(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 366 385 A1

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.08.2018 Bulletin 2018/35

(21) Application number: **17305219.2**

(22) Date of filing: **28.02.2017**

(51) Int Cl.:
B22C 1/02 *(2006.01)* ***B22C 9/02*** *(2006.01)*
B22D 21/00 *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(71) Applicant: **Safran Transmission Systems**
92700 Colombes (FR)

(72) Inventors:
- **PIWOWAR, Katarzyna**
  77550 Moissy-Cramayel (FR)
- **MOCEK, Jan**
  38-213 Kolaczyce (PL)
- **MYSZKA, Marcin**
  31-228 Krakow (PL)
- **ZYCH, Jerzy**
  30-611 Krakow (PL)

(74) Representative: **Robert, Mathias et al**
Ernest Gutmann - Yves Plasseraud S.A.S.
3, rue Auber
75009 Paris (FR)

(54) **MOLDING SAND INCLUDING GRAPHITE NANOPARTICLES AND MOLD MADE OF SUCH A MOLDING SAND**

(57) Molding sand (**5**) comprising:
- Quartz sand (**6**);
- A binder (**7**) including sodium or potassium silicate and graphite nanoparticles;
- A radical initiator (**8**).

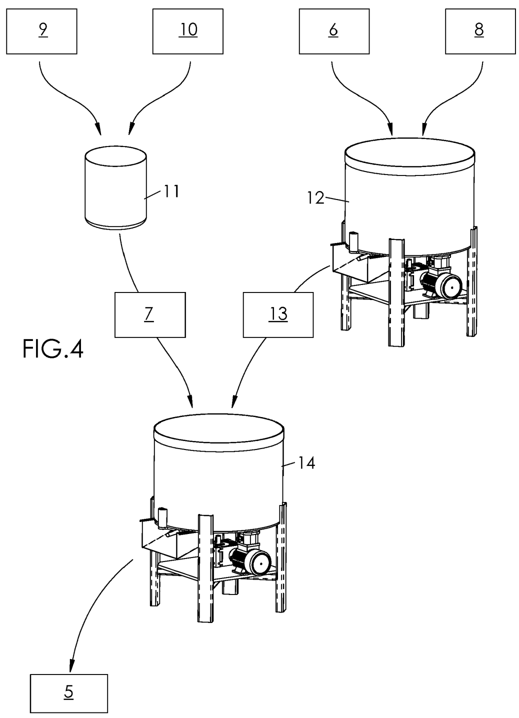


FIG.4

EP 3 366 385 A1

Description

FIELD OF THE INVENTION

[0001] The invention generally relates to the field of foundry, particularly to the foundry of aluminum alloy cast pieces, more specifically of pieces serving as components of turbomachines such as aircraft turbojet engines.

BACKGROUND OF THE INVENTION

[0002] Many components of turbojet engines are made of cast aluminum alloys, due to their good mechanical performances, resistance to thermal fatigue and lightness.

[0003] Such is the case of an accessory gear box (better known by its acronym: AGB), which includes, in a metal surrounding made of an aluminum alloy, gears connected to components e.g. an electric generator or a starter and driven by an input shaft of the turbomachine.

[0004] An AGB architecture is disclosed in international PCT application WO 2012/175883 (Snecma).

[0005] The surrounding of an AGB is commonly casted in an aluminum alloy such as one of the 42000 series (AlSi7Mg).

[0006] The surrounding is ordinarily casted within a mold made of a material (called molding sand) the main component of which is sand (typically silica sand), and further including a binding agent (or binder) together with a radical initiator - or curing agent - which gives the material its mechanical strength.

[0007] It is known that the mechanical performances of the cast piece depend a lot upon the solidification rate of the alloy within the mold.

[0008] The solidification rate depends in turn of the thermal conductibility of the mold, i.e. its capability to evacuate calories from the liquid alloy.

[0009] To increase the cooling rate, it is known to use chillers which have the exact shape of the cast piece. Those chillers are commonly made of metal. It is also known, however, to make those chillers out of graphite powder mixed with a binder (such as sodium silicate or a thermosetting resin) and hardened through carbon dioxide, see e.g. French patent FR 2 138 358 (Messier).

