content between 24 and 25 wt. %;

a Chrome between 21 and 23 wt. %;

a Silicon content between 1.7 and 1.8 wt. %;

50

a Manganese content between 0.9 and 1 wt. %;

a Carbon content between 0.5 and 0.6 wt.%;

55

a Molybdenum content between 0.6 and 0.7 wt. %

a Tungsten content between 1.4 and 1.7 wt. %;

a Niobium content between 0.4 and 0.5 wt. %.

[0034] Also encompassed is a refractory steel comprising:

a Carbon content between 0.4 and 0.6 wt.%;

5 a Nickel content between 20 and 22 wt. %;

a Chrome content between 24 and 25 wt. %;

10 a Molybdenum content between 0.6 and 0.7 wt. %;

a Silicon content between 1.6 and 1.7 wt. %

a Manganese content between 0.9 and 1 wt. %.

15 a Tungsten content between 0 and 0.3 wt. %;

a Niobium content 0 and 0.3 %.

[0035] A further refractory steel within the scope of the invention comprises:

20

a Nickel content between 20 and 22 wt. %;

a Chrome content between 24 and 25 wt. %;

25 a Silicon content between 1.6 and 1.8 wt. %;

a Manganese content between 0.9 and 1 wt. %;

30 a Carbon content 0.5 and 0.6 wt.%;

a Molybdenum content between 0.55 and 0.65 wt. %;

a Tungsten content between between 0 and 0.3 wt. %;

35 a Niobium content between 0 and 0.3 %.

[0036] The inventors of the present invention have achieved to improve creep properties of the refractory steel according to the present invention, by increasing carbon content, thus generating a higher number of chrome carbides, which are further stabilized with the introduction of Molybdenum in certain ranges. The inventors have achieved to further improve these properties by the introduction of different quantities of Tungsten (W) and Niobium (Nb), in particular amounts, and in preferred relationship one with another, which unexpectedly has generated high temperature strengthening phases.

40

[0037] As is shown in Figure 7, the refractory steels of the invention having increased carbon content and comprising Molybdenum, presents a microstructure, which consists of a matrix of austenite, with variable quantities of carbides. The introduction of Tungsten and Niobium has been observed to unexpectedly generate eutectic carbides in grain boundaries, which, without wishing to be bound to theory, seems to be behind the reduction in the deformation and cracks propagation (see Figure 1).

45

[0038] In terms of microstructure:

- Reference refractory steel (1.4848) presents a microstructure consisting of an austenitic matrix with Chrome carbides precipitated in interdendritic spaces (see Figure 7).

50

- However, Steel 1 and Steel 3 according to the present invention present a microstructure consisting of an austenitic matrix with carbides precipitated in interdendritic spaces. The carbides in interdendritic spaces are mainly eutectic in the case of Niobium carbides and separated from those ones are found mixed carbides of molybdenum, tungsten and chrome (see Figure 1 and Figure 7).

55

[0039] The refractory steels of the present invention can be used for e.g. for manufacturing complex components integrated in furnaces that can work continuously and discontinuously, using radiation tubes, electrical resistances, or

open burners inside the equipment to heat the load. They can be used in cyclic or static loads in the range of 20-50 MPa, at temperatures from 600-1000°C. These refractory steels are prepared to withstand wear conditions due to the stability at high temperature given by the Molybdenum, Niobium and Tungsten carbides in a corrosive environment consisting of combustion gases or dry air conditions.

5 **[0040]** In an additional aspect, the invention provides a process for the preparation of the refractory steel defined above, which comprises the following steps:

10 (i) Charging a furnace with the elements defined above, each at a purity between 99 and 100 wt. % or corresponding ferroalloys necessary to reach the refractory steel as defined above;

(ii) Increasing the temperature of the charge up to between 1550 and 1700°C;

(iii) Maintaining the charge in its molten condition for at least 3 minutes for homogenization;

15 (iv) Deoxidizing the melt obtained in step (iii) by the addition of 0.05 to 0.30 wt. % FeSiCa and from 0.05 to 0.1 wt. % pure aluminium;

(v) Transferring the molten metal obtained in step (iv) to a tea-pot ladle and pouring into a keel block type mold;

20 (vi) Submitting the obtained refractory steel to a temperature of between 780-1000°C during between 1 and 30 hours in a non-controlled atmosphere heat treatment furnace;

(vii) Extracting the sample and leaving it cool down in calm air.

25 **[0041]** In step (iii) the charge may be maintained in its molten condition for any desired time, but for energy saving purposes, will not be maintained in its molten condition for more than 10 minutes, but maintaining for a longer time would not be detrimental to the refractory steel. According to particular embodiments, the molten condition is maintained for between 3 and 10 minutes or between 4 and 8 minutes.

[0042] Step (vi) is an ageing heat treatment, to increase wear and creep resistance properties.

30 **[0043]** The introduction of the ageing heat treatment assures the precipitation of a homogeneous network of carbides inside grains, assuring a higher wear resistance (see Fig 2).

[0044] According to a particular embodiment, the furnace is a conventional furnace, such as an Open-air medium frequency induction furnace or vacuum Induction Melting (VIM) furnace.

