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

(11) EP 2 749 658 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
02.07.2014 Bulletin 2014/27

(21) Application number: **12382541.6**

(22) Date of filing: **27.12.2012**

(51) Int Cl.:
C21D 5/00 *(2006.01)*
C21D 1/20 *(2006.01)*
C22C 37/04 *(2006.01)*
C21D 1/68 *(2006.01)*
C21D 1/70 *(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

(71) Applicants:
- **Veigalan Estudio 2010 S.L.U.**
  48200 Durango (Vizcaya) (ES)
- **Thermal Quality Control Technologies S.L.U.**
  48200 Durango (Vizcaya) (ES)
- **Casa Maristas Azterlan**
  48200 Durango, Vizcaya (ES)

(72) Inventors:
- **Suarez Creo, Ramón**
  48200 Durango (Vizcaya) (ES)
- **Garay Abascal, Jon**
  48200 Durango (Vizcaya) (ES)
- **de la Torre Ugarte, Urko**
  48200 Durango (Vizcaya) (ES)

(74) Representative: **Stiebe, Lars Magnus et al**
Balder IP Law, S.L.
Paseo de la Castellana 120
28046 Madrid (ES)

(54) Method for as-cast production of ausferritic ductile iron

(57) The present invention discloses a method for the manufacturing of ausferritic ductile iron alloy which comprises the following steps: (i) casting a melt of a ductile iron alloy in a mould; (ii) solidification of the casting in the mould and subsequent cooling until the casting temperature is between 800ºC and 950ºC; (iii) shaking out the casting at said temperature between 800ºC and 950ºC; (iv) cooling the casting until the temperature of the casting reaches a value between 275ºC to 450ºC with a high enough cooling rate in order to avoid the pearlitic nose; (v) introducing the casting in an insulating material and leaving the casting inside for a period of time until a completely ausferritic microstructure is obtained. The invention also discloses the ausferritic ductile iron alloy produced by the present method.

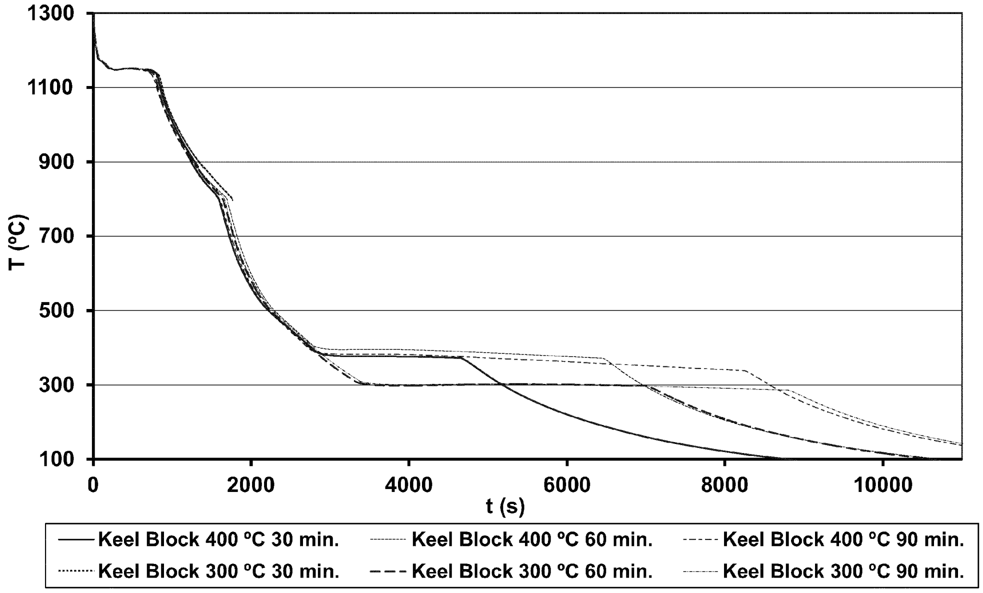

FIG. 1

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention is encompassed within the sector of metallurgical industry. Particularly, it relates to a new method for the manufacturing of ductile iron with a completely ausferritic matrix which has proved to be a more economical, simple and faster alternative method to the methods currently used.

BACKGROUND OF THE INVENTION

[0002] Ausferritic ductile iron is a high strength, wear resistance, fatigue and rolling contact resistant material with good toughness that finds a wide variety of applications.