[0010] That document does not state the thickness needed for the chiller to efficiently evacuate the calories and hence promote the increase of the solidification rate of the cast piece.

[0011] The solution provided by French patent FR 2 138 358 implies several difficulties.

[0012] Firstly, it requires to grind the graphite down to the particle size of the sand commonly used for the making of the mold, which increases its complexity and manufacturing time.

[0013] Secondly, the evacuation of calories is limited by the low thermal conductibility of the underlying molding sand.

[0014] A first objective of the invention is to enhance mechanical performances of the cast pieces, particularly pieces made from aluminum alloy, and more specifically pieces serving as components in turbomachines.

[0015] A second objective of the invention is to provide a material intended for the manufacturing of a casting mold which promotes a greater solidification rate of the cast alloy.

[0016] A third objective of the invention is to provide a method for preparing such a material, which is simple to implement.

SUMMARY OF THE INVENTION

[0017] It is therefore provided, according to a first aspect, a molding sand comprising:

- Quartz sand;
- A binder including sodium or potassium silicate and graphite nanoparticles;
- A radical initiator.

[0018] According to various embodiments, taken either separately of in combination:

- the size of the graphite nanoparticles is comprised between 500 nm and 800 nm;
- the radical initiator is chosen among the following agents: acetic acid, carbonic acid, ester acid, carbon dioxide;
- the mass proportion of binder, with respect to quartz sand, is comprised between 2.5% and 5%;
- the mass proportion of radical initiator, with respect of sodium or potassium silicate, is comprised between 10% and 15%;
- the quartz sand is composed of grains of quartz the size of which is comprised between 200 and 300 μm.

[0019] It is provided, according to a second aspect, a method for preparing a molding sand such as disclosed hereinbefore, comprising the following steps:

- preparing the binder by mixing a colloidal graphite solution with water glass,
- preparing a primary mixture including the radical initiator and the quartz sand;
- adding the binder to the primary mixture;
- mixing the resulting mixture.

[0020] According to various embodiments, taken either separately or in combination:

- the mass proportion of colloidal graphite with respect to glass water is comprised between 5% and 20%;
- the mass proportion of binder with respect to quartz sand is comprised between 2.5% and 5%;
- the colloidal graphite is in powder form.
- the radical initiator is chosen among the following agents: acetic acid, carbonic acid, ester acid, carbon

dioxide.

- the mass proportion of radical initiator with respect to binder is comprised between 10% and 15%.
- the mixing time of the resulting mixture is about 2 min.

[0021] It is provided, according to a third aspect, a casting mold made of a molding sand as disclosed hereinbefore.

[0022] It is provided, according to a fourth aspect, a method of manufacturing a cast piece in an aluminum alloy comprising a step of casting the alloy within such a mold.

[0023] The above and further objects and advantages of the invention will become apparent from the detailed description of preferred embodiments, considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] In the drawings:

FIG.1, FIG.2 and **FIG.3** are schematic cut views showing steps of manufacturing a cast piece within a mold made of molding sand.

FIG.4 is a schematic representation of several steps of preparing a molding sand according to the invention.

FIG.5 is a graphical diagram including two curves showing variation of temperature vs. time, and illustrating, on the one hand, in solid line, the cooling of the cast piece in a mold made in a molding sand according to the invention and, on the other hand, in dash-dotted line, the cooling of a similar cast piece in a mold made of a conventional molding sand;

FIG.6A is a photograph showing, at micrometric scale, a section of a cast aluminum alloy from a mold made of a molding sand according to the invention.

FIG.6B is a photograph showing, at micrometric scale, a section of a cast aluminum alloy from a mold made of a conventional molding sand.

DETAILED DESCRIPTION

[0025] A casting mold **1** is shown on **FIG.1** to **FIG.3.** This mold **1** comprises a hollow molding cavity **2** made as a print from a piece **3** to be made by the casting, within the cavity **2,** of a metal alloy **4,** e.g. an aluminum alloy.

