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(54) INOCULATION PROCESS FOR GRAIN REFINEMENT OF A NICKEL BASE ALLOY

(57) An inoculation process of a nickel base alloy, wherein the process is carried out in a vacuum furnace and comprises: a) providing a melt of a nickel base alloy in vacuum conditions, characterized in that the inoculation process further comprises: b) introducing an encapsulated inoculant comprising a mixture of Co_3FeNb_2 and CrFeNb(Ni) inside the melt of the nickel base alloy at a temperature from 1450 to 1500 °C for a period from 5 to 30 seconds, c) immediately pouring the inoculated nickel base alloy of step b) into a mold, preferably at a temperature from 1450 to 1500 °C, and d) cooling said inoculated nickel base alloy.

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Description

FIELD OF INVENTION

[0001] The present invention is encompassed within the sector of metallurgical industry. Particularly it is related to an inoculation process for a nickel base alloy to achieve grain refinement. The process of the present invention comprises using a mixture of Co_3FeNb_2 and CrFeNb(Ni) as inoculant, where such compounds are introduced inside the melt nickel base alloy encapsulated, and the inoculation step is carried out at a temperature from 1450 to 1500 °C for a period from 5 to 30 seconds. Advantageously, the inoculant process described in this document can produce a fine and equiaxial grain size, which promotes high mechanical properties such as tensile stress, yield stress and elongation and, at the same time, this process can provide a complete filling of the mold.

[0002] In particular embodiments, the invention further comprises the manufacture of the encapsulated inoculant and adaption for its introduction inside the melt nickel base alloy.

BACKGROUND OF THE INVENTION

[0003] Nickel base alloys and, in particular, the so-called nickel base superalloys, are frequently used for elevated mechanical strength and high temperature performance applications, mainly for aeronautics and energy sectors (G. Marahleh, A. R. I. Kheder, H. F. Hamad, CREEP-LIFE PREDICTION OF SERVICE-EXPOSED TURBINE BLADES, Materials Science, Vol. 42, No. 4, 2006). One of the most common examples of a nickel base superalloy known as IN718.

[0004] Some components for engines are manufactured by conventional casting in an open-air furnace but most of them by investment casting process using a Vacuum Induction Melting (VIM) furnace as equipment for the melting, casting and pouring of the melt. Common problems associated to the investment casting are high pouring temperature ($\geq$1450°C) of the melt and the use of preheated mold, both practices assure a good filling of the components but result in long solidification time and thus coarse and columnar grain sizes. Columnar grain sizes larger than 3-6 mm average length are frequently observed representing unfavorable microstructures in terms of mechanical properties such as elongation, yield strength and tensile strength (Kumar, S., Sudhakar Rao, G., Chattopadhyay, K., Mahobia, G.S., Santhi Srinivas, N.C., Singh, V., Effect of Surface Nanostructure on Tensile Behavior of Superalloy IN718, Materials and Design (2014)).

[0005] Inoculation process is a well-known technology for the modification of internal microstructure of metallic alloys. Addition of FeSi to cast iron, and Titanium and Boron to AlSi7Mg alloys are some traditional examples of inoculation processes for grain refinement performed in metallic alloys with great mechanical properties improvement and reduction of porosity. In the case of the turbine engines made with superalloys for industrial and aircraft applications, the demands of better performance have led to the development of methods to obtain fine and uniform grain sizes in the microstructure.

[0006] Historically, the control of the grain size in alloys and, more specifically, in superalloys, has been carried out by mechanical and thermal methods (LI Ying-ju, MA Xiao-ping, YANG Yuan-sheng, Grain refinement of as-cast superalloy IN718 under action of low voltage pulsed magnetic field, Trans. Nonferrous Met. Soc. China 21 (2011) 1277-1282). In the early 1980s, Howmet developed the first fine grain casting technique and consisted in agitation of the casting during the solidification of the alloy (J.R. Brinegar, L.F. Norris, L. Rosenberg, in: M. Gell, C.S. Kortovich, R.H. Bricknell, W.B. Kent, J.F. Radavich (Eds.), Superalloy 1984, The Metallurgical Society of AIME, 1984, p. 23; D.E. Macha, G.R. Cole, J.A. Butzer, in: G.J. Abbaschian, S.A. David (Eds.), Grain Refinement in Casting and Welds, The Metallurgical Society of AIME, 1983, p. 197). Few years later the same authors introduced an improved method based on pouring at low temperature (melting point temperature plus 10°C) accompanied by turbulence in the molten alloy (B.A. Ewing, K.A. Green, in: M. Gell, C.S. Kortovich, R.H. Bricknell, B.W. Kent, J.F. Radavich (Eds.), Superalloys 1984, The Metallurgical Society of AIME, 1984, p. 33; J.M. Lane, Microcast-x Fine Grained Castings for Aerospace Industry, in: Presented at AeroMat'93 Conference, Anaheim, 1993), while at the same time Air Research Casting Company established low superheating temperature and local chills in the mold for the obtention of grain refinement (M. Woulds, H. Benson, in: M. Gell, C.S. Kortovich, R.H. Bricknell, W.B. Kent, J.F. Radavich (Eds.), Superalloys 1984, The Metallurgical Society of AIME, 1984, p. 3). However, both factors difficult mold filling and thus casting soundness as it was previously aforementioned.

[0007] Meantime, other researched alternatives of grain refinement of superalloys have been focused on chemical methods based on inoculation of the metal before pouring. Boron (A.F. Denzine, T.A. Kolakowski, J.F. Wallance, in: Proceeding AGARD Conference on Advanced Casting Technology, AGARD Conference Proceeding no. 325, 1982), metallic oxides and refractories (A. N. Cherepanov, V. E. Ovcharenko, Effect of Nanostructured Composite Powders on the Structure and Strength Properties of the High_Temperature Inconel 718 Alloy, The Physics of Metals and Metallography, 2015, Vol. 116, No. 12, pp. 1279-1284) were studied to be used as refiners but finally were not applied to industrial processes because of the detrimental effect of the introduction of them as inclusions. Thus, more recently Lin Liu et al. proposed the addition of two compounds based on elements present in the chemical composition of the target superalloy for avoiding the generation of inclusions (Lin Liu, Taiwen Huang, Yuhua Xiong, Aimin Yang, Zhilong Zhaoa, Rong Zhang, Jinshan Li, Grain refinement of superalloy K4169 by addition of refiners: cast structure and refinement mechanisms, Materials Science and Engineering A 394, 2005, 1-8). Low pouring temperature of 1380-1420°C was used in this work. However, from the practical point of view low pouring temperature and long inoculation time could derive in problems associated to incomplete filling of the castings and the fading effect due to dissolution of the inoculants in the melt respectively, which would not achieve grain refinement.

[0008] Therefore, there is a need for developing an inoculation process for grain refinement of a nickel base alloy that avoid the above-mentioned problems of previously known processes.

DESCRIPTION OF THE INVENTION

[0009] The present invention provides an improved inoculation process, which is able to achieve successful grain refinement of castings at industrial pouring temperatures, preferable from 1450°C to 1500°C. The chemical composition of the encapsulated inoculant used in this process does not introduce strange elements or modify seriously the chemical composition of the nickel base alloy.

[0010] In particular, the invention disclosed in this patent application refers to an inoculation process of a nickel base alloy, wherein the process is carried out in a vacuum furnace and comprises:

a) providing a melt of a nickel base alloy in vacuum conditions, characterized in that the inoculation process further comprises:
b) introducing an encapsulated inoculant comprising a mixture of Co_3FeNb_2 and CrFeNb(Ni) inside the melt of the nickel base alloy at a temperature from 1450 to 1500 °C for a period from 5 to 30 seconds to obtain an inoculated nickel base alloy,
c) immediately pouring the inoculated nickel base alloy of step b) into a mold, preferably at a temperature from 1450 to 1500 °C, and
d) cooling said inoculated nickel base alloy.