[0003] For the manufacturing of ausferritic ductile iron with high quality basically the most common and easiest to reproduce method consists in an austempering process. The ausferritic ductile iron obtained accordingly is usually referred to as austempered ductile iron (ADI). The austempering process is a three-step heat treatment which comprises the austenitization of the casting at a temperature higher than 850ºC until the matrix structure attains a reasonably uniform carbon content; quenching to an intermediate temperature range of 260 to 400ºC and austempering, which consists in the transformation to austenitic-ferritic structure at the isothermal temperature. This process is characterized mainly by its remarkable inherent cost, representing a large percentage of the total cost of cast parts.

[0004] Other methods without austenitization for the manufacturing of ausferritic ductile iron have been developed in the state of the art. The method disclosed in Int.J.Cast Metals Res., 1999, 11, 483-488, for example, is based on controlled cooling in a salt bath furnace. The method comprises pouring the melt into a permanent mould, hot knocking-out the casting of the permanent mould at a temperature above 870ºC, and quenching the casting to an austempering temperature using a salt bath furnace. This method has been developed under laboratory conditions; and it is costly and highly complicated to be implemented in the foundry industry because most of the foundries do not have the possibility to introduce an expensive salt bath furnace in the facility, in order to manufacture ausferritic ductile iron cast parts by means of this method. Another known method for manufacturing ausferritic ductile iron without austenitization is disclosed in Ali Reza Kiani-Rashid et al., International Foundry Research 63 (2011) No. 1. The method applies a special heat treatment of the casting in the mold during solidification to obtain the desired ausferritic matrix. First ductile iron is cast in a metallic mold, after casting the specimens are rapidly transferred to an electrical furnace at an austempering temperature of 350ºC and held there for one hour, and finally air cooled to room temperature. This method presents some disadvantages, such as the need of an electrical furnace which use implies additional energy consumption and costs.

[0005] In view of the above there is the need in the state of the art to provide an alternative method for obtaining ausferritic ductile iron alloy with high quality which overcomes at least part of the disadvantages above mentioned.

DESCRIPTION OF THE DRAWINGS

[0006]

Figure 1: The registered cooling curves of the keel blocks Y2 of Example 1 are shown.
Figure 2: The microstructure of the samples of Example 1 are shown

DESCRIPTION OF THE INVENTION

[0007] In a first aspect the present invention relates to a method for the manufacturing of an ausferritic ductile iron alloy of high quality, at much lower production costs than the conventional methods of the state of the art without the necessity to use costly heat treatments and salt bath or electrical furnaces. Therefore, a significant reduction of energy, costs and production time is advantageously obtained.

[0008] In the context of the present invention an ausferritic ductile iron alloy of high quality means that it presents mechanical properties equal to those obtained for ADI by means of conventional treatment methods according to norm UNE-N 1564:2011 (see Example). Said ausferritic ductile iron alloy presents a completely ausferritic microstructure.

[0009] The method of the invention yields an ausferritic ductile iron alloy of high quality which contains the following typical alloying constituents for ductile iron: carbon, silicon and magnesium, and optionally one or more of the following elements: copper, nickel, manganese, molybdenum, the balance being iron and incidental impurities such as phosphorous, sulfur, etc. In a particular embodiment the method of the invention yields an ausferritic ductile iron alloy that contains the following constituents: carbon, silicon, magnesium, copper, nickel, manganese and molybdenum the balance being iron and incidental impurities such as phosphorous, sulfur, etc.

[0010] In another particular embodiment the method of the invention yields an ausferritic ductile iron alloy that presents the following chemical composition (percentages expressed by weight with respect to the total weight of the ausferritic ductile iron alloy):

C	3.20-3.90%
Si	1.90-4.00%
Mn	≤1.2%;
P	≤0.035%;
S	≤0.015%;
Cu	≤1.10%
Mg	0.020-0.060%
Ni	0.5-4.00%
Mo	≤0.90%

the rest of the chemical composition being Fe and other residual elements.

[0011] The method of the invention comprises the following steps:

(i) casting a melt of a ductile iron alloy in a mould;
(ii) the solidification of the casting and subsequent cooling in the mould until the casting temperature is between 800ºC and 950ºC;
(iii) shaking out the casting at said temperature between 800ºC and 950ºC;
(iv) cooling the casting until the temperature of the casting reaches a value between 275ºC to 450ºC with a high enough cooling rate in order to avoid the pearlitic nose; and
(v) introducing the casting in an insulating material and leaving the casting inside for a period of time until an ausferritic ductile iron alloy is obtained.

