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Czekaj et al.(10) **Pub. No.: US 2014/0190653 A1**(43) **Pub. Date: Jul. 10, 2014**(54) **METHOD FOR PRODUCING INVESTMENT
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Krakow (PL)(21) Appl. No.: **14/237,360**(22) PCT Filed: **Aug. 10, 2012**(86) PCT No.: **PCT/PL2012/000068**§ 371 (c)(1),
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B22D 27/04 (2006.01)(52) **U.S. Cl.**CPC **B22D 27/04** (2013.01)USPC **164/121**(57) **ABSTRACT**

A method for producing investment castings, preferably in ceramic moulds, from alloys based on Al, Mg, Cu, Zn and Fe, characterised in that the ceramic mould is baked at temperatures of 800-1000° C. for 2-4 hours, then the mould is cooled to a temperature of 20-950° C. and is held at this temperature for 10-40 minutes, then it is poured with liquid alloy overheated by from 50 to 200° C. above the initial melting point and after a lapse of 10-100 seconds, the mould is immersed at a fixed or variable speed in a liquid cooling medium, which is a 1-99 volume percent aqueous solution of liquid polymer at a temperature of 15-85° C.

The liquid polymer is a polymer of the PAG or PVP, or ACR, or PEO type. The ceramic moulds made of aluminosilicate, or high alumina refractory materials, especially based on synthetic sand, for example Molochite, are used.

METHOD FOR PRODUCING INVESTMENT CASTINGS

[0001] This invention relates to a method for producing investment castings, preferably in ceramic moulds, from alloys based on aluminium, magnesium, copper, zinc and iron.

[0002] After pouring the ceramic mould cavity with liquid alloy, a rapid, bulk or directional, cooling of this alloy is required to get a compact casting without porosity, characterised by relatively homogeneous and fine-grain structure and, consequently, by high mechanical properties.

[0003] The ceramic moulds used in investment casting are characterised by low thermal conductivity and therefore the time of the liquid metal solidification is relatively long. As a result of the slow solidification, a coarse-grain structure is formed, which is the cause of reduced mechanical properties of the casting.

[0004] To obtain the required compact structure in castings, a directional solidification of the metal should be provided. For example, a method to produce investment castings according to patent specification DE-OS 3629079 consists in this that it uses ceramic moulds with "pockets" made in the selected parts of mould. Before pouring of mould with liquid metal, these pockets are filled with steel shot. Because of the heat capacity of the steel shot considerably higher than the heat capacity of the aluminium alloy, an intense heat transfer from the liquid metal is thereby provided, which allows making castings with the areas of directional solidification. In patent specification EP571703, as a cooling medium for the ceramic mould poured with liquid alloy a fluid coolant is used, preferably in liquid state, at varying degrees of overheating, wherein the boiling point is lower than the temperature of the metal poured. The liquid coolant should have an appropriate viscosity, and it is a mixture of substances characterised by different boiling points. As an example, a composition comprising wax, glycol, ester and/or oil is given. Due to the flammability of the components of the coolant, the process is carried out in a closed container under inert gas atmosphere. According to patent specification U.S. Pat. No. 6,622,774, ceramic moulds poured with aluminium alloy are cooled in an oil bath, which has a high flash point and low viscosity. On the other hand, in patent specification US 2008/0011442, the ceramic foundry mould filled with liquid metal is kept at a pressure of at least 20 MPa for the time of about 300 seconds, and then it is introduced into a liquid coolant at a temperature of -100°C ., or lower. It is advantageous to subject the solidifying metal to the effect of ultrasounds, or to another alternative treatment.

[0005] A method for producing investment castings according to the invention, preferably in ceramic moulds, from alloys based on Al, Mg, Cu, Zn and Fe characterised in that the ceramic mould is baked at a temperature of $800-1000^{\circ}\text{C}$. for 2-4 hours, is cooled next to a temperature in the range of $20-950^{\circ}\text{C}$., and is held at this temperature for 10-40 minutes, and after a lapse of this time, the said mould is poured with liquid alloy overheated by 50 to 200°C . above the initial melting point, and after a lapse of 10-100 seconds, it is immersed at a fixed or variable speed in a liquid cooling medium, the said liquid cooling medium being a 1-99 volume percent aqueous solution of liquid polymer at a temperature in the range of $15-85^{\circ}\text{C}$.

[0006] Preferably, the liquid polymer is a polymer of the PAG, or PVP, or ACR, or PEO type. Preferably, the ceramic

moulds made from the aluminosilicate or high alumina refractories, especially based on synthetic sand, for example Molochite, are used.

[0007] Liquid polymers are solutions, suspensions or alloys of polymers, which belong to a particular group of liquids characterised by a measurable shape stability, reveal some characteristics of a solid body, and are characterised by a measurable elasticity. They represent polymolecular carbon and hydrogen compounds, containing also oxygen, nitrogen, phosphorus and sulphur, as well as modifiers, inhibitors and other additives. Liquid polymers exhibit non-Newtonian fluid properties at high shear rates, which means that their flow curves are not straight lines.