[0026] In one embodiment, the alloy **4** is an aluminum alloy from the EN AC-4000 series (according to European standard EN 1780-1), i.e. having silica as main additive element. The alloy is, for example, AlSi7Mg, including 7% silica and less than 1% magnesium. Such alloy is most appropriate for the casting of components of a turbomachine (and more specifically a turbojet engine).

[0027] In the example depicted on **FIG.1** to **FIG.3,** the mold **1** comprises several (two here) blocks **1A, 1B** each having embossings **2A, 2B** (either hollow or protruding) which, whenever the blocks **1A, 1B** are side by side (**FIG.1, FIG.2**), together define the molding cavity **2.**

[0028] The mold **1** is made of a molding sand **5** comprising:

- silica sand **6** as main component (called matrix);
- a binder **7** the function of which is to aggregate the grains of sand **6;**
- a radical initiator **8** which acts as a curing agent to polymerize and harden the aggregate.

[0029] When, as in the depicted example, the mold **1** includes several blocks **1A, 1B,** each block **1A, 1B** is made of the same molding sand **5.**

[0030] The sand **6** used for the matrix is a quartz sand; it is preferably made of grains of quartz the size of which is comprised between 200 and 300 μm.

[0031] The binder **7** comprises sodium or potassium silicate together with graphite particles of nanometric size.

[0032] A particle of nanometric size, called nanoparticle, is a particle the size of which is lower than 100 nm, according to ISO/TS 80004-2:2015 standard.

[0033] In a preferred embodiment, the size of the graphite nanoparticles is comprised between 500 nm and 800 nm.

[0034] The mass proportion of binder **7,** with respect to the matrix (i.e. the quartz sand **6**) is preferably comprised between 2.5% and 5%.

[0035] The radical initiator **8** is a chemical which is characterized by its capability to form free radicals, i.e. molecules in which the outer shell electrons have not formed bonds yet and hence give those molecules a great chemical reactivity.

[0036] The radical initiator **8** is here initially chosen (i.e. before it is in contact with the binder **7,** with which it is to react) among the following compounds:

- acetic acid (chemical formula CH_3COOH)
- carbonic acid (chemical formula H_2CO_3),
- ester (formula RCOOR') acid,
- carbon dioxide (CO_2).

[0037] The mass proportion of radical initiator **8,** with respect of the sodium or potassium silicate, is preferably comprised between 10% and 15%.

[0038] The preparation of the molding sand **5** comprises three phases.

[0039] A first phase consists of preparing the binder **7.** To this end, water glass **9** is mixed with colloidal graphite **10.** Water glass is a common name for a sodium or potassium silicate solution. The proportion of the colloidal graphite **10** with respect to water glass **9** is preferably comprised between 5% and 20%.

[0040] The water glass **9** and the colloidal graphite solution **10** are poured into a mixer **11.** Mixing the water glass **9** and the colloidal graphite solution **10** within the mixer **11** produces the binder **7.**

[0041] A second phase, which may be conducted before, during or after the first phase, consists of mixing the radical initiator **8** with the matrix (i.e. the quartz sand **6**). To this end, the radical initiator **8** and the quartz sand **6** are poured into a mixer **12** in which they are mixed to form a primary mixture **13.** The mass proportion of the radical initiator **8** is measured with respect to the liquid glass **9.** More precisely, the mass proportion of radical initiator **8,** with respect to the water glass **9,** is preferably comprised between 10% and 15%. This phase is based upon the assertion that the radical initiator **8** is under liquid form (which is the case with acetic acid, carbonic acid and ester acid).

[0042] A third phase comprises adding the binder **7** resulting from the first phase to the primary mixture **13,** and mixing the resulting mixture - which is the molding sand **5** in a pasty form. The mixing may be achieved in the mixer **12** used to obtain the primary mixture **13,** or in a different mixer **14** (**FIG.4** is merely schematic and covers both cases).