[0012] The melt of the ductile iron alloy to be poured in the mould is prepared from conventional raw materials such as pig iron, steel, soft iron, graphite, ferroalloys, among others. The raw materials are put in contact according to conventional methods which include steps such as mixing of components, melting, adjusting the alloy composition by adding further components, treatment with known magnesium containing compounds, and inoculation with known inoculating materials. The melt thus required to prepare the ausferritic ductile iron alloy of any one of the above mentioned compositions can be easily prepared by the skilled person in the art. The mould can be a metallic mould or a sand mould. Casting of the melt is done in any conventional manner. The solidification of the casting and subsequent cooling in the mould until the casting temperature is between 800ºC and 950ºC is also carried out in a conventional manner. Shaking out the casting at said temperature between 800ºC and 950ºC is also carried out by means known in the art.

[0013] Step (iv) of cooling the casting until the temperature of the casting reaches a value between 275ºC to 450ºC can be carried out by air cooling, forced air cooling, quenching into any adequate quench medium such as oil, water, or mixtures of water and at least one polymer. The way of cooling and the cooling means are conventional and are employed at room temperature.

[0014] During this step of cooling the casting, it is important to avoid the pearlitic nose. In this sense a certain cooling rate which is higher than a determined value is needed. This value can be readily determined by the skilled person in the art. Said value depends for example on the composition of the alloy. Thus, it is well known that alloying elements like nickel or molybdenum displace the pearlitic nose to longer times, so that lower cooling rates are needed to avoid this nose. It is also well known that depending on the geometry and size of the casting more or less severe cooling means are needed, to achieve the above mentioned needed cooling rate. For thin or small castings, air cooling is in general enough, to achieve the required cooling rate, while for bigger parts, forced air or quenching is usually preferred.

[0015] The step (v) of introducing the casting in an insulating material and leaving the casting inside it, is carried out until a completely ausferritic microstructure is obtained.

[0016] In the context of the present invention introducing the casting in an insulating material means that the casting is completely surrounded or covered by the insulating material.

[0017] Insulating materials useful in the present invention are any material or combination of materials which retard the heat flow and have a low thermal conductivity. In principle any insulating material within which the casting temperature does not decrease below the martensite start formation temperature before the austenite transforms completely into ferrite needles and carbon enriched austenite, can be used. According to a particular embodiment the insulating material presents a conductivity of equal or less than 1 W/mK, preferably equal or less than 0.5 W/mK, and more preferably equal or less than 0.08 W/mK.

[0018] Said materials may be in the solid or the liquid state. They can also be of different compositions (i.e. glass, ceramic, plastic) and different internal structure (i.e. cellular, fibrous). Non limiting illustrative examples of insulating materials are: silica, rock wool, slag wool, glass fibers, foamed plastics such as polystyrene, polyurethane, polyisocyanurate, agricultural waste products such as rice husks; calcium silicate, expanded vermiculite, hereinafter also referred to as vermiculite, expanded perlite, hereinafter also referred to as perlite, cellulose and diatomaceous earth.

[0019] In addition, insulation materials can be used in the present method in a variety of suitable forms. Non limiting illustrative examples are rigid or flexible boards, blocks, bricks, sheets, blankets, foams, loose fills, such as granulates, pellets or particles, and pre-formed shapes

[0020] Step (v) can be carried out in many different ways depending for instance on the size of the castings and the selected insulating material. In a particular embodiment a container comprising the insulating material is used, in which case the casting is introduced therein and is completely surrounded or covered by the insulating material. According to another particular embodiment a container comprising insulating material in form of a loose fill (particles, pellet, granulates, etc.,) is used; the casting is introduced therein, and is completely surrounded or covered by the loose fill of insulating material.

[0021] During this step (v) the following reaction takes place: the austenite decomposes to ferrite needles and carbon enriched austenite. This reaction thus must take place at a temperature above the martensite formation start temperature (M_s) to avoid formation of martensite in the casting. Because of this reason, and in order to obtain a completely ausferritic microstructure the insulating material maintains the temperature of the casting above (M_s).

[0022] According to a particular embodiment the insulating material is in the form of a loose fill. Loose fill can be particles, pellets, granulates, which may have different sizes and shapes.

[0023] In a particular embodiment expanded perlite, which has a thermal conductivity of less than 0.059 W/mK, is used as insulating material. In another particular embodiment expanded vermiculite is used.