35 **[0045]** In the frame of the present invention, the term "calm air" refers to an environment in absence or nearly absence of air currents or wind, i.e. wind or air currents moving at less than 1 knot, or "zero" (0) on the international scale of wind force known as "Beaufort scale". The temperature in "calm air" conditions is intended to be ambient or room temperature, taken in the broad sense, i.e. generally between 15 and 30 °C, more specifically between 20 and 27 °C, or between 20 and 25 °C, or between 20 and 22°C.

40 **[0046]** In order to obtain the desired composition of the refractory steel of the invention and prevent oxidation of aluminium and manganese in open air, the alloying elements Mn, Al, Si, Fe and C, according to a particular embodiment, may be added to the furnace in step (i) in the following forms:

◦ Pure graphite (99-100 wt. % C)

45 ◦ Pure nickel (99-100 wt. % Ni)

◦ Pure chromium (99-100 wt. % Cr)

◦ Pure manganese (99-100 wt. % Mn)

50 ◦ Pure silicon (99-100 wt. % Si),

◦ Pure Molybdenum (99-100 wt. % Mo)

55 ◦ Pure tungsten (99-100 wt. % W)

◦ Pure Niobium (99-100 wt. % Nb)

- Pure iron (99-100 wt. % Fe)
- Being the sum of Nb, W y Mo in the range of 0.5-4.0.

5 **[0047]** Alternatively, corresponding ferroalloys necessary to reach the weight percentages in the final refractory steel as defined above, may be used.

[0048] As already noted earlier, according to a particular embodiment, the W content is about 2-4 times the Nb content, and about 2-4 times of the Mo content.

[0049] The adjustment of the additions and the desired composition are within the skills of a person skilled in the art.

10 **[0050]** During the process according to the present invention, according to a preferred embodiment the heating or temperature increasing of step (ii) is carried out progressively. The heating is carried out by increasing the power of the furnace progressively to higher power, over at least 20 - 30 minutes, to assure no refractory cracking takes place during heating up. The time to reach the final temperature of the mixture obtained in step (i) is not relevant, although it is recommended, as noted above, to heat the mixture progressively. As a reference, the time to reach the final temperature may be between 20 minutes and e.g 10 or 5 hours. According to further particular embodiments, the time to reach the final temperature is between 20 minutes and 3 hours, between 20 minutes and 1 hour, or between 20 minutes and 30 minutes. The average heating rate during step (ii) should be between 1 °C/min and 90 °C/min, according to particular embodiments is between 10 and 85 °C/min, or between 25°C/min and 85°C, or between 50 °C/min and 85 °C/min.

15 **[0051]** The mixture of elements is heated up to between 1550 and 1700°C, for example to about 1650°C, so that sufficient homogenization of the charge takes place.

[0052] Before pouring the melt into the mould, the mixture must remain molten for a period of time, to allow a correct homogenization of the elements. Typically, time is not less than between 3 and 10 minutes. Then from 0.05 to 0.30 wt. % of FeSiCa (preferably, from 0.05 to 0.15 wt. %) and from 0.05 to 0.10 wt.% of pure aluminum are added into the furnace to assure a correct deoxidation of the metal. The molten mixture is transferred to a tea pot ladle that previously has been heated up with a gas torch. The melt is poured directly into a keel-block mold, manufactured with chemically bonded sand.

25 **[0053]** As already noted, the process for preparing the refractory steel of the invention further comprises submitting the refractory steel of the invention to a heat treatment (see step (vi)), which is designated as an ageing heat treatment. This heat treatment process can be carried out in any conventional manner known to the skilled person and comprises the steps of: submitting the high creep resistant refractory steel of the invention as-cast to a high temperature, and subsequently cooling, this heat treatment is known as ageing and deals with the precipitation of secondary carbides that enhances high temperature mechanical properties. The heat treatment is done in a furnace, such as for example an electrical resistance non-controlled atmosphere heat treatment furnace.

30 **[0054]** The ageing treatment applied consists in heating up the metallic sample, preferably a keel-block sample (see Figure 1), to a temperature of between 780-1000°C; preferred temperature ranges are between 820 and 950 °C, between 835 and 930 °C, for example at about 930°C. The time the refractory steel as cast is submitted to heat treatment varies depending on factors like the size of the part, the selected temperature, and is typically from 1 to 30 hours, for example during between 1 and 20 hours, between 1 and 10 hours, between 1 and 5 hours, between 1.5 and 2.5 hours, for example during about 2 hours, in a 11 kW power Termolab furnace with open air atmosphere. The metallic sample is extracted from the furnace and cooled down in calm air until reaching room temperature.

35 **[0055]** This ageing heat treatment represents a significant advance in comparison with the current delivery conditions of refractory stainless steels. The controlled precipitation of secondary carbides allows that initial wear is lower and crack initiation and growth is slower. This effect is due to the presence of carbides in the microstructure non-generating a preliminary high wear rate and assuring higher mechanical resistance to crack initiation.

40 **[0056]** Therefore, the present invention is also related to a machinery part comprising the refractory steel as-cast or the heat-treated refractory steel of the invention.

[0057] Illustratively, the heat-treated high creep resistant refractory steels are preferably but non-limiting to examples of parts such as radiation tubes for heat treatment furnaces, buckets to contain parts in heat treatment furnaces used in the steel and aluminium flat product, beams, and rolls for parts transport in hot stamping sector, trays and rails in the investment casting and ceramic sector and entrance and outside segments in the mining and cement roasting furnaces.

50 **[0058]** The following examples are merely illustrative and should not be considered as limiting the invention.