[0043] The time of mixing the pasty molding sand **5** is preferably of about 2 min. The pasty (i.e. not hardened yet) molding sand **5** may then be given the shape of the mold **1 -** and more specifically the shape of each mold block **1A, 1B.** The radical initiator **8** fulfills its curing agent function after this shaping, whereby strength of the molding sand **5** forming each mold block **1A, 1B** is sufficient to allow the latter to maintain its shape.

[0044] In an alternate embodiment, wherein the radical initiator is carbon dioxide, which is in a gaseous form, the binder **7** resulting from the first step is directly mixed with pure quartz sand **6,** under carbon dioxide atmosphere, which then plays the role of curing agent while the binder **7** and sand **6** are mixed in mixer **13** or **14.**

[0045] Manufacturing the cast piece **3** comprises a step of assembling various mold blocks **1A, 1B** to form the molding cavity **2** (**FIG.1**), and a step of casting the alloy **4,** which has previously been molten, in the molding cavity **2** (**FIG.2**). AlSi7Mg is molten at about 800°C.

[0046] Thermal exchange occurs between the molten alloy **4** and the mold **1:** the alloy **4** cools while giving calories to the mold **1** which absorbs and diffuses those calories.

[0047] Due to its composition, the molding sand **5** forming the mold **1** absorbs and diffuses the calories at a rate greater than that of a conventional molding sand, which gives the alloy **4** a cooling rate greater than the known cooling rates (with equal shape), as shown by **FIG.5** on which there is drawn:

- in solid line, a first curve **C** representing variations of temperature (in °C) of the piece **3** within a mold **1** according to the invention, vs. time (in s);
- in dash-dotted line, a second curve **C'** representing variations of temperature of a piece of identical shape, in a conventional mold.

[0048] Each curve **C, C'** has a global similar shape, and comprises a first section **S1, S1'** (where **S1**, for the first curve **C,** is comprised between 0 and about 70s, whereas **S1',** for the second curve **C',** is comprised between 0 and about 130s).

[0049] The first section **S1, S1'** corresponds to the liquid form of the alloy, in which the variation of temperature is nonlinear.

[0050] Each curve **C, C'** also comprises a second section **S2, S2'** (where **S2,** for the first curve **C,** extends from about 70s, whereas **S2',** for the second curve **C',** extends from about 130s).

[0051] The second section **S2, S2'** corresponds to the solid form of the alloy, in which variation of temperature is globally linear. The temperature (of about 550°C) corresponding to the junction between section **S1** (respectively **S1'**) and the second section **S2** (respectively **S2'**) is the solidification temperature of the alloy (referred to as **TS**).

[0052] As can be seen on **FIG.5:**

- solidification temperature **TS** is reached more quickly on curve **C** (in a ratio of about 2), corresponding to a manufacturing in a mold **1** according to the invention;
- cooling rate of the solidified alloy remains greater on curve **C** (in a ratio of about 2, corresponding to the ratio of the slopes of the linear sections **S2, S2'** of the curves **C, C'**), corresponding to a manufacturing in a mold **1** according to the invention.

[0053] Therefore, the manufacturing time (and hence the production rate) with a mold **1** according to the invention is shorter.

[0054] In addition, the lowered cooling rate gives the piece **3** a crystal structure of better quality, due to thinner crystal grains, as depicted on:

- **FIG.6A,** which shows crystal structure, at micrometric scale, of a AlSi7Mg alloy casted in a mold **1** according to the invention;
- **FIG.6B** which, by comparison, shows crystal structure, at similar scale, of the same alloy casted in a conventional mold of same shape.

[0055] Accordingly, the alloy solidified in the mold **1** according to the invention has a greater hardness, and hence a greater mechanical strength.

[0056] It is therefore possible to design differently the piece **3,** in particular by reducing its weight with equivalent mechanical strength, which is a true benefit in the field of turbojet engines.

[0057] Those benefits are a consequence of the better thermal conductibility of the mold **1** (i.e. of the molding sand **5**) according to the invention, which is made possible through the presence of graphite nanoparticles.

Claims

1. Molding sand (**5**) comprising:

- Quartz sand (**6**);
- A binder (**7**) including sodium or potassium silicate;
- A radical initiator (**8**);

Characterized in that the binder (**7**) includes graphite nanoparticles.