[0024] The period of time during which the casting is leaved inside the insulating material can vary depending on factors such as the casting size. Castings are however to be left inside, at least until the austenite transforms completely into ferrite needles and carbon enriched austenite, which is stable at room temperature, that is until a completely ausferritic microstructure is achieved. In general said period is typically comprised between 30 and 120 minutes although greater and lesser durations are also foreseeable depending on each particular case. Said period can be easily determined in each case by the skilled person in the art.

[0025] The method of the invention comprises further, the steps of taking the casting out of the insulating material after step (v) is concluded and cooling it to room temperature, for instance on the air.

[0026] The method of the invention yields ausferritic ductile iron alloys. In particular the alloys are obtained as components or castings which have may different applications such as for instance, as automotive or railroad components or components for the construction, mining and agricultural industries. The method presents the advantage that the manufacturing of ausferritic ductile iron alloys does not require the application of either subsequent conventional heat treatments after casting, nor controlled cooling and austempering in either a salt bath furnace nor in an electric furnace.

[0027] In another aspect the invention refers to ausferritic ductile iron alloys produced by the method of the invention.

[0028] In this text, the term "comprises" and its derivations (such as "comprising", etc.) should not be understood in an excluding sense, that is, these terms should not be interpreted as excluding the possibility that what is described and defined may include further elements, steps, etc.

[0029] The following examples are non-limiting and are merely representative of the invention.

EXAMPLES

Example 1: method of the invention of preparing ausferritic ductile iron alloy

[0030] In a middle frequency induction furnace, with a capacity of 100 kg, the following components in the following amounts (percentages by weight) were introduced:

> 50 kg of soft iron of the following composition (0.002 % C; 0.005 % Si; 0.17 % Mn, 0.013 % P and 0.011 % S the rest being Fe);
>
> 2.0 kg of graphite (minimum with 99% by weight of C);
>
> 1.00 kg of FeSi75% (74.6 % Si; 0.83 % Al and 0.12 % C the rest being Fe),
>
> 0.025 kg of FeMo (69.41 % Mo; 0.23 % Si; 0.02 % C; 0.03 % S; 0.038 % P the rest being Fe) and
>
> 1.6 kg of nickel (minimum with 99% by weight of Ni).

[0031] To adjust the chemical composition to the one desired, the following further components were added:

0.65 kg of graphite (minimum with 99% by weight of C);

0.325 kg of FeSi75%, (as above)

0.10 kg Ni (minimum with 99% by weight of Ni);

0.085 kg Cu (minimum 99% by weight of Cu),

0.05 kg of FeMo (as above) and

0.05 kg of FeMn (75.16% Mn; 5.16 % N; 1.38 % C; 0.57 % Si; 0.13 % P; 0.009 %S the rest being Fe).

[0032] The extraction of the melt from the furnace to the ladle was made at a temperature of 1525°C. The magnesium treatment was carried out following the sandwich methodology adding 1.2% (by weight with respect to the total weight of the ductile iron alloy) of a FeSiMg alloy (Si = 45.39%, Mg = 6.48%, Ca = 1.07%, Al = 0.67%, Rare Earth elements = 0.91%, the rest being Fe). The inoculation was made in mould using 0.2% (by weight with respect to the total weight of the ductile iron alloy) of a FeSi alloy (Si = 69.9%, Ca = 1.38%, Bi = 0.49%, Al = 0.93%, Zr = 0.19%, Ce = 0.24, La = 0.13%, the rest being Fe) with a grain size of 0.2-0.5 mm.

[0033] The castings were keel Blocks Y2 following the standard norm UNE-EN 1563:1998.

[0034] A thermocouple (type k) was inserted in the centre of the samples or keel Blocks Y2 in order to obtain the cooling curves (figure 1). The moulds were made of chemical bonded sand. Once the solidification was carried out, the castings were early shaken out of the mould at the temperature of 800ºC. In total six keel blocks Y2 were poured.

[0035] Three of these were air cooled until their temperature reached 400ºC, and then they were each introduced in an insulating material. In this particular case the keel blocks Y2 were introduced into a metallic container (110 mm x 80 mm x 80 mm) comprising perlite in an amount enough to completely cover the keel blocks therein introduced. Perlite has thermal conductivity between 0.04-0.06 W/mK. Perlite had the following characteristics: mesh size of below 5 mm and density between 40-120 kg/m^3. The keel blocks Y2 were easily introduced in the container, and were easily completely covered with expanded perlite only due to their own weight.

[0036] Each keel block Y2 remained in the container for 30, 60 and 90 minutes respectively.