EXAMPLES

55 **[0059]** Examples of the refractory steels according to the present invention are gathered in Table 1; the steels represented in the table 1 have gone over different high temperature related validation tests, such as long term creep, thermal fatigue and creep crack growth rate.

Table 1: Chemical composition of high creep resistant refractory steel (wt. %)

Refractory Steel	Chemical composition (wt. %)								
	C	Ni	Cr	Mo	Si	Mn	W	Nb	Fe
1.4848 refractory steel (comparative)	0.32	18.7	23.8	< 0.5	1.28	1.01	/	/	to balance
Steel 1	0.4	20,8	24,7	0,62	1,63	0,94	/	/	to balance
Steel 2	0,55	24,5	21,5	0,61	1,71	0,93	1,46	0,46	to balance
Steel 3	0.52	20.6	19.2	0.6	1.77	0.98	1.65	0.48	to balance
Steel 4	0.52	21.0	24.7	0.57	1.69	0.92	/	/	to balance

* This wt. % includes unavoidable impurities, being the total sum lower than 0.1 wt. %.

[0060] The steels of Table 1 were prepared according to the procedure described in the following examples:

Example 1: preparation of Steel 1, Steel 2, Steel 3 and Steel 4 according to the present invention

[0061] Proper amounts of each of the elements indicated in Table 1 for each of the aimed refractory steels, the elements being in pure form (purity higher than 99.0 wt.%), the elements summing 50 kgs in total, were introduced into an open air medium frequency induction furnace of 100 kg capacity.

[0062] Melting of the mixture of elements was performed, until a temperature of 1650°C was reached. Deoxidation was carried out, by introducing 0,15% of FeSiCa and 0,10% of pure aluminium into the furnace.

[0063] Once the mixture of elements was molten, the metal was maintained molten for about 4 minutes. The mixture of metals was transferred to a tea pot ladle, heated up with a gas burner. Pouring was performed into keel blocks Y2, particularly chemically bonded sand moulds, following the standard norm UNE-EN 1563:1998; the casted keel blocks Y2 were then extracted from the moulds and cleaned by shot blasting.

[0064] After casting, the obtained samples were submitted to a heat treatment consisting in heating up the sample, from room temperature to 930 °C, and maintaining it at 930°C during about 2 hours, in a 11kW power Termolab furnace, with non-controlled atmosphere. The heat treated samples were taken out from the furnace and cooled down, in calm air, until reaching room temperature, thus obtaining samples for subsequent testing.

Example 2: Mechanical properties and ageing heat treatment process of the steels according to the present invention

[0065] The mechanical properties indicated in Tables 2 to 4 below were determined on keel block samples of each of the refractory steels, prepared according to the process described in Example 1. Figures 3 to 6 show details about the shape and dimensions of the respective samples that were prepared.

[0066] The keel blocks were cut and test samples for micrographic inspection of rectangular dimensions of approximately 25 x 20 x 20 mm were prepared by surface polishing and their microstructures were then analysed with a field emission gun scanning electron microscope (SEM) (Model ULTRA PLUS, Zeiss).

[0067] Test samples for short creep and long creep were machined from the bottom rectangular part of the keel block of each of the refractory steels, of dimensions 25*40*140 mm, according to the dimensions indicated in Figure 4, and were tested according to EN-ISO 204 standard.

[0068] Test samples for creep crack growth rate were machined from the bottom rectangular part of the keel block of each of the refractory steels, of dimensions 25*40*140 mm, according to the dimensions indicated in Figure 5.

[0069] Test samples for thermal fatigue tests were machined from the bottom rectangular part of the keel block of each of the refractory steels, of dimensions 25*40*140 mm, according to the dimensions indicated in Figure 6.

[0070] Table 2 below shows how Steel 1, Steel 2, Steel 3 and Steel 4, which are according to the present invention, present significantly better results, in comparison to the reference refractory steel 1.4848, in terms of long term creep.

Table 2: Long term creep properties at 930 °C at different loads

Refractory Steel	Time to rupture in hours at 48 MPa	Time to rupture in hours at 25 MPa
1.4848 refractory steel (comparative)	38,25	636,25
Steel 1	47,75	2500

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(continued)

Refractory Steel	Time to rupture in hours at 48 MPa	Time to rupture in hours at 25 MPa
Steel 2	69,25	4230,5
Steel 3	236,25	>5000
Steel 4	68	3869

[0071] Table 3 below shows how Steel 1, Steel 2 and Steel 3 according to the present invention present better results in terms of creep crack growth rates, at different loads, than comparative 1.4848 refractory steel; Steel 4 in terms of creep crack growth rate shows a performance which is similar to comparative 1.4848 refractory steel.

Table 3: Creep crack growth rates at different loads

Refractory Steel	Hours before breaking at 110 MPa	Hours before breaking at 90 MPa
1.4848 refractory steel (comparative)	32	146,25
Steel 1	67,17	196,12
Steel 2	102,33	469,92
Steel 3	62,83	215,8
Steel 4	35,25	150,67

[0072] Table 4 below shows how Steel 1 shows better thermal fatigue resistance at thermal cycles from 700 to 300°C, in comparison to comparative 1.4848 refractory steel. The table gathers the average of 8 samples tested under the same conditions.