[0011] Thus, the inoculation process of the present invention can successfully achieve grain refinement of the nickel base alloy, more specifically the inoculated nickel base alloy, obtained by such process.

[0012] In order to assess the grain refinement of the nickel base alloy, the ratio between the mean length (L) and the mean width (W) has been evaluated for the definition of the columnar or equiaxial morphology of the grain. Thus, the approach taken for the grain refinement measurement is defined by two parameters: the grain size value and the grain morphology, which should correspond to mean grain length (L) below 2 mm and L/W ratio equal or below 1.5 for equiaxial grain, respectively.

[0013] In the inoculation method of the present invention, the pouring of the inoculated nickel base alloy takes place immediately after the inoculation period has finished, this means that steps b) and c) shall be done consecutively, without any delay between them.

[0014] The inoculation process described herein is carried out in a vacuum furnace, preferably a Vacuum Induction Melting (VIM) furnace. In particular, this process can be carried out by introduction of the encapsulated inoculant inside a melt of a nickel base alloy in a VIM furnace, which comprises internally communicated two chambers (charging and main chamber) with vacuum pressure, which can be measured by Pirani and Penning gauges. Thus, the encapsulated inoculant can be placed in the charging chamber and the main chamber is used for the melting and inoculation process of the nickel base alloy.

[0015] In some preferred embodiments of the present invention, the vacuum furnace (in particular, VIM furnace) wherein the inoculation process is to be carried out has been modified, so that it further comprises means for introducing the encapsulated inoculant inside the melt of nickel base alloy, such as, for example a pulley system.

[0016] In some preferred embodiments, the melt of nickel base alloy to be inoculated in the process of the invention comprises Ni, Cr, Co, Nb and Fe. These elements are present in the inoculant mixture used in the process herein described and, therefore, such process can provide the desired grain refinement without introducing strange elements or significantly modifying the chemical composition of the alloy.

[0017] The melt of nickel base alloy provided in step a) of the inoculation process more preferably comprises:

Ni: 50 wt. % to 65 wt. %,
Cr: 10 wt. % to 25 wt. %,
Mo: 2 wt. % to 5 wt. %,
Co: 0.01 wt. % to 1 wt. %,
Nb: 0.04 wt. % to 5.5 wt. %, and
Fe: 1 wt. % to 24 wt. %,

wherein percentages are expressed by weight with respect to the total weight of the nickel base alloy.

[0018] In particularly preferred embodiments of the present invention, the melt of nickel base alloy to be inoculated in the process described is an alloy, commonly known as IN718, which comprises:

Ni: 50 wt. % to 55 wt. %,
Cr: 17 wt. % to 21 wt. %,
Mo: 2.8 wt. % to 3.3 wt. %,
Co: 0.01 wt. % to 1 wt. %,
Nb: 4.75 wt. % to 5.5 wt. %,
Fe: 12 wt. % to 22 wt. %,
Ti: 0.65 wt. % to 1.15 wt. %,
Al: 0.2 wt. % to 0.8 wt. %,
C: not more than 0.08 wt. %,
Si: not more than 0.35 wt. %,
Mn: not more than 0.35 wt. %,
P: not more than 0.015 wt. %,
S: not more than 0.015 wt. %, and
B: not more than 0.006 wt. %,

wherein percentages are expressed by weight with respect to the total weight of the nickel base alloy.

[0019] The melt of a nickel base alloy of step a) can be obtained by any suitable means known by the skilled person in the art. In particular, such melt can be obtained by melting one or more nickel base alloy ingots or, alternatively, the melt of a nickel base alloy can be obtained from raw materials of the elements comprised such alloy, preferably, raw materials with purity between 99-100 wt. %.

[0020] As previously mentioned in this document, the inoculation process is carried out in a vacuum furnace, preferably a VIM furnace. Thus, step a) of the inoculation process can comprise progressively heating either the nickel base alloy ingots or raw materials of the alloying elements in vacuum conditions, for example, at a pressure from $5x10^{-3}$ to $5x10^{-4}$ mbar, until the melt of nickel base alloy is obtained.

[0021] From the beginning of the heating process the temperature of the alloy can be continuously measured by a Spectropyrometer (FAR Associates FMP2 multi-wavelength pyrometer) instead of a conventional two-color optical pyrometer or immersion thermocouple. The advantage of the Spectropyrometer is that the emissivity behavior is determined from data collected every measurement by means of the use of hundreds of narrow wavebands which allows accurate temperature control.

[0022] The encapsulated inoculant preferably comprises a mixture of

from 45 to 55 wt. % of Co_3FeNb_2, and
from 55 to 45 wt. % of CrFeNb(Ni),

wherein percentages are expressed by weight with respect to the total weight of the mixture of Co_3FeNb_2 and CrFeNb(Ni).

[0023] More preferably, the Co_3FeNb_2 and CrFeNb(Ni) contained in the encapsulated inoculant are powders with a particle size from 1 to 80 μm. In particularly preferred embodiments of the present invention, the encapsulated inoculant comprises a mixture of:

20 wt. % to 30 wt. % of Co_3FeNb_2 powders with particle size from 1 to 20 μm, and
20 wt. % to 30 wt. % of Co_3FeNb_2 powders with particle size from above 20 to 80 μm, provided that the total weight of Co_3FeNb_2 powders is from 45 to 55 wt. % of the total weight of Co_3FeNb_2 and CrFeNb(Ni); and
20 wt. % to 30 wt. % of CrFeNb(Ni) powders with particle size from 1 to 20 μm, and
20 wt. % to 30 wt. % of CrFeNb(Ni) powders with particle size from above 20 to 80 μm; provided that the total weight of CrFeNb(Ni) powders is from 55 to 45 wt. % of the total weight of Co_3FeNb_2 and CrFeNb(Ni).

[0024] The above-mentioned particle size distribution provided is particularly advantageous because an improved grain refinement effect can be achieved. More specifically, the combination of the powder size of the inoculants, time used for inoculation and temperature of the molten metal during inoculation are relevant to achieve a better effectiveness of the inoculation process. The control of these features results in the repeatability of the process.

[0025] Inoculants used in the process of the invention, i.e., Co_3FeNb_2 and CrFeNb(Ni), preferably have an amount of C lower than 0.05 %wt. Carbon is an impurity that might be present on the raw materials used to manufacture these inoculant. A higher amount of C in the inoculant could give rise to carbide formation, which could negatively affect mechanical properties of the inoculated nickel base alloy.

[0026] In the inoculation process of the invention, the powders of Co_3FeNb_2 and CrFeNb(Ni) are introduced inside the melt nickel base alloy encapsulated in a sealed container of a material compatible with the nickel base alloy, i.e., a material not comprising significant amounts of any elements strange to the nickel base alloy. Preferably, such material is iron based and, more preferably, the sealed container of the encapsulated inoculant is made of an iron base alloy comprising

C: 0 to 0.08 wt. %,
S: 0 to 0.03 wt. %,
P: 0 to 0.045 wt. %,
B: 0 to 0.045 wt. %, and
Si: 0 to 0.075 wt. %,

wherein percentages are expressed by weight with respect to the total weight of the iron base material of the container. A high content of C, S, P, B and Si could be detrimental to the alloy properties and, therefore, it is preferable to use an iron base alloy with the above-mentioned maximum content of these elements.