[0008] The applied cooling medium has nearly 2-times higher specific heat than the quenching oils, owing to which the temperature increase of the medium will be for a given batch weight reduced by approximately one half.

[0009] The aqueous solution of liquid polymers penetrating through the ceramic mould walls forms in contact with molten metal a thin separating polymer coating, which enables making castings with excellent surface quality. Applying the method according to the invention, the outer surfaces of castings are not contaminated with oil or wax, and therefore they do not require degreasing or other cleaning processes. The residues of the cooling medium that can remain on castings when the said medium occurs in high concentrations in the cooling bath are not carbonised, but fully decompose at high temperatures to form water vapour and carbon oxides. The cooling rate depends on the type of the polymer, on its concentration, and on the temperature of the aqueous solution. The applied cooling medium is non-flammable and environmentally friendly. Due to these characteristics, for the implementation of the method according to the present invention, no sealed space is required but a sucking-off installation is sufficient, since larger amounts of smoke can arise only in the case of the premature removal of moulds from the cooling medium.

[0010] Casting immersed in the polymer coolant crystallises and solidifies in a bottom-up manner, and the down-gate crystallises as the last part of the casting, performing at the same time the role of a feeding system. Rapid bulk crystallisation and cooling from the liquid state occur when the whole ceramic mould, poured with liquid alloy, is immediately immersed in the cooling medium, this technique being applied to castings of practically equal wall thickness and smooth transition from one section to another. Rapid directional crystallisation occurs when the ceramic mould poured with liquid alloy is immersed at a constant or variable speed in the liquid cooling medium.

[0011] Ceramic moulds made of aluminosilicate or high-alumina refractories are characterised by stable properties during changes in temperature. Higher temperature of the ceramic mould favours alloy castability, and thus enables making thin wall or ultra-thin wall castings.

[0012] Castings made by the method according to the invention have very good quality of the outer surface, characterised by a low degree of roughness, by glossy appearance, and by absence of defects of the gas microporosity type. The directional solidification provides good internal compactness, measured by density. Moreover, the castings are characterised by high homogeneity of the macro- and microstructure in the wall cross-sections, the thicknesses of which are not greater than 2-3 times. Their structure is more refined with respect to similar castings solidifying according to the tradi-

tional methods of the investment casting process, in particular, the average values of the secondary dendrite arm spacing are reduced, and in eutectic alloys a fine-grain eutectic is formed. All these factors affect the increase of strength parameters R_m and $R_{p0.2}$ and ductility A_5 in the tensile test, while the magnitude of these parameters depends on the alloy type and cooling conditions.

[0013] Examples of practical embodiments of the method for producing investment castings according to the invention are given below.

Example 1

[0014] A ceramic mould for a pilot conical casting of $\varnothing 20 \times \varnothing 30 \times 100$ mm is made of quartz flour and silica sand with SiO_2 content above 90 weight percent, with a binder of the LUDOX® PX30 type in the form of an aqueous solution of colloidal silica containing 20 to 40 weight percent of SiO_2 . The mould is baked at a temperature of 800-850° C. for 2 hours. Then it is slowly cooled to a temperature of 750° C., held at this temperature for 15 minutes, and next poured with an aluminium alloy, which is a hypoeutectic EN AC- AlSi7Mg0.6 silumin at a temperature of 700-720° C. The ceramic mould poured with liquid alloy is after 10 seconds immersed at a speed of 7.5 mm/s in a 20 volume percent aqueous solution of the liquid polymeric quenching agent such as Aqua-Quench 260 at a temperature of 20° C.

[0015] The use of an aqueous solution of the liquid polymer makes its reaction with the ceramic mould and liquid alloy very weak, and the resulting casting is compact and free from any internal gas-type porosity, while its outer surface is bright and glossy, with only traces of roughness.

Example 2

[0016] A ceramic mould for a tapered casting, as in Example 1, wherein the said mould is made of an aluminosilicate material in the form of a synthetic filler under the trade name of Molochite and the LUDOX® PX30 binder, and wherein the said mould is baked at 900° C. for 2 hours, and then cooled to room temperature. After preheating the said mould to a temperature of 300° C., it is held at this temperature for 15 minutes and poured with liquid cast MgAl9Zn1 magnesium alloy at a temperature of 690-710° C. Then, after 10 seconds, the mould poured with molten metal is immersed at a constant speed of 7.5 mm/s in a 20 volume percent aqueous solution of the liquid POLIHARTENOL-E8 polymer at a temperature of 20° C.

[0017] After crystallisation and cooling of the alloy in a cooling medium, the mould shell does not show any signs of adherence to the outer surface of the casting. The casting is compact, free from any external and internal porosity, while its density is close to the theoretical one typical for an alloy of a given chemical composition. When hit with a metal tool