Table 4: Time until failure for test samples submitted to thermal cycles from 700 to 300°C

Refractory steel	External diameter of the test bar (mm)	Internal diameter of the test bar (mm)	Time to rupture (hours).
1.4848 refractory steel	8	2,4	567
Steel 1	8	2,4	955

Claims

1. A refractory steel, comprising, in weight percentages based on the total weight of the steel:

- 18.0 - 26.0 wt. % Nickel (Ni);
- 16.0 - 26.0 wt. % Chrome (Cr);
- 1.0 - 2.0 wt. % Silicon (Si);
- 0.5 - 1.5 wt. % Manganese (Mn);
- 0.4 - 0.7 wt. % Carbon (C);
- 0.2 - 1.0 wt. % Molybdenum (Mo);
- 0 - 2.0 wt. % Tungsten (W);
- 0 - 1.0 wt. % Niobium (Nb);
- ≤ 0.1 wt. % impurities;
- the balance being iron;

with the proviso that the sum of weight percentages of Molybdenum, Tungsten and Niobium is from 0.5 to 4.0 wt. %.

2. A refractory steel according to claim 1, wherein the Carbon content is between 0.5 and 0.7, preferably between 0.5 and 0.6 wt. %.

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3. A refractory steel according to any one of claims 1 and 2, wherein the Nickel content is between 20 and 26 wt.%, preferably between 20 and 25 wt.%.
- 5 4. A refractory steel according to any one of claims 1 to 3, wherein the Chrome content is between 19 and 25 wt. %, preferably between 19 and 22 wt. %.
5. A refractory steel according to any one of claims 1 to 4, wherein the Molybdenum content is between 0.5 and 0.8 wt. %, preferably between 0.6 and 0.7 wt. %.
- 10 6. A refractory steel according to any one of claims 1 to 5, wherein the Silicon content is between 1.5 and 2 wt %, preferably between 1.5 and 1.8 wt. %.
7. A refractory steel according to any one of claims 1 to 6, wherein the Manganese content is between 0.8 and 1 wt %, preferably between 0.9 and 1 wt. %.
- 15 8. A refractory steel according to any one of claims 1 to 7, wherein the Tungsten content is between 0 and 1.7 wt. %, preferably between 1.4 and 1.7 wt. %.
9. A refractory steel according to any one of claims 1 to 8, wherein the Niobium content is between 0 and 0.6 wt. %, preferably between 0.4 and 0.6 wt. %.
- 20 10. A refractory steel according to any one of claims claims 1 to 9, wherein the Tungsten content is between 2 and 4 times the Niobium content and between 2 and 4 times the Molybdenum content.
- 25 11. A process for preparing a refractory steel as defined in any one of claims 1 to 10, which comprises the following steps:
- (i) Charging a furnace with the elements defined in claim 1, each at a purity between 99 and 100 wt. % or corresponding ferroalloys necessary to reach the weight percentages in the final refractory steel as defined in any one of claims 1 to 10;
 - 30 (ii) Increasing the temperature of the charge up to between 1550 and 1700°C;
 - (iii) Maintaining the charge in its molten condition for at least 3 minutes for homogenization;
 - (iv) Deoxidizing the melt obtained in step (iii) by the addition of 0.05 to 0.30 wt. % FeSiCa and from 0.05 to 0.1 wt. % pure aluminium;
 - (v) Transferring the molten metal obtained in step (iv) to a tea-pot ladle and pouring into a keel block type mold;
 - 35 (vi) Submitting the obtained refractory steel to a temperature of between 780-1000°C during between 1 and 30 hours, in a non-controlled atmosphere heat treatment furnace;
 - (vii) Extracting the sample and leaving it cool down in calm air.
- 40 12. A piece of industrial equipment comprising the refractory steel as defined in any one of claims 1 to 10 or obtained by the process of claim 11.
- 45 13. A piece of industrial equipment according to claim 12, selected from radiation tubes, especially for heat treatment furnaces; buckets, especially to contain parts in heat treatment furnaces used in the steel and aluminium flat product; beams; rolls for parts transport in hot stamping sector; trays and rails in the investment casting and ceramic sector; and entrance and outside segments in the mining and cement roasting furnaces.
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Figure 1