[0027] The container where the inoculants are encapsulated may have different dimensions and different forms such as tubular form. In the process of the invention, however, it is preferable that such container will be as small as possible, with the proviso that the inoculant powders can be stored into the container. Additionally, the thickness of the container's walls are preferably lower than 2 mm, so that the minimum amount of the container's material is incorporated at the nickel base alloy in the inoculation process.

[0028] The container of the encapsulated inoculant has to be sealed, so that the inoculant powders cannot left the container prior to the introduction of said encapsulated inoculant inside the melt nickel base alloy. Any conventional sealing means can be used, for example, pressure and/or spot welding.

[0029] In other preferred embodiments of the inoculation process described in this document, the total content of Co_3FeNb_2 and CrFeNb(Ni) contained in the encapsulated inoculant introduced inside the melt nickel base alloy is from 0.1 wt. % to 0.8 wt. %, preferably from 0.4 wt. % to 0.6 wt. %, of the weight of the melt nickel base alloy weight in step a).

[0030] More preferably, the total content of Co_3FeNb_2 and CrFeNb(Ni) in the encapsulated inoculant is 0.6 wt. % of the weight of the nickel base alloy weight in step a), both Co_3FeNb_2 and CrFeNb(Ni) are powders with a particle size from 1 to 80 μm, and the encapsulated inoculant is introduced, preferably for a period of 10 seconds, inside the melt mixture of alloying elements at a temperature of 1485 °C.

[0031] Once the melt of nickel base alloy is obtained and before introducing the encapsulated inoculant into this melt, a power supply of the vacuum furnace is reduced or, preferably, switched off to avoid electromagnetic stirring. The inventors have found that a high electromagnetic stirring during the inoculation step can jeopardize grain refinement, among other things due to quick dissolution of the inoculants. In order to avoid this negative effect, a reduced power supply in the heating process to obtain the melt of nickel base alloy can be used or, preferably, the power supply required to achieve a melt in a suitable time can be reduced or even switched off, once the melt is obtained.

[0032] An important advantage of the inoculation process of the present invention is that the mixture of inoculant powders with the required particle size, preferably between 1 μm and 80 μm, are contained in the encapsulated inoculant within a sealed container and, therefore, they can be properly introduced inside the melt of nickel base alloy, preferably in the central part of said melt, without electromagnetic stirring. If such powders would be left (un-encapsulated) on the surface of the melt, they would be mixed with the slag and, therefore, the inoculant compounds could not disperse thought the melt alloy.

[0033] Another important advantage of using encapsulated inoculants is that the dissolution rate of the inoculant powder can be reduced, so that a greatest grain refinement effect is achieved with the process of the present invention.

[0034] An alumina crucible can be used to obtain the melt of nickel base alloy. In particular, such crucible is preferably a high alumina crucible with a content of alumina higher than 60 wt. %, because this material avoids the formation of impurities during the procedure.

[0035] In the inoculation process of the invention, the mold can be positioned close to the alumina crucible, in particular, the distance between the mold and the alumina crucible containing the melt inoculated nickel base alloy is about 300 mm, so that turbulence when pouring can be avoided.

[0036] In other preferred embodiments of the invention, the encapsulated inoculant is manufactured by the following method:

i) providing Co_3FeNb_2 powders with a particle size from 1 to 80 μm;
ii) providing CrFeNb(Ni) powders with a particle size from 1 to 80 μm;
iii) preparing a mixture comprising from 45 wt. % to 55 wt. % of the Co_3FeNb_2 powders of step i) and from 55 wt. % to 45 wt. % of the CrFeNb(Ni) powders of step ii);
iv) introducing the mixture prepared in step iii) into an iron base container, preferable a tube, and

v) sealing the container, preferably by pressure and spot welding, in order to avoid extraction of the inoculant powders from the encapsulated inoculant.

[0037] Preferably, the encapsulated inoculant comprises a handling system, which can be used for introducing it inside the melt of nickel base alloy, for example, using any suitable means incorporated to the vacuum furnace such as a pulley system. In particular, the handling system can be a wire of similar material than the container. In particular, a material compatible with the nickel base alloy as defined in this document in relation with the material of the container.

[0038] If the encapsulated inoculant comprises a handling system, the method for manufacturing it further comprises attaching the handling system to the container.

[0039] Besides that, Co_3FeNb_2 and CrFeNb(Ni) powders to be used as inoculant can be separately manufactured using conventional methods. In particular, these inoculants can be manufactured, for example in the 20 kg single chamber Consarc VIM furnace, by a method comprising the following steps:

- Introducing the raw materials of elements of the inoculant in a high alumina crucible, i.e., an alumina crucible with a content of alumina higher than 60 wt. %. Raw materials of the elements of the inoculant preferably have a purity higher than 99 wt. % and, more preferably, the total content of C is such that the content of C in the inoculant compounds is lower than 0.05 wt. %. Vacuum pumping of the VIM furnace, preferably within $5x10^{-3}$ - $5x10^{-4}$ mbar range.
- Progressive heating up until melting and uniform mixing of the constituents of the inoculant compound in vacuum.
- Switching off the power of the VIM and cooling of the cast inoculant, preferably natural cooling of the cast inside the crucible.
- Crushing the inoculant ingot using a mechanical method (such as a standard hammer or similar) to approximately 20 mm size pieces.
- Milling the inoculant pieces, for example, using a Retsch vibrating mill to obtain fine powders, preferably for 5-10 minutes.
- Separating the inoculant powders using the four following sequence of sieves: 1-20 μm, 20-80 μm, 80-160 μm and 160-400 μm.

[0040] 1-80 μm powder size of Co_3FeNb_2 and CrFeNb(Ni) inoculants are preferably selected for the inoculation process.

[0041] In order to analyze the grain structure of the inoculated nickel base alloy, the cast inoculated can be sectioned and specimen can be prepared by conventional grinding and polishing methods. Then, ADLER chemical etching (40-60% hydrogen chloride, 5-25% iron trichloride, 2-5% diammonium tetrachlorocuprate) for nickel alloys can be used to reveal grain structure. The average grain length and width size can be obtained according to the length and the width of 10-25 grain measurement performed in two 11 mm x 8 mm regions of the central area of the cast part (metallic sample of 30 mm x 30 mm x 35 mm) with 10X magnification in a Olympus SZH binocular magnifier.

[0042] The ratio between the mean length (L) and the mean width (W) has been also evaluated for the definition of the columnar or equiaxial morphology of the grain. The approach taken for the grain refinement method is defined by two parameters: the grain size and the grain morphology which should correspond to mean grain length below 2 mm and L/W ratio equal or below 1.5 for equiaxial grain, respectively.