[0037] As above stated is necessary to maintain the keel blocks Y2 in the insulating material long enough until the austenite transforms completely into ferrite needles and carbon enriched austenite which is completely stable at room temperature, that is, until a completely ausferritic microstructure is obtained. Afterwards, the keel blocks Y2 were taken out of the insulating material and simply air cooled until room temperature.

[0038] The other three keel blocks Y2 were air cooled until their temperature reached 300ºC and were then each introduced into the same insulating material, also for 30, 60 and 90 minutes respectively. As it can be seen in Fig. 1, the cooling curve corresponding to the keel Block 300ºC and 30ºC could not be completely registered since the corresponding thermocouple broke when the keel block was shaken out. Afterwards, the keel blocks Y2 were taken out of the insulating material and simply air cooled until room temperature.

[0039] The ausferritic ductile iron alloy obtained this way had the following chemical composition (percentages expressed by weight with respect to the total weight of the alloy): C = 3.48%; Si = 2.04%; Mn = 0.19%; P = 0.018%; S = 0.0013%; Cu = 0.16%; Mg = 0.049%; Ni = 2.83%; Mo = 0.21% the rest of the composition being Fe and the usual residual elements.

[0040] The mechanical properties of the resulting keel blocks Y2 were determined and the results are shown in the following Table. The tests were carried out following these standards:
Tensile tests: UNE-EN 1563:2012 - UNE-EN ISO 6892-1:2010 B which render the tensile strength (T.S.), yield strength (Y.S) and Elongation (E);
Brinell Hardness (HB) tests: UNE-EN ISO 6506-1:2006; and
Charpy impact tests (unnotched room temperature) (J): UNE-EN ISO 148-1: 2011.

	T.S. (MPa)	Y.S. (MPa)	E (%)	Impact Resistance room temperature unnotched (J)				Brinell Hardness (HB)
				Unitary values			Average	
Keel Block Perlite 400 ºC 30 min.	894	503	8,8	68	58	63	63	277
Keel Block Perlite 400 ºC 60 min.	862	552	13,3	103	102	103	102,67	268

(continued)

	T.S. (MPa)	Y.S. (MPa)	E (%)	Impact Resistance room temperature unnotched (J)				Brinell Hardness (HB)
				Unitary values			Average	
Keel Block Perlite 400 ºC 90 min.	864	620	16,9	104	107	104	105	274
Keel Block Perlite 300 ºC 30 min.	987	580	8,4	52	61	73	62	302
Keel Block Perlite 300 ºC 60 min.	1036	626	9,7	88	70	93	83,67	311
Keel Block Perlite 300 ºC 90 min.	1001	665	8,1	68	75	90	77,67	315

[0041] The microstructure of the samples is shown in Figure 1. These micrographies have been taken using an optical microscope (LEICA MEF 4) at 500 and 1000 magnifications. It can be seen, that completely ausferritic microstructures were achieved. Completely ausferritic in the context of the present invention means 85% or more by volume of ausferrite, preferably 90% or more, more preferably 95% or more, and even more preferably 99% or more, the rest being pearlite and/or martensite.

[0042] The micrographies show that the shape of the ferrite needles changes depending on the temperature at which the samples are introduced and then held in the insulating material. It has been observed that the mechanical properties vary as follows: for higher remaining temperatures (400ºC), the tensile strength decreases while the elongation and the impact resistance at room temperature for an unnotched specimen increase.

Claims

1. A method for the manufacturing of ausferritic ductile iron alloy containing carbon, silicon and magnesium, and optionally one or more of the following elements: copper, nickel, manganese, molybdenum; with the balance being iron and incidental impurities:

which comprises the following steps:

(i) casting a melt of a ductile iron alloy in a mould;
(ii) solidification of the casting in the mould and subsequent cooling until the casting temperature is between 800ºC and 950ºC;
(iii) shaking out the casting at said temperature between 800ºC and 950ºC;
(iv) cooling the casting until the temperature of the casting reaches a value between 275ºC to 450ºC with a high enough cooling rate in order to avoid the pearlitic nose; and
(v) introducing the casting in an insulating material and leaving the casting inside for a period of time until a completely ausferritic microstructure is obtained.

2. A method according to claim 1 wherein the ausferritic ductile iron alloy presents carbon, silicon, magnesium, copper, nickel, manganese and molybdenum, with the balance being iron and incidental impurities.