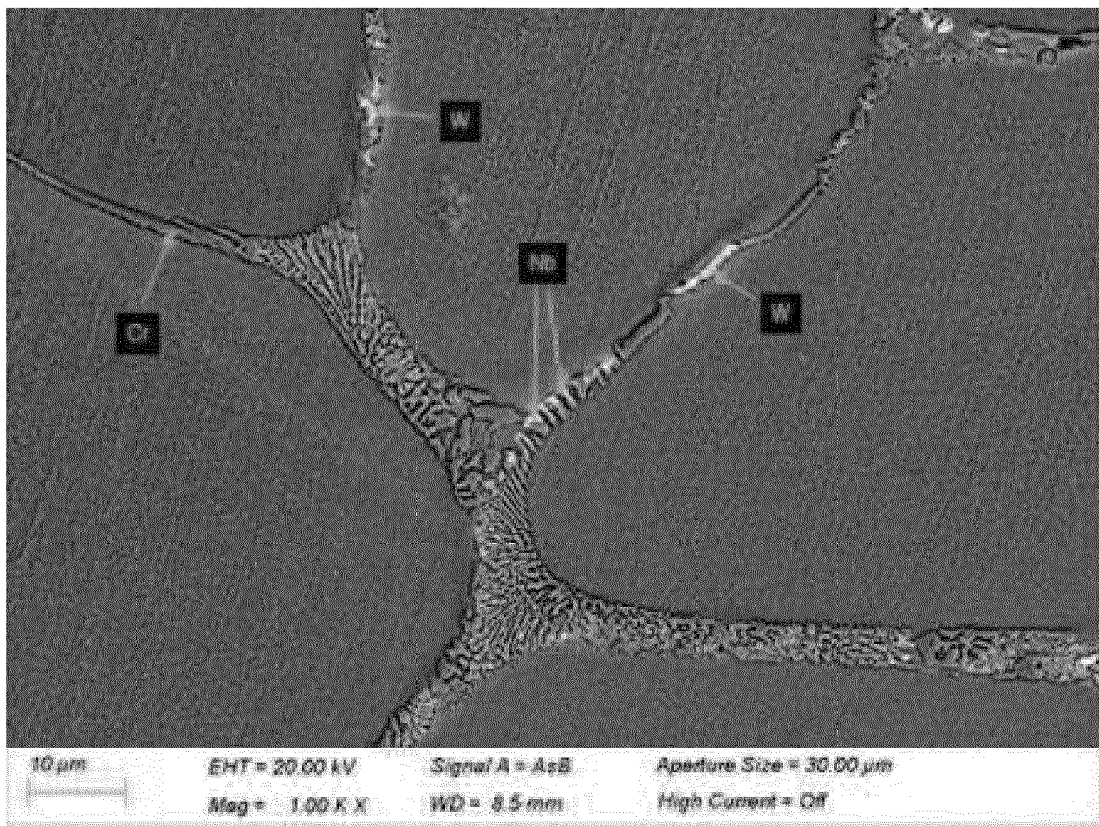


Figure 2a

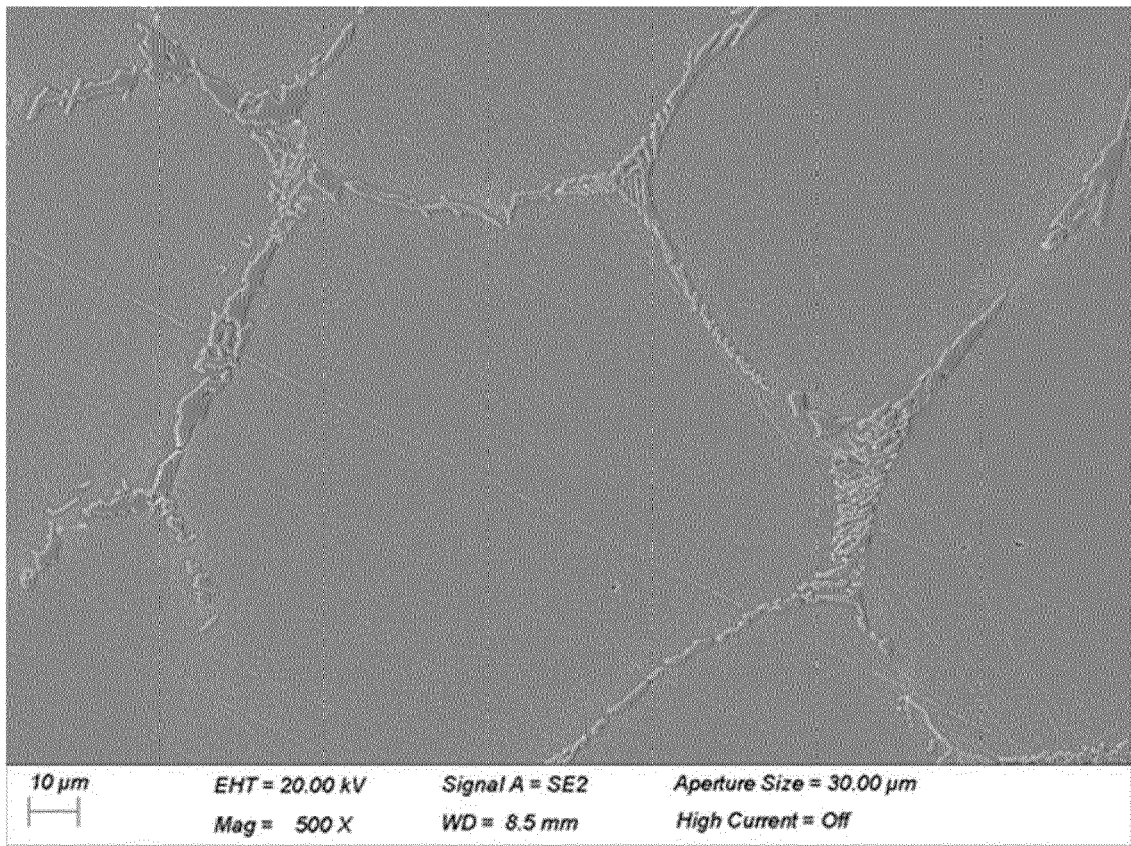


Figure 2b

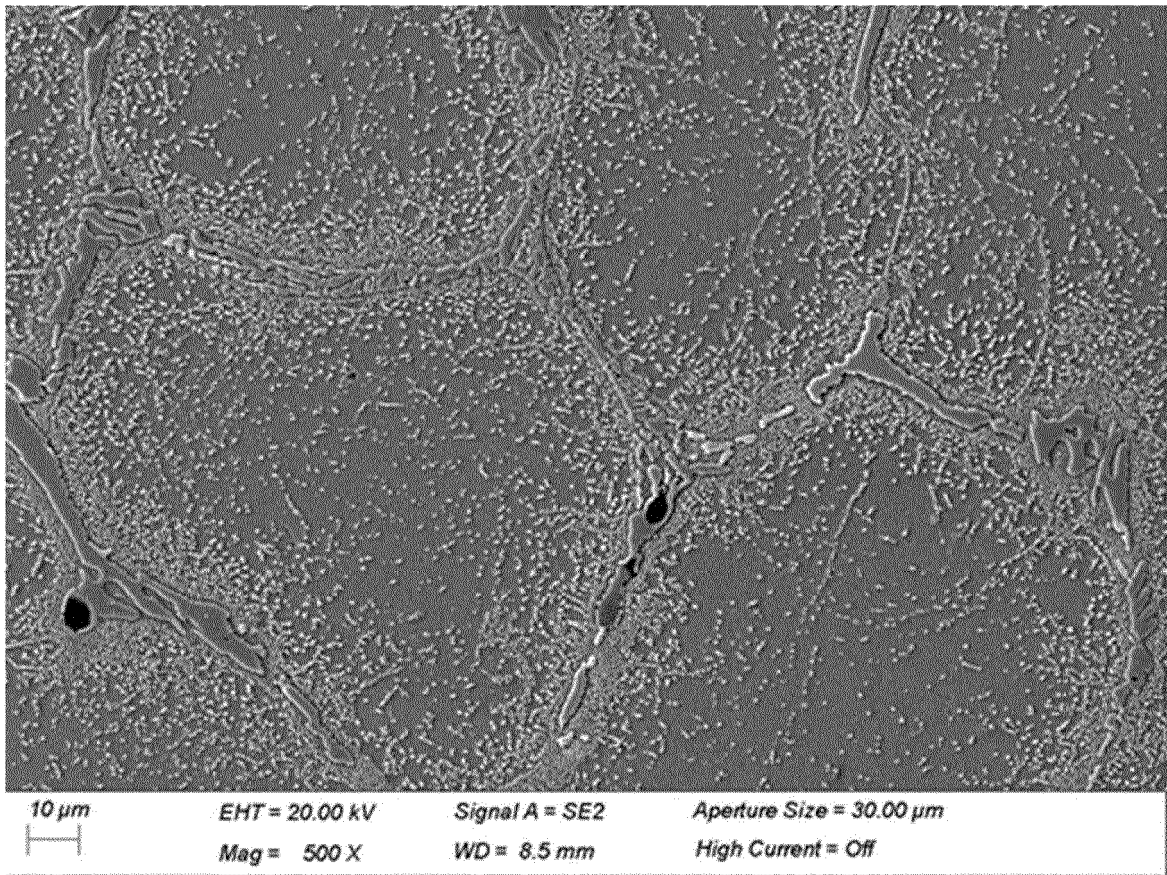


Figure 3

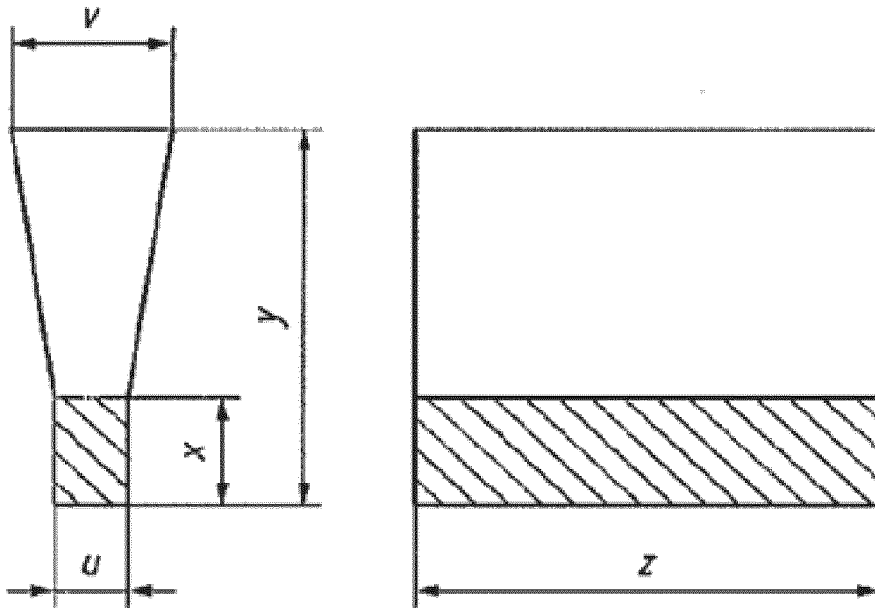


Figure 4

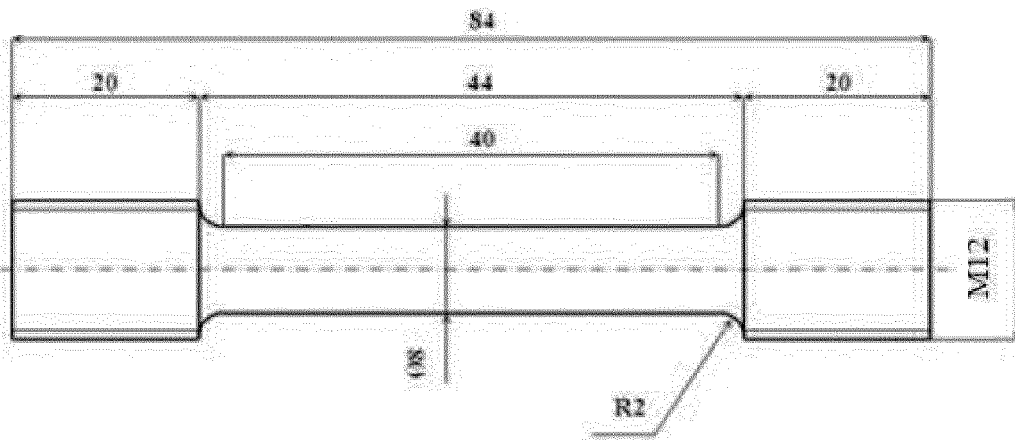


Figure 5

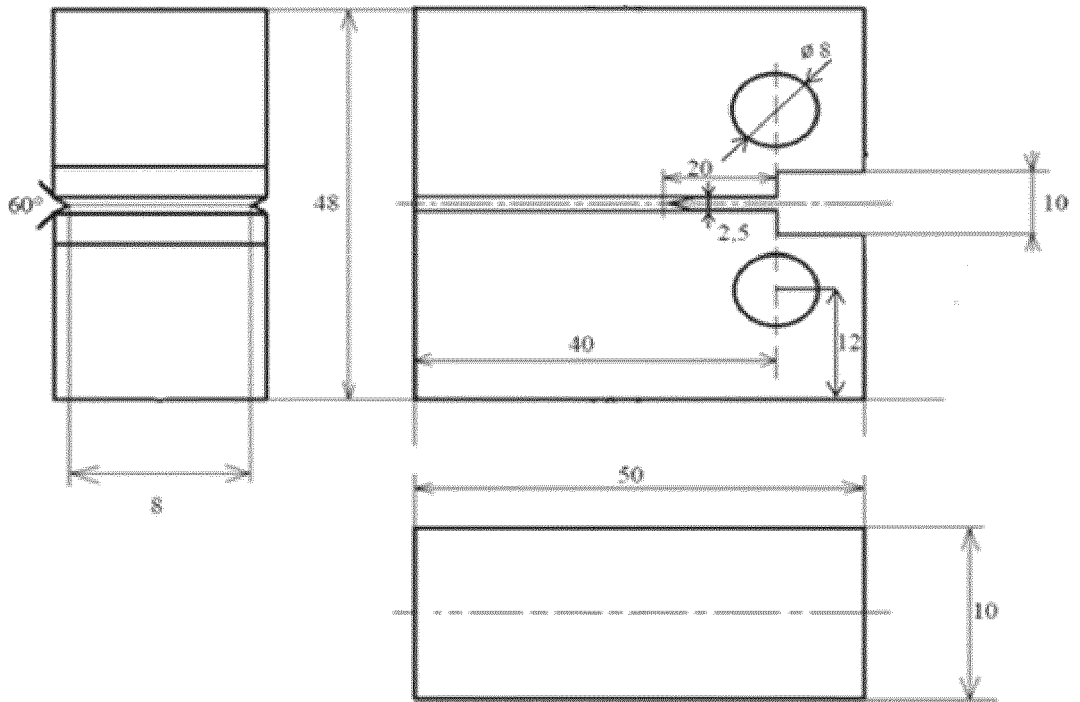


Figure 6

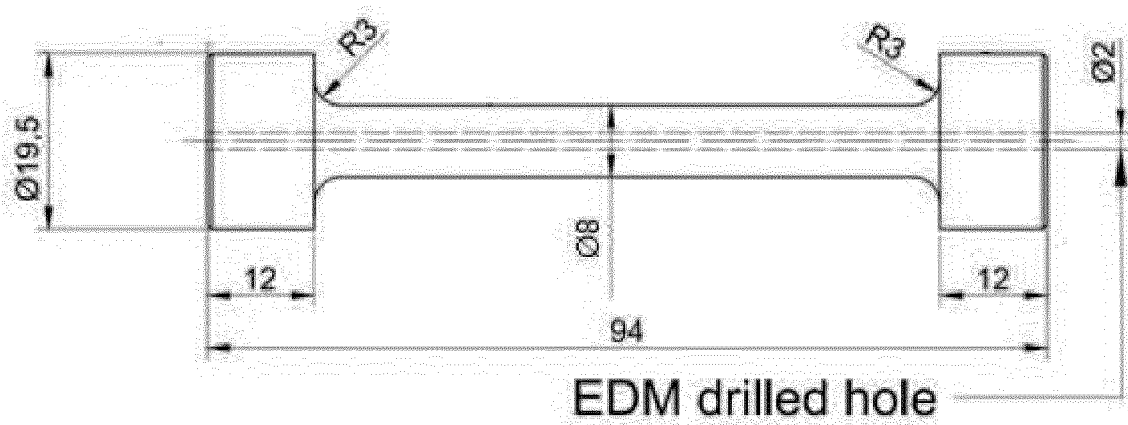
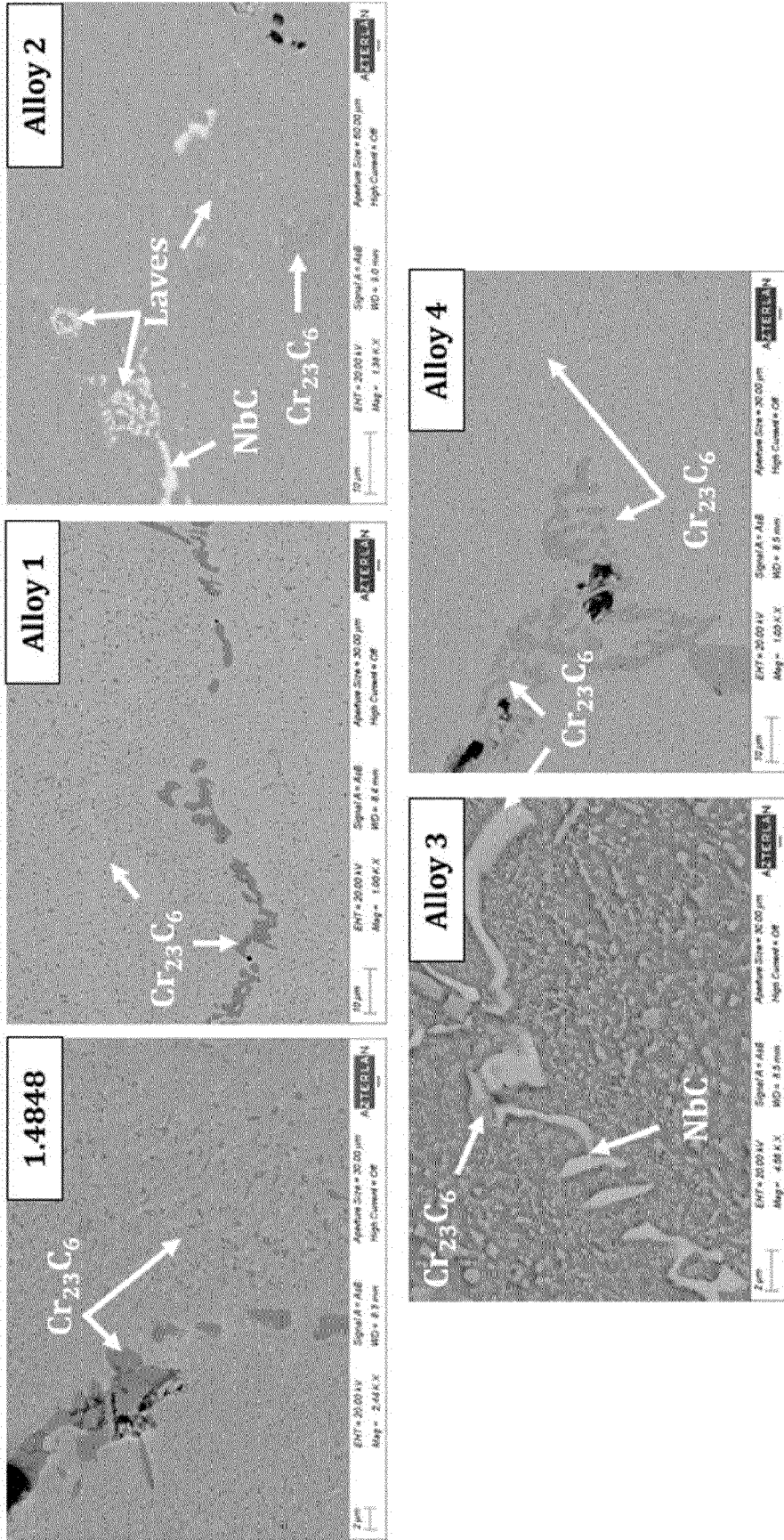


Figure 7





EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 741 799 A1 (HITACHI METALS LTD [JP]) 10 January 2007 (2007-01-10)	1-10, 12, 13	INV. C22C38/02
A	* 0034, 0037, 0048, 0050, 0125; tab. 1-2, 32 *	11	C21C5/00 C21C7/00 C22C38/04
A	US 4 861 547 A (CULLING JOHN H [US]) 29 August 1989 (1989-08-29) * tables I-II *	1-13	C22C38/44 C22C38/48 C21D9/00
A	EP 1 043 417 A1 (HITACHI METALS LTD [JP]) 11 October 2000 (2000-10-11) * tab. 1 *	1-13	
A	GB 1 241 081 A (ABEX CORP [US]) 28 July 1971 (1971-07-28) * p. 4-8 *	1-13	
			TECHNICAL FIELDS SEARCHED (IPC)
			C22C C21C
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		20 October 2023	Kreutzer, Ingo
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 23 38 2534

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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20-10-2023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1741799	A1	10-01-2007	CN 1942598 A
			04-04-2007
			EP 1741799 A1
			10-01-2007
			JP 4985941 B2
			25-07-2012
			JP WO2005103314 A1
			13-03-2008
			KR 20060135864 A
			29-12-2006
			US 2007217941 A1
			20-09-2007
			WO 2005103314 A1
			03-11-2005

US 4861547	A	29-08-1989	NONE

EP 1043417	A1	11-10-2000	DE 60025860 T2
			05-10-2006
			EP 1043417 A1
			11-10-2000
			JP 4379753 B2
			09-12-2009
			JP 2000291430 A
			17-10-2000
			US 6383310 B1
			07-05-2002

GB 1241081	A	28-07-1971	DE 1900300 B1
			08-10-1970
			FR 1596359 A
			15-06-1970
			GB 1241081 A
			28-07-1971