DESCRIPTION OF THE DRAWINGS

[0043]

Figure 1: SEM image of the crushed CrFeNb(Ni) inoculant
Figure 2: SEM image of the crushed Co_3FeNb_2 inoculant
Figure 3: A particular embodiment of the sealed container with encapsulated inoculant ready for the inoculation process
Figure 4: Scheme of the pouring system, wherein it is represented a crucible for obtaining the melt of nickel base alloy (1), a pouring platform (2) and a mold (3), in particular, a mold for the 30 x 30 x 35 mm part.
Figure 5: Spectropyrometer measurement at the end of the heating process
Figure 6: Section of cutting from the cast part for the grain size analysis
Figure 7: Grain size measurements in Zone 1 of 0.6 % cast inoculated part
Figure 8: Grain size measurements in Zone 2 of 0.6 % cast inoculated part
Figure 9: Grain size measurements in non-inoculated cast part

EXAMPLES

Example 1: Manufacturing process of the CrFeNb(Ni) inoculant

[0044] 2340 g of CrFeNb(Ni) inoculant have been prepared and cast in the 20 kg single chamber Consarc VIM furnace following the next steps:

- Cleaning of the solid raw materials with acetone and introduction in the high alumina crucible (i.e., a crucible with a content of alumina higher than 60 wt. %) in the indicated amounts: 608.4 gr of Cr, 655.2 g of Fe and 1076.4 g of Nb. Vacuum pumping of the VIM furnace to $7x10^{-4}$ mbar.
- Progressive heating of the solid materials with 5 KW power increase steps until 20 KW has been reached. This power has been maintained during 5 minutes until melting at 1560 °C of all the solid charge.
- The metal is left for mixing and homogenization at 20 KW power for 3-4 minutes.
- The power of the VIM is switched off and the mixed alloy is cooled down naturally inside the crucible. The vacuum pressure indicated $3x10^{-3}$ mbar when the furnace was switched off.

Example 2: Manufacturing process of the Co_3FeNb_2 inoculant

[0045] 2340 g of Co_3FeNb_2 inoculant have been prepared and cast in the 20 kg single chamber Consarc VIM furnace following the next steps:

- Cleaning of the solid raw materials with acetone and introduction in the high alumina crucible (i.e., a crucible with a content of alumina higher than 60 wt. %) in the indicated amounts: 982.8 g of Co, 304.2 g of Fe and 1053 g of Nb.
- Vacuum pumping of the VIM furnace to $5x10^{-4}$ mbar.
- Progressive heating of the solid materials within 3-5 KW power increase steps until 17 KW has been reached. This power has been maintained during 5 minutes until melting at 1565 °C of all the solid charge.
- The metal is left for mixing and homogenization at 17 KW power for 3-4 minutes.
- The power of the VIM is switched off and the mixed alloy is cooled down naturally inside the crucible. The vacuum pressure indicated $6x10^{-3}$ mbar when the furnace was switched off.

Analysis of the inoculants

[0046] The chemical composition of the inoculants obtained in Examples 1 and 2 has been analyzed in six different zones of each ingot by X-ray fluorescence. Table 1 and Table 2 show the results for the CrFeNb(Ni) and Co_3FeNb_2 inoculants, respectively. In addition to this, presence of carbon has been also measured in order to test the possible presence of contaminants. Results have been showed below 0.05 %C in both cases, as detailed in Table 3.

Table 1. Chemical analysis (wt. %) of the CrFeNb(Ni) inoculant obtained by X-ray fluorescence

Region of analysis	Chemical analysis (wt. %)			
	%Nb	%Fe	%Cr	%Ni
Zone 1	46.4	28.0	23.3	1.5
Zone 2	45.0	29.1	24.4	1.4
Zone 3	44.8	29.9	23.5	1.7
Zone 4	45.4	29.3	22.9	1.6
Zone 5	45.8	29.0	23.6	1.6
Zone 6	45.3	29.5	23.7	1.5

Table 2. Chemical analysis (wt. %) of the Co_3FeNb_2 inoculant obtained by X-ray fluorescence

Region of analysis	Chemical analysis (wt. %)		
	%Fe	%Co	%Nb
Zone 1	12.4	40.9	46.2

(continued)

Region of analysis	Chemical analysis (wt. %)		
	%Fe	%Co	%Nb
Zone 2	13.0	40.1	46.8
Zone 3	12.5	40.6	46.7
Zone 4	12.6	39.6	47.8
Zone 5	13.2	41.1	45.8
Zone 6	13.6	40.6	44.4

Table 3. Carbon chemical analysis of CrFeNb(Ni) and Co_3FeNb_2 inoculants in wt. %

Reference	%C	Reference	%C
CrFeNb(Ni)	0.030	Co_3FeNb_2	0.040
	0.022		0.041
	0.023		0.039

Example 3: Preparation of the inoculant powders

[0047] The following procedure has been separately applied to the 2.34 kg ingots of CrFeNb(Ni) and Co_3FeNb_2 inoculants obtained as described in Examples 1 and 2:

- The inoculant ingots have been crushed using a standard hammer to approximately 20 mm size pieces.
- The inoculant pieces have been milled using a Retsch vibrating mill. Four two-minute cycles have been applied for both inoculants and the obtained powder size has been 1-400 μm for the CrFeNb(Ni) compound and 1-720 μm for the Co_3FeNb_2 compound. Figure 1 and Figure 2 show SEM images from CrFeNb(Ni) and Co_3FeNb_2 powders, respectively.
- Powders of each of the inoculants have been separated using the four following sequence of sieves: from 1 μm to 20 μm, above 20 μm to 80 μm, above 80 to 160 μm, above 160 to 400 μm. In the case of the Co_3FeNb_2 inoculant powders bigger than 400 μm have been again milled and separated through the mentioned sieves.

Example 4: Preparation of the encapsulated inoculant

[0048] A total amount of 18 g of Co_3FeNb_2 and CrFeNb(Ni), following the size ranges and amounts indicated in Table 4, has been weighed. This amount of inoculant mixture corresponds to a 0.6 wt. % of the weight of IN718 melt alloy to be used in the inoculation process (see Example 5 below).

Table 4. Amount and powder size range of the inoculant compounds

	Amount (g)
from 1 μm to 20 μm of Co_3FeNb_2	4.5
from above 20 μm to 80 μm of Co_3FeNb_2	4.5
from 1 μm to 20 μm of CrFeNb(Ni)	4.5
from above 20 μm to 80 μm of CrFeNb(Ni)	4.5

[0049] The 18 g of Co_3FeNb_2 and CrFeNb(Ni) have been introduced into an AISI 316L tube of 10 mm external diameter and 0.5 mm thickness and both sides have been closed by pressure after introducing a steel wire through it for handling, as that of Figure 3. Then, both ends of the tube have been spot welded to avoid the inoculant powder getting out from the tube.

Example 5: Inoculation process of IN718 alloy

[0050] The encapsulated inoculant prepared in Example 4 has been placed in the charging chamber of the VIM furnace.

[0051] Additionally, solid raw materials of the elements for 3 kg of IN718 alloy with purity 99-100 wt. have been introduced in the high alumina crucible (i.e., a crucible with a content of alumina higher than 60 wt. %) located at the main chamber of such VIM furnace. The amount of these raw materials is detailed in Table 5 below:

Table 5. Raw materials load for 3 kg of IN718 alloy

	Amount (g)
Cr	571
Mo	92.5
Ti	31
Nb	152.5
Fe	558
Al	19
Ni	1576

[0052] A defined mold for the 30 x 30 x 35 mm part has been positioned close to the crucible (in particular, at the distance of 300 mm) to avoid the turbulence when pouring the mold, as shown in Figure 4. The VIM furnace has been vacuum pumped to 5×10^{-4} mbar pressure and then the melt of the alloy has been obtained by manual control of the power settings to allow slow heating of the crucible following this sequence: 5 KW for 20 minutes, 10 KW for 10 minutes and 15 KW for 10 minutes.

[0053] Finally, the power has been slightly increased to 18 KW to reach the preferred temperature range for industrial process (1480-1490 °C). The temperature of the nickel base alloy during the heating process has been continuously measured by a Spectropyrometer (FAR Associates FMP2 multi-wavelength pyrometer), showing the temperature at the end of the heating process in Figure 5. The solid materials have been progressively melted until reaching 1484 °C, at this moment the power of the furnace has been switched off and the encapsulated inoculant (obtained as described in Example 4) has been introduced into the molten alloy. The container of the encapsulated inoculant has been melted in approximately 10 seconds and then the inoculant powders have been left for 5-10 seconds inside the metal. Finally, the inoculated alloy has been poured into the mold and left for natural cooling inside the furnace.