3. A method according to claim 1 or 2, wherein the ausferritic ductile iron alloy presents the following composition (percentages expressed by weight with respect to the total weight of the ausferritic ductile iron alloy):

C 3.20-3.90%
Si 1.90-4.00%
Mn ≤1.2%;
P ≤0.035%;
S ≤0.015%;
Cu ≤1.10%
Mg 0.020-0.060%

Ni 0.5-4.00%
Mo ≤0.90%

the rest of the chemical composition being Fe and other residual elements.

4. The method according to any one of claims 1 to 3, further comprising the steps of taking the casting out of the insulating material and cooling it to room temperature.

5. A method according to any one of claims 1 to 4, wherein the mould is a metallic mould or a sand mould.

6. A method according to any one of claims 1 to 5, wherein cooling in step (iv) is carried out by air cooling, forced air cooling, quenching in oil, water, or a mixture of water and at least one polymer.

7. A method according to any one of claims 1 to 6, wherein the insulating material has a thermal conductivity equal or less than 1 W/mK.

8. A method according to claim 7, wherein said insulating material is selected from the group consisting of : silica, rock wool, slag wool, glass fibers, foamed plastics, agricultural waste products; calcium silicate, expanded vermiculite, expanded perlite, cellulose and diatomaceous earth.

9. A method according to claim 8, wherein said insulating material is in one of the following forms: boards, blocks, bricks, sheets, blankets, foams, loose fills, and pre-formed shapes

10. A method according to claim 8 or 9, wherein said insulating material is expanded perlite.

11. A method according to claim 10, wherein expanded perlite is in form of particles of mesh size below 5 mm and has a density between 40-120 kg/m^3.

12. A method according to any one of claims 1 to 11, wherein the casting is maintained in step (v) in the insulating material during a period of time comprised between 30 and 120 minutes.

13. An ausferritic ductile iron alloy produced by the method of any one of the preceding claims.

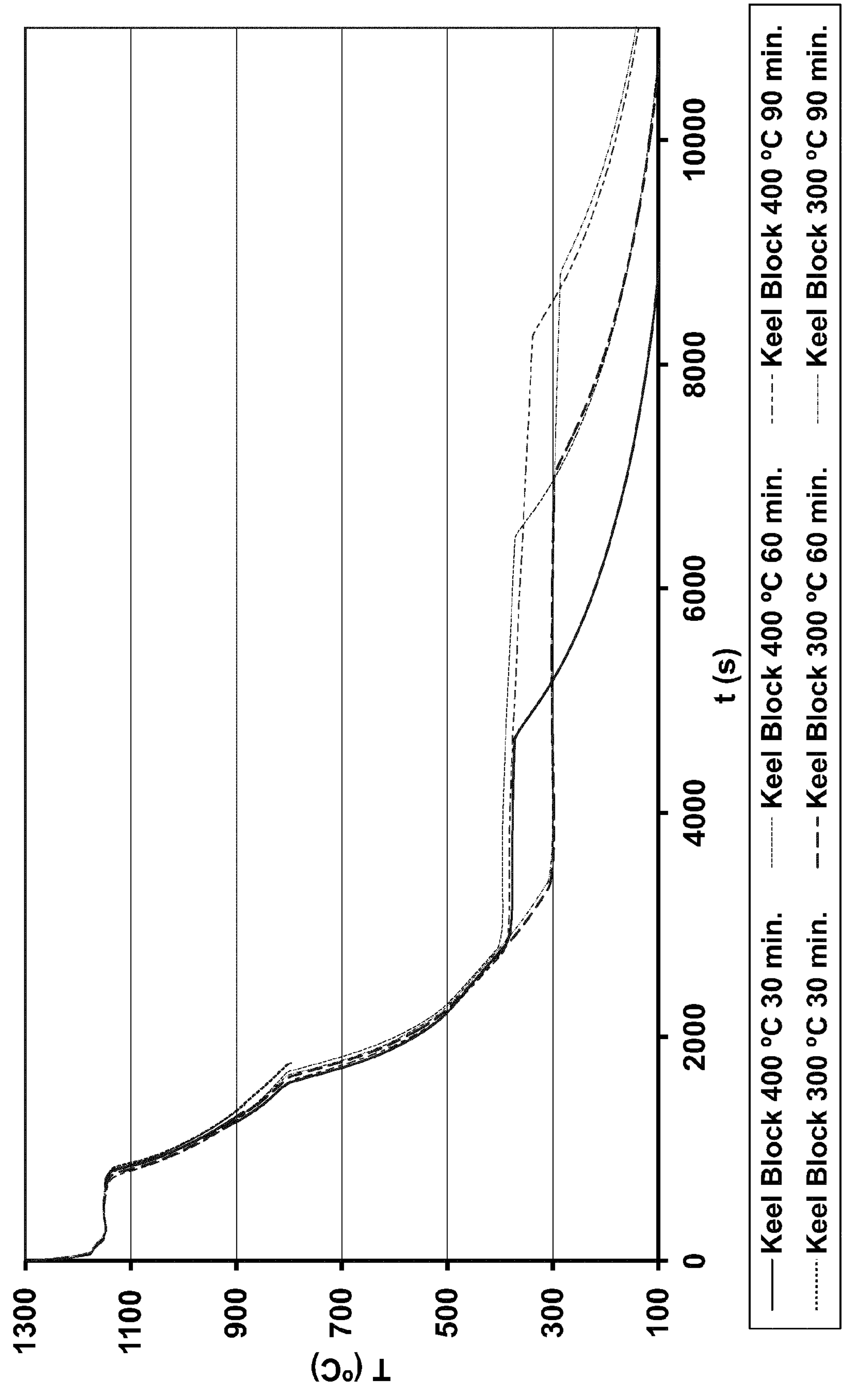
T (oC)
1300
1100
900
700
500
300
100
t (s)
0
2000
4000
6000
8000
10000
Keel Block 400 °C 30 min.
Keel Block 400 °C 60 min.
Keel Block 400 °C 90 min.
Keel Block 300 °C 30 min.
Keel Block 300 °C 60 min.
Keel Block 300 °C 90 min.