2. Molding sand (**5**) according to claim 1, wherein the size of the graphite nanoparticles is comprised between 500 nm and 800 nm.

3. Molding sand (**5**) according to claim 1 or claim 2, wherein the radical initiator (**8**) is chosen among the following agents: acetic acid, carbonic acid, ester acid, carbon dioxide.

4. Molding sand (**5**) according to any of the preceding claims, wherein the mass proportion of binder (**7**), with respect to quartz sand (**6**), is comprised between 2.5% and 5%.

5. Molding sand (**5**) according to any of the preceding claims, wherein the mass proportion of radical initiator (**8**), with respect of sodium or potassium silicate, is comprised between 10% and 15%.

6. Molding sand (**5**) according to any of the preceding claims, wherein the quartz sand (**6**) is composed of grains of quartz the size of which is comprised between 200 and 300 μm.

7. Method for preparing a molding sand (**5**) according to any of the preceding claims, **characterized in that** it comprises the following steps:

- preparing the binder (**7**) by mixing a colloidal graphite solution (**10**) with water glass (**9**),
- preparing a primary mixture (**13**) including the radical initiator (**8**) and the quartz sand (**6**);
- adding the binder (**7**) to the primary mixture (**13**);
- mixing the resulting mixture.

8. Method according to claim 7, wherein the mass proportion of colloidal graphite (**10**) with respect to glass water (**9**) is comprised between 5% and 20%.

9. Method according to claim 7 or claim 8, wherein the mass proportion of binder (**7**) with respect to quartz sand (**6**) is comprised between 2.5% and 5%.

10. Method according to any of claims 7-9, wherein the colloidal graphite (**10**) is under the form of powder.

11. Method according to any of claims 7-10, wherein the radical initiator (**8**) is chosen among the following agents: acetic acid, carbonic acid, ester acid, carbon dioxide.

12. Method according to any of claims 7-11, wherein the mass proportion of radical initiator (**8**) with respect to binder is comprised between 10% and 15%.

13. Method according to any of claims 7-12, wherein the mixing time of the resulting mixture is about 2 min.

14. Casting mold (**1**), **characterized in that** it is made of a molding sand according to any of claims 1-6.

15. Method of manufacturing a cast piece (**3**) in an aluminum alloy, **characterized in that** it comprises a step of casting the alloy (**4**) within a mold (**1**) according to claim 14.