Example 6: Grain size analysis

[0054] The cast inoculated 30 x 30 x 35 mm part has been sectioned as presented in Figure 6 and specimen has been prepared by conventional grinding and polishing methods. In particular, grinding has been carried out according to the use of SiC papers in this order: P80, P220, P1200 and P2400 and polishing with diamond paste of 3, 0.25 and 0.04 μm. Then ADLER chemical etching (40-60% hydrogen chloride, 5-25% iron trichloride, 2-5% diammonium tetrachlorocuprate) for nickel alloys has been used to reveal grain structure by immersion. The average grain size has been obtained according to the length and the width of 10-25 grains. Grain size measurements have been carried out in two 11mm x 8mm regions (Figure 7 and Figure 8) of 0.6 wt. % inoculated cast part. Images have been taken with 10X magnification by a Olympus SHZ binocular magnifier. The ratio between the mean length (L) and the mean width (W) has been also measured for the definition of the morphology (columnar or equiaxial) of the grain. Mean values of length and width and the morphology of the grains from both regions are detailed in Table 6. It is demonstrated that the requirements of grain size below 2 mm and ratio morphology equal or below 1.5 are fulfilled and therefore grain refinement has been successfully achieved. Finally, as for comparison, Figure 9 shows an image of a non inoculated cast part with large grains up to 4 mm length and columnar grain microstructure with approximate ratio of 3 between the length and the width.

Table 6. Mean grain size measurements from Zone 1 and Zone 2 of 0.6 wt. % inoculated cast part

	Mean length (μm)	Mean width (μm)	Grain morphology (Length/Width)
Zone 1	915	625	Equiaxial 1.46

(continued)

	Mean length (μm)	Mean width (μm)	Grain morphology (Length/Width)
Zone 2	1010	680	Equiaxial 1.49

Claims

1. An inoculation process of a nickel base alloy, wherein the process is carried out in a vacuum furnace and comprises:

   a) providing a melt of a nickel base alloy in vacuum conditions, **characterized in that** the inoculation process further comprises:
   b) introducing an encapsulated inoculant comprising a mixture of Co_3FeNb_2 and CrFeNb(Ni) inside the melt of the nickel base alloy at a temperature from 1450 to 1500 °C for a period from 5 to 30 seconds,
   c) immediately pouring the inoculated nickel base alloy of step b) into a mold, preferably at a temperature from 1450 to 1500 °C, and
   d) cooling said inoculated nickel base alloy.

2. The inoculation process of claim 1, wherein the melt nickel base alloy comprises Ni, Cr, Co, Nb and Fe.

3. The inoculation process of any one of claims 1 to 2, wherein the melt nickel base alloy comprises:

   Ni: 50 wt. % to 65 wt. %,
   Cr: 10 wt. % to 25 wt. %,
   Mo: 2 wt. % to 5 wt. %,
   Co: 0.01 wt. % to 1 wt. %,
   Nb: 0.04 wt. % to 5.5 wt. %, and
   Fe: 1 wt. % to 24 wt. %,

   wherein percentages are expressed by weight with respect to the total weight of the nickel base alloy.

4. The inoculation process of any one of claims 1 to 3, wherein the melt of nickel base alloy comprises:

   Ni: 50 wt. % to 55 wt. %,
   Cr: 17 wt. % to 21 wt. %,
   Mo: 2.8 wt. % to 3.3 wt. %,
   Co: 0.01 wt. % to 1 wt. %,
   Nb: 4.75 wt. % to 5.5 wt. %,
   Fe: 12 wt. % to 22 wt. %,
   Ti: 0.65 wt. % to 1.15 wt. %,
   Al: 0.2 wt. % to 0.8 wt. %,
   C: not more than 0.08 wt. %,
   Si: not more than 0.35 wt. %,
   Mn: not more than 0.35 wt. %,
   P: not more than 0.015 wt. %,
   S: not more than 0.015 wt. %, and
   B: not more than 0.006 wt. %,

   wherein percentages are expressed by weight with respect to the total weight of the nickel base alloy.

5. The inoculation process of any one of claims 1 to 4, wherein the encapsulated inoculant comprises a mixture of

   from 45 to 55 wt. % of Co_3FeNb_2, and
   from 55 to 45 wt. % of CrFeNb(Ni),

   wherein percentages are expressed by weight with respect to the total weight of the mixture of Co_3FeNb_2 and

CrFeNb(Ni).

6. The inoculation process of any one of claims 1 to 5, wherein the Co_3FeNb_2 and CrFeNb(Ni) contained in the encapsulated inoculant are powders with a particle size from 1 to 80 μm.

7. The inoculation process of claim 6, wherein the encapsulated inoculant comprises a mixture of:

   20 wt. % to 30 wt. % of Co_3FeNb_2 powders with particle size from 1 to 20 μm, and
   20 wt. % to 30 wt. % of Co_3FeNb_2 powders with particle size from above 20 to 80 μm, provided that the total weight of Co_3FeNb_2 powders is from 45 to 55 wt. % of the total weight of Co_3FeNb_2 and CrFeNb(Ni);
   20 wt. % to 30 wt. % of CrFeNb(Ni) powders with particle size from 1 to 20 μm, and
   20 wt. % to 30 wt. % of CrFeNb(Ni) powders with particle size from above 20 to 80 μm; provided that the total weight of CrFeNb(Ni) powders is from 55 to 45 wt. % of the total weight of Co_3FeNb_2 and CrFeNb(Ni).

8. The inoculation process of any one of claims 1 to 7, wherein both Co_3FeNb_2 and CrFeNb(Ni) has an amount of C lower than 0.05 %wt.

9. The inoculation process of any one of claim 1 to 8, wherein the mixture of Co_3FeNb_2 and CrFeNb(Ni) is encapsulated in an iron base sealed container.

10. The inoculant process of claim 9, wherein the iron base sealed container comprises:

   C: 0 to 0.08 wt. %,
   S: 0 to 0.03 wt. %,
   P: 0 to 0.045 wt. %,
   B: 0 to 0.045 wt. %, and
   Si: 0 to 0.075 wt. %,

   wherein percentages are expressed by weight with respect to the total weight of the iron base material of the container.

11. The inoculation process of any one of claims 1 to 10, wherein the total content of Co_3FeNb_2 and CrFeNb(Ni) is from 0.1 wt. % to 0.8 wt. %, preferably from 0.4 wt. % to 0.6 wt. %, of the melt nickel base alloy.