FIG. 1

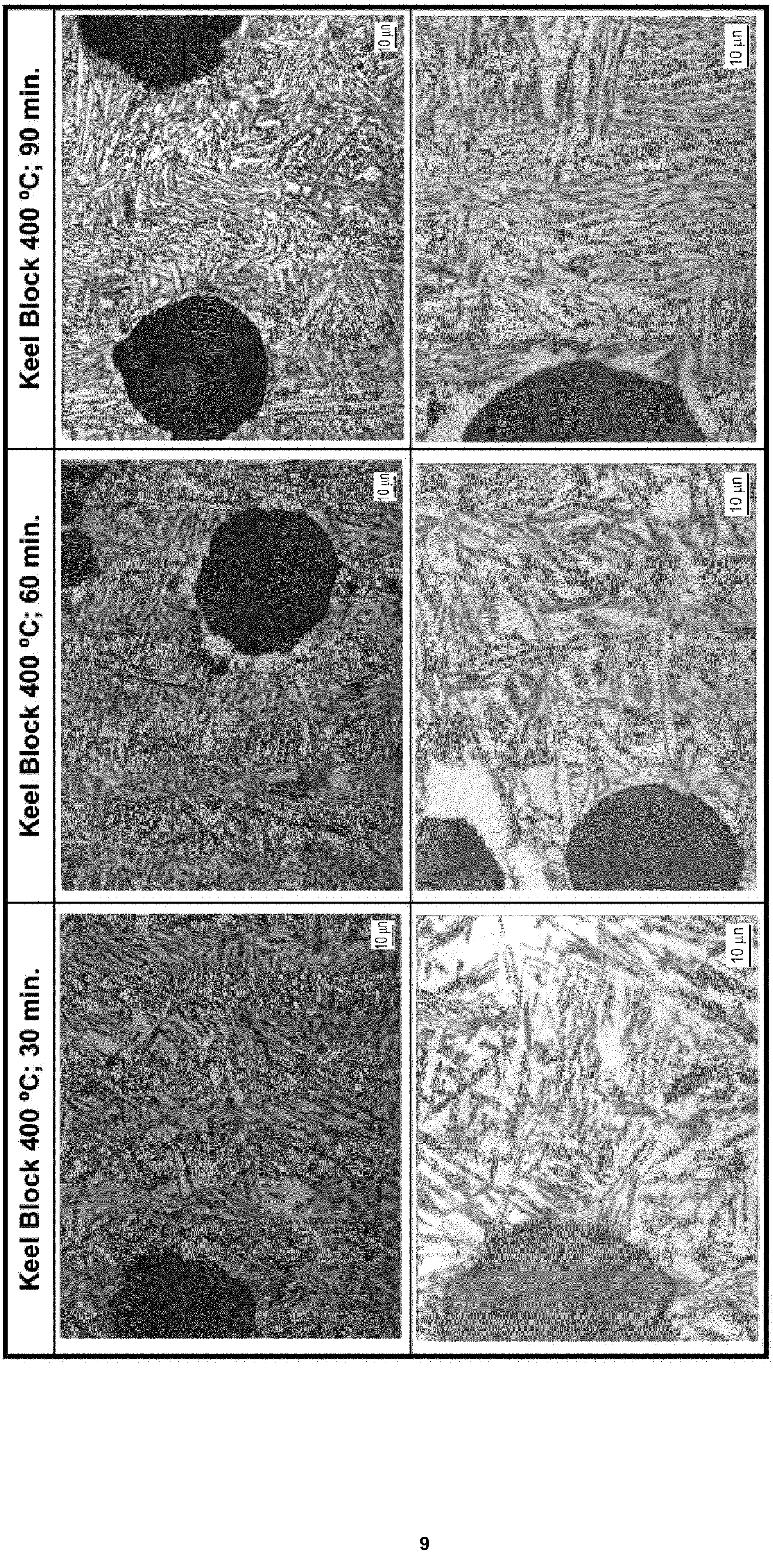
Keel Block 400 °C; 30 min.
Keel Block 400 °C; 60 min.
Keel Block 400 °C; 90 min.
10 µm
10 µm
10 µm
10 µm
10 µm
10 µm