FIG.1

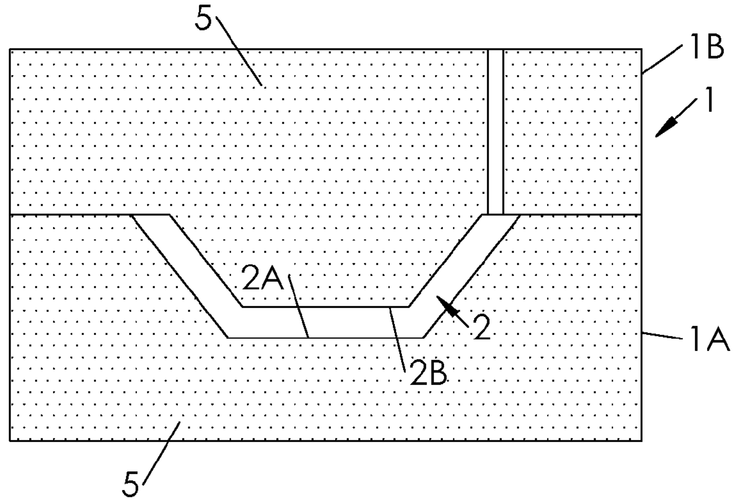


FIG.2

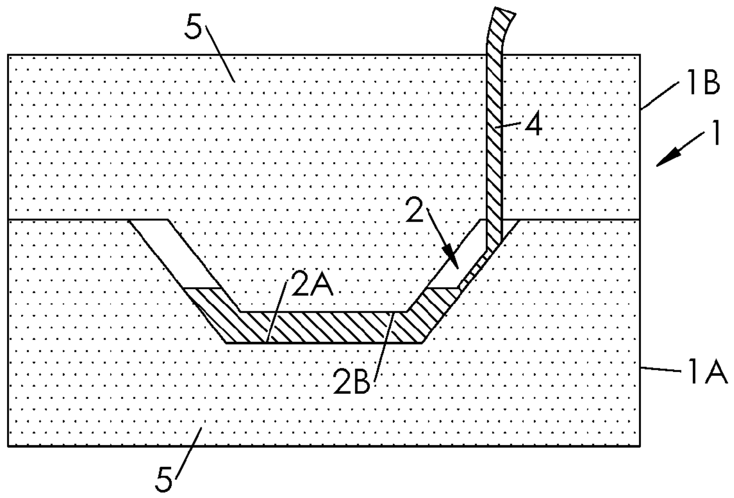
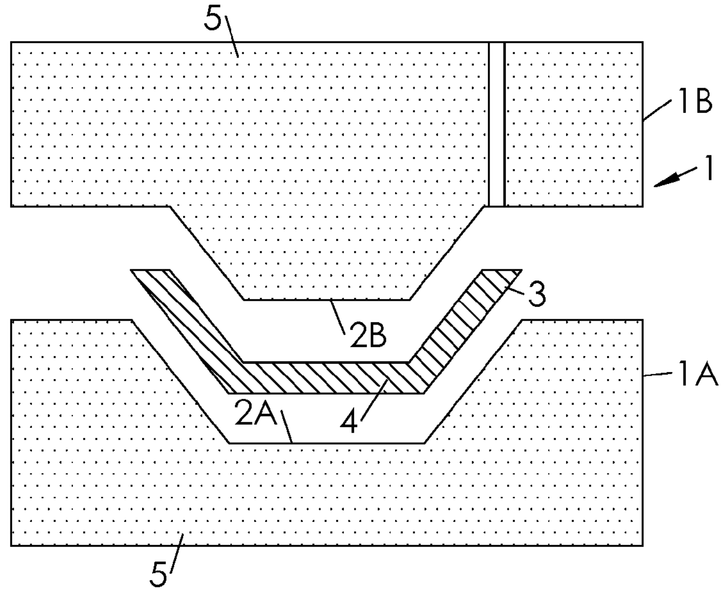