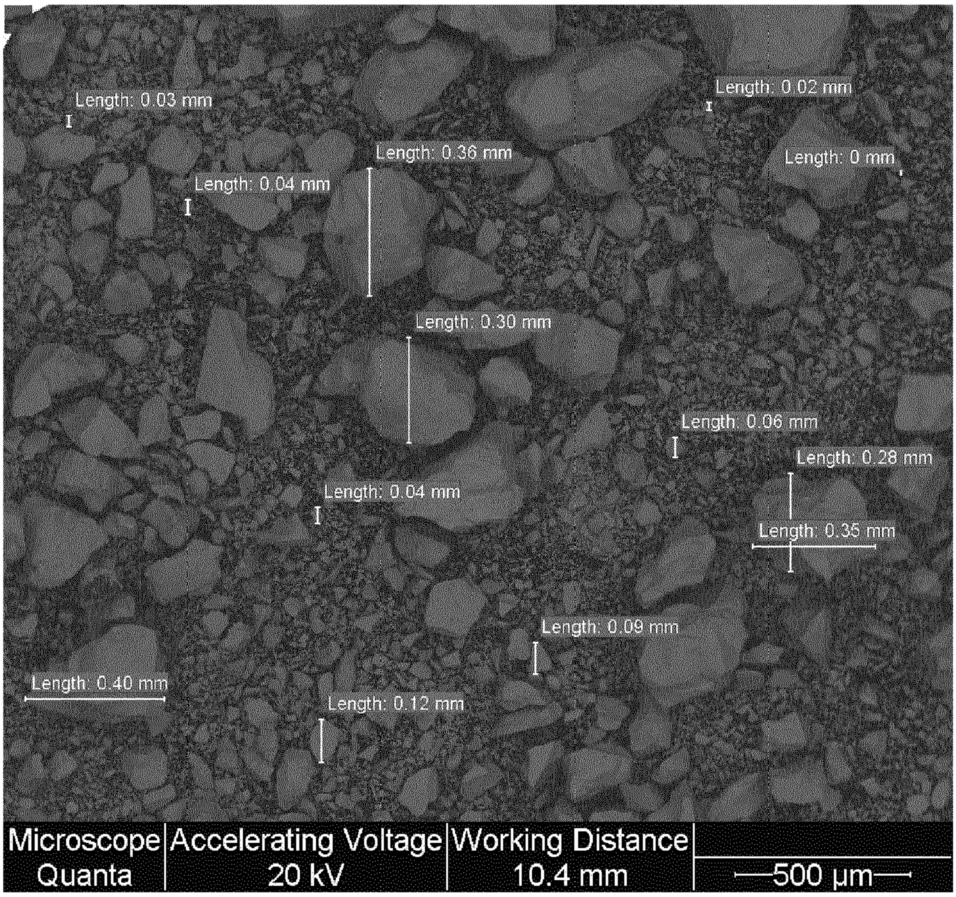
12. The inoculation process of claim 11, wherein the total content of Co_3FeNb_2 and CrFeNb(Ni) in the encapsulated inoculant is 0.6 wt. % of the melt nickel base alloy, both Co_3FeNb_2 and CrFeNb(Ni) are powders with a particle size from 1 to 80 μm, and the encapsulated inoculant is introduced, preferably for a period of 10 seconds, inside the melt mixture of alloying elements at a temperature of 1485 °C.

13. The inoculation process of any one of claims 1 to 12, wherein the power supply of the vacuum furnace is reduced or, preferably, switched off before introducing the encapsulated inoculant inside the melt nickel base alloy.

14. The inoculation process of any one of claims 1 to 13, wherein the encapsulated inoculant is manufactured by the following method:

   i) providing Co_3FeNb_2 powders with a particle size from 1 to 80 μm;
   ii) providing CrFeNb(Ni) powders with a particle size from 1 to 80 μm;
   iii) preparing a mixture comprising from 45 wt. % to 55 wt. % of the Co_3FeNb_2 powders of step i) and from 55 wt. % to 45 wt. % of the CrFeNb(Ni) powders of step ii);
   iv) introducing the mixture prepared in step iii) into an iron base container, preferable a tube, and
   v) sealing the container, preferably by pressure and spot welding.

15. The inoculation process of claim 14, wherein the encapsulated inoculant comprises a handling system and, preferably, the method for manufacturing such encapsulated inoculant further comprises attaching the handling system to the container.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Length: 0.35 mm
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Length: 0.40 mm
Length: 0.12 mm
Microscope
Quanta
Accelerating Voltage
20 kV
Working Distance
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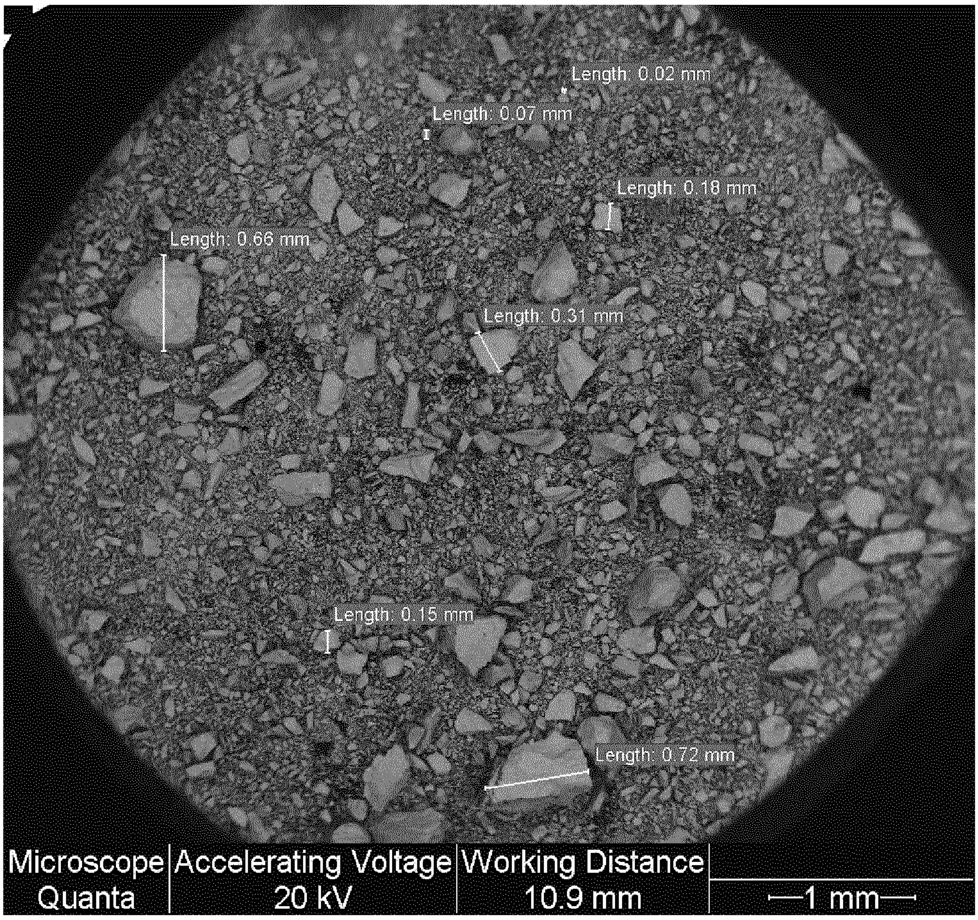
500 µm

FIG 1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Quanta
Accelerating Voltage
20 kV
Working Distance
10.9 mm
1 mm