FIG. 2

Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 12 38 2541

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	US 5 139 579 A (KOVACS BELA V [US] ET AL) 18 August 1992 (1992-08-18) * claims 3,5; figure 1 * -----	1-13	INV. C21D5/00 C21D1/20 C22C37/04 C21D1/68 C21D1/70
X	JANOWAK J F ET AL: "APPROACHING AUSTEMPERED DUCTILE IRON PROPERTIES BY CONTROLLED COOLING IN THE FOUNDRY", INTERNATIONAL CONFERENCE ON AUSTEMPERED DUCTILE IRON, XX, XX, 2 April 1984 (1984-04-02), pages 63-69, XP001182603, * page 66 - page 68; figures 7-12 * -----	1-13	
A	"Austempered ductile-iron castings - advantages, production, properties and specifications", MATERIALS AND DESIGN, LONDON, GB, vol. 13, no. 5, 1 January 1992 (1992-01-01), pages 285-297, XP024153210, ISSN: 0261-3069, DOI: 10.1016/0261-3069(92)90191-J [retrieved on 1992-01-01] * page 287, right-hand column; figures 1-8 * * page 291 * -----	1-13	TECHNICAL FIELDS SEARCHED (IPC) C21D C22C
A	US 4 504 527 A (HARA SADAO [JP] ET AL) 12 March 1985 (1985-03-12) * the whole document * -----	1-13	
A	US 5 753 055 A (LIU XIAOJUN [US]) 19 May 1998 (1998-05-19) -----	1-13	
A	US 2004/071584 A1 (MOLINARI ALBERTO [IT] ET AL) 15 April 2004 (2004-04-15) -----	1-13	
A	US 5 878 897 A (LAZZARO FRANK [US] ET AL) 9 March 1999 (1999-03-09) -----	1-13	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	29 May 2013	Catana, Cosmin

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

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 38 2541

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.

29-05-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5139579 A	18-08-1992	NONE	
US 4504527 A	12-03-1985	DE 3206297 A1	18-11-1982
		FR 2500335 A1	27-08-1982
		JP S6121287 B2	26-05-1986
		JP S57140814 A	31-08-1982
		US 4504527 A	12-03-1985
US 5753055 A	19-05-1998	CA 2218788 A1	05-05-1998
		US 5753055 A	19-05-1998
US 2004071584 A1	15-04-2004	AT 327351 T	15-06-2006
		DE 60305389 T2	03-05-2007
		EP 1384794 A1	28-01-2004
		ES 2264507 T3	01-01-2007
		IT MI20021670 A1	26-01-2004
		PT 1384794 E	31-10-2006
		US 2004071584 A1	15-04-2004
US 5878897 A	09-03-1999	AU 729310 B2	01-02-2001
		AU 1912597 A	12-03-1998
		CA 2194254 A1	05-03-1998
		US 5878897 A	09-03-1999
		ZA 9701611 A	03-08-1998

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

Non-patent literature cited in the description

- *Int.J.Cast Metals Res.,* 1999, vol. 11, 483-488 **[0004]**
- **ALI REZA KIANI-RASHID et al.** *International Foundry Research,* 2011, vol. 63 (1 **[0004]**