FIG.3



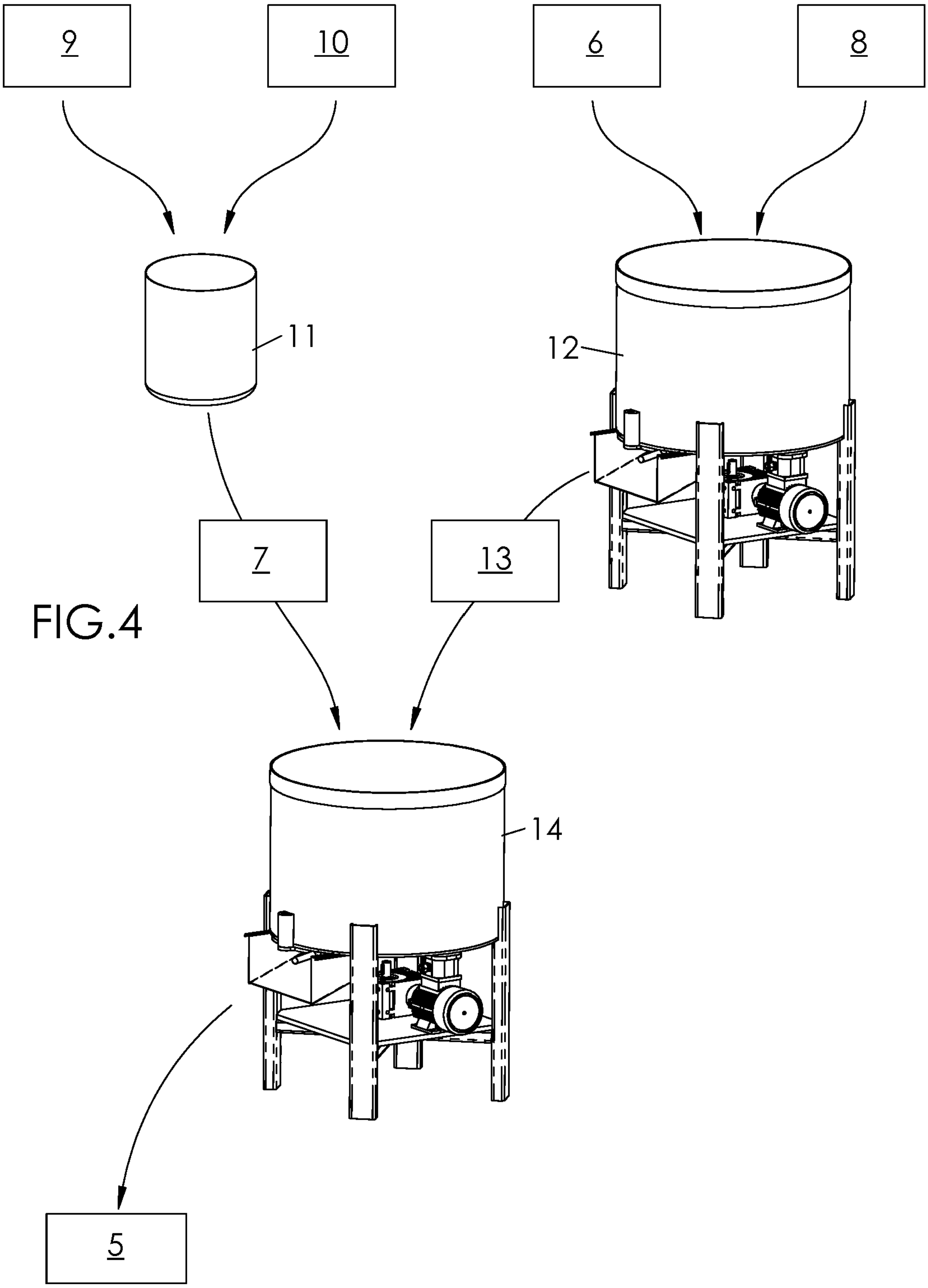


FIG.4

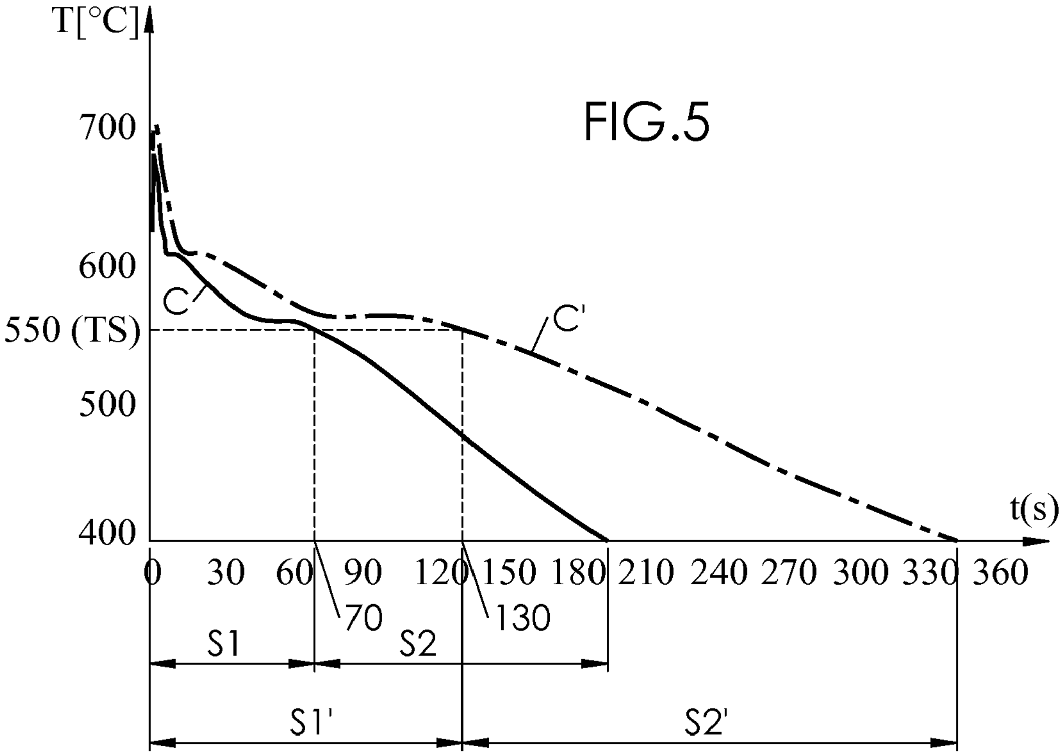


FIG.5

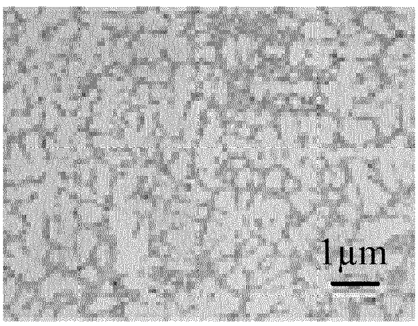


FIG.6A

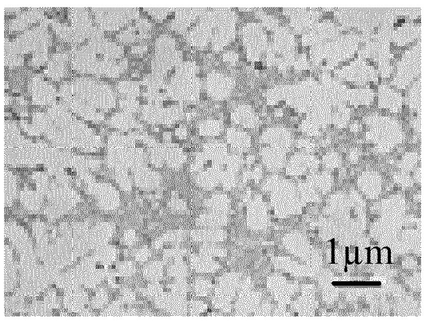


FIG.6B

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 17 30 5219

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	Satoshi Horikoshi ET AL: "Introduction to Nanoparticles" In: "Microwaves in Nanoparticle Synthesis", 24 April 2013 (2013-04-24), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, XP055198443, ISBN: 978-3-52-733197-0 pages 1-24, DOI: 10.1002/9783527648122.ch1, * table 1.1 *	1-15	INV. B22C1/02 B22C9/02 B22D21/00
A	"Nanotechnologies - Vocabulary - Part 2: Nano-objects", ISO TS 80004-2:2015, IEC, 3, RUE DE VAREMBÉ, PO BOX 131, CH-1211 GENEVA 20, SWITZERLAND, 4 January 2015 (2015-01-04), pages 1-10, XP082006389, [retrieved on 2015-01-04] * section 4.4 * * Annex A.1.2-A.1.3 *	1-15	
X	CN 105 414 465 A (HEFEI LINUO NEW MAT TRADE CO LTD) 23 March 2016 (2016-03-23) * abstract * * paragraphs [0002], [0005], [0007], [0008], [0011] * * claims 1,3 *	1-15	TECHNICAL FIELDS SEARCHED (IPC): B22C B22D
X	CN 104 057 017 A (ANHUI XINRUN NEW MATERIALS CO LTD) 24 September 2014 (2014-09-24) * paragraphs [0002] - [0006], [0009], [0010] * * claim 1 *	1-15	

-/--

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	28 July 2017	Grave, Christian

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

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 17 30 5219

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	J. ZYCH ET AL: "Thermal Conductivity of Moulding Sand with Chemical Binders, Attempts of its Increasing", ARCHIVES OF METALLURGY AND MATERIALS, vol. 60, no. 1, 1 January 2015 (2015-01-01), XP055393704, Poland ISSN: 1733-3490, DOI: 10.1515/amm-2015-0058 * sections 1, 2.1, 2.3.2 * * figure 5 * -----	1-14	

TECHNICAL FIELDS SEARCHED (IPC)

1

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	28 July 2017	Grave, Christian

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

EPO FORM 1503 03.82 (P04C01)

page 2 of 2

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 17 30 5219

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 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-07-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 105414465 A	23-03-2016	NONE	
CN 104057017 A	24-09-2014	NONE	

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2012175883 A **[0004]**
- FR 2138358 **[0009] [0011]**