FIG 2

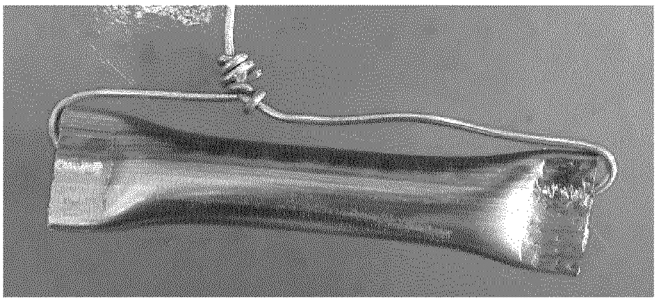


FIG 3

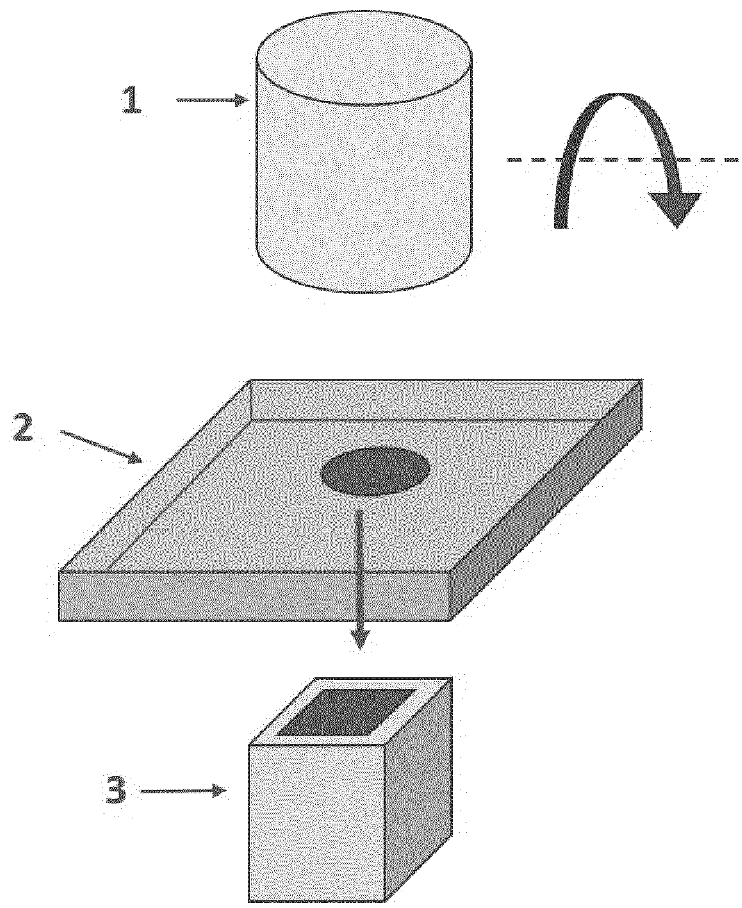
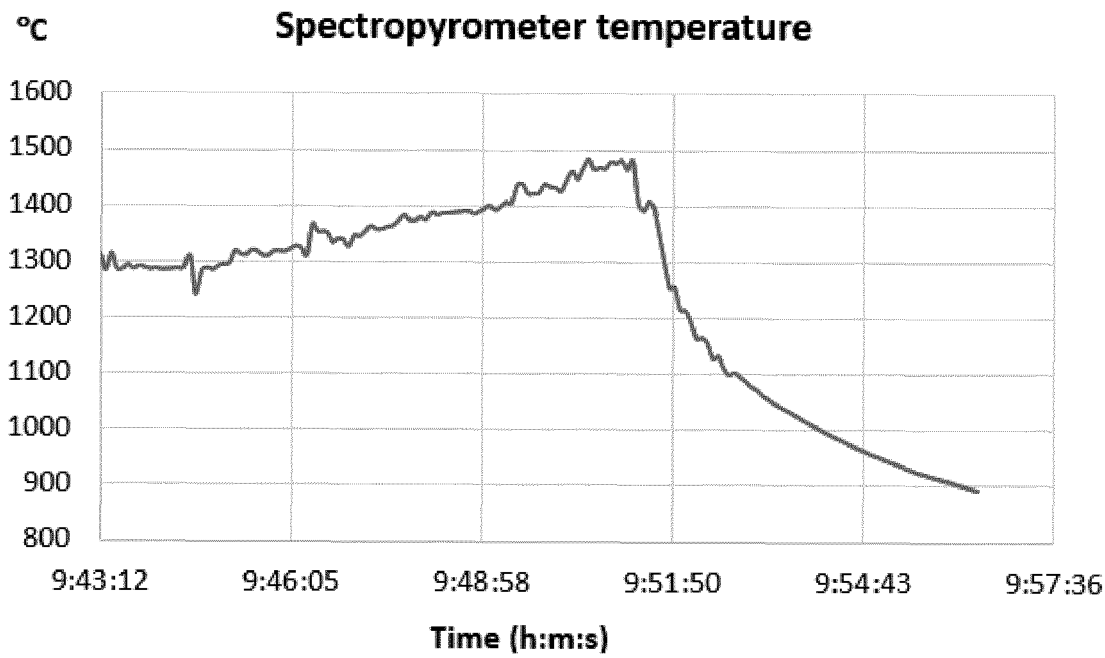


FIG 4


°C
Spectropyrometer temperature
1600
1500
1400
1300
1200
1100
1000
900
800
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9:48:58
9:51:50
9:54:43
9:57:36
Time (h:m:s)

FIG 5

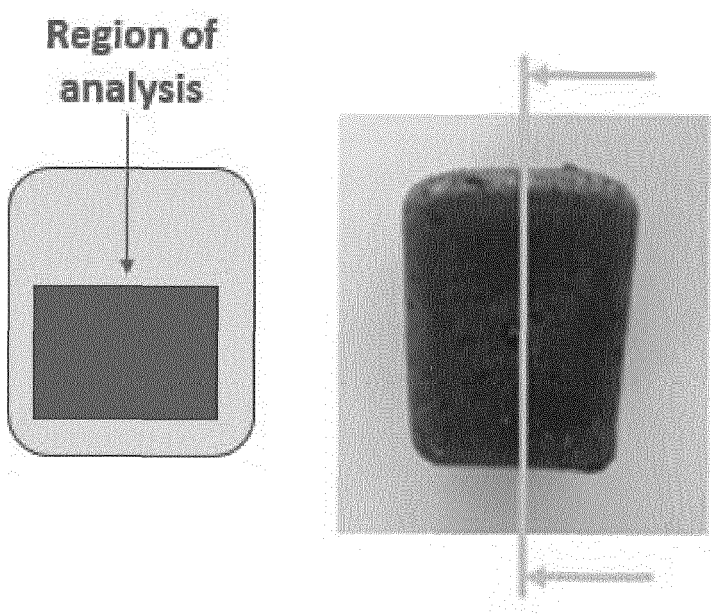
Region of analysis

FIG 6

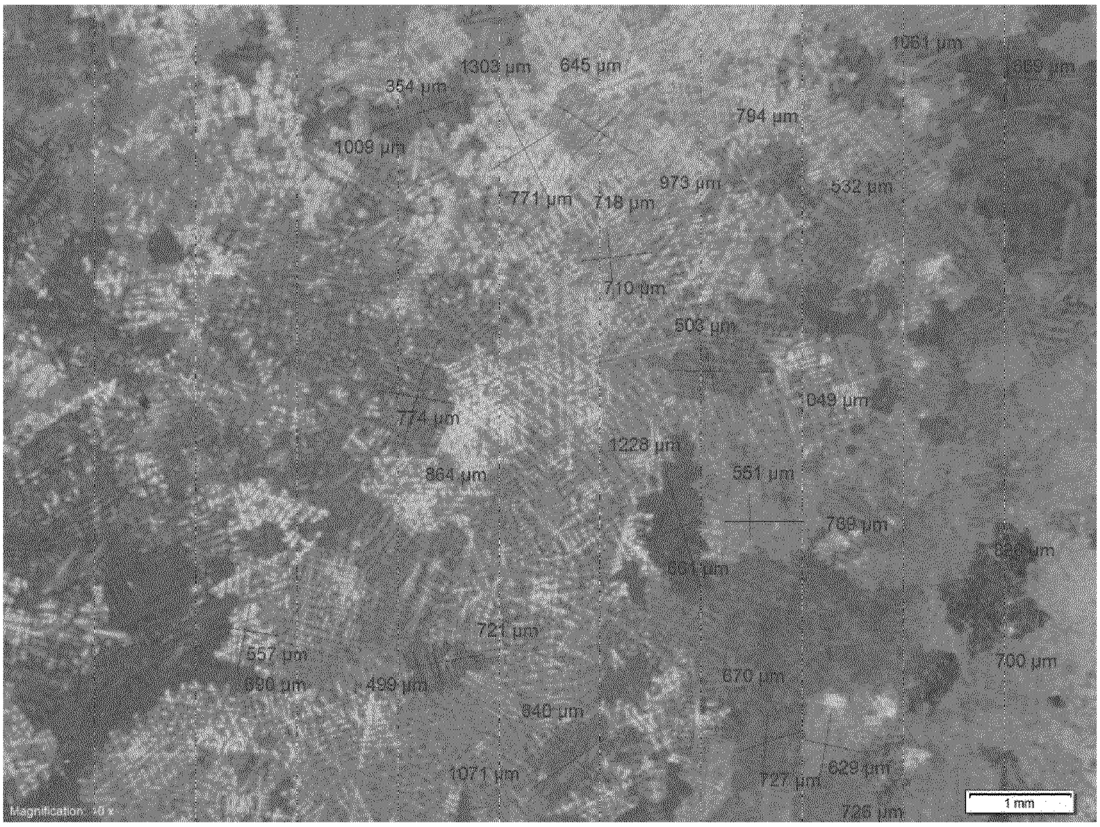

FIG 7

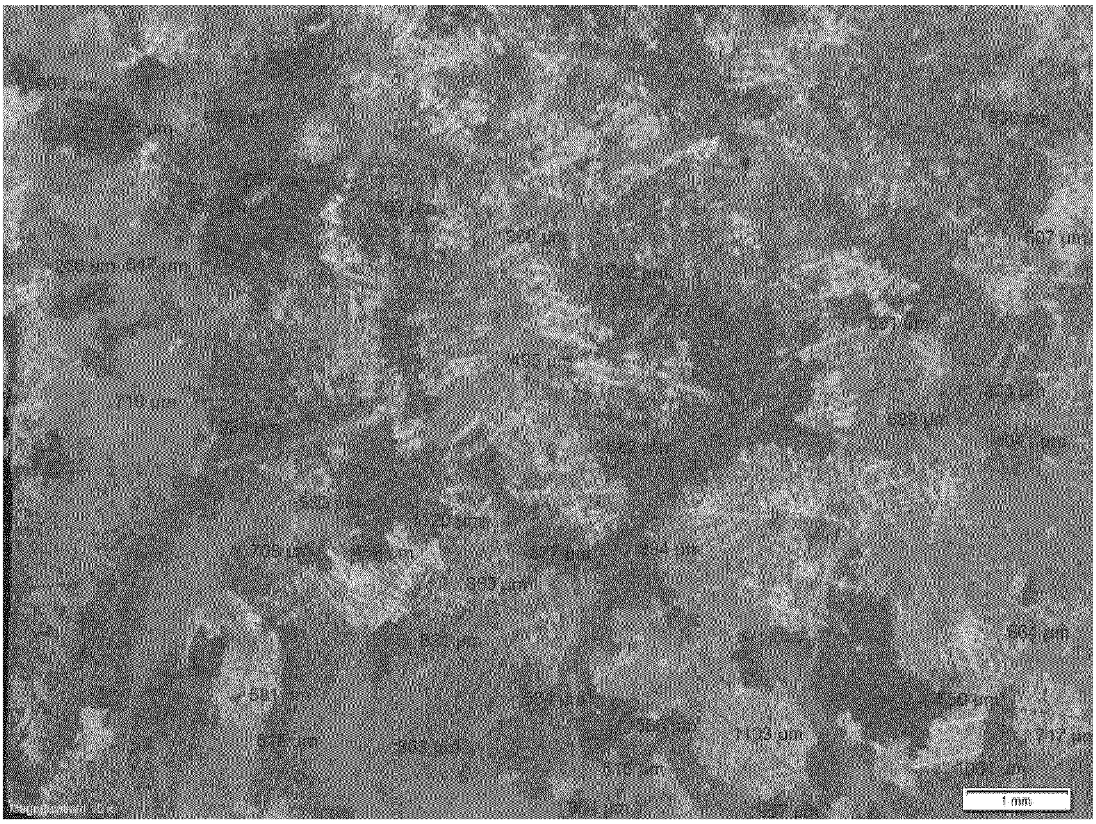

FIG 8

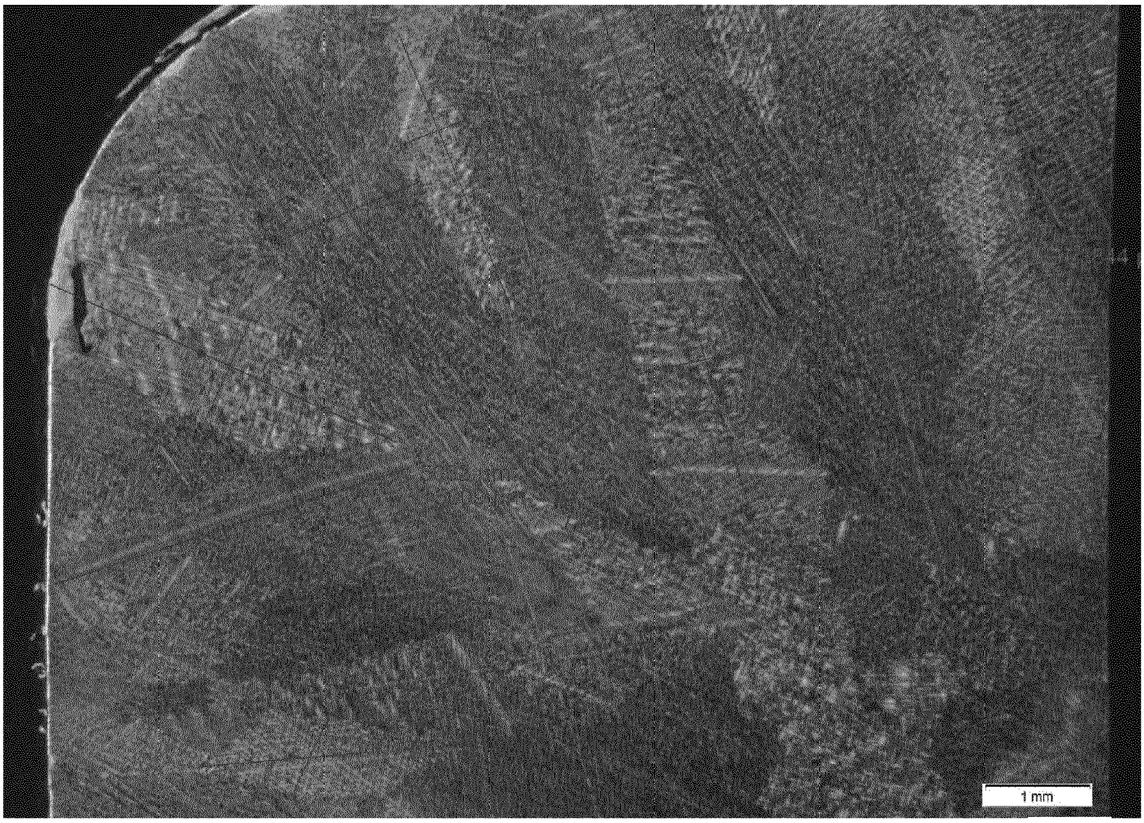

FIG 9

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

2

Place of search	Date of completion of the search	Examiner
The Hague	17 March 2020	Vermeulen, Yves

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EUROPEAN SEARCH REPORT

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L : document cited for other reasons

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page 2 of 2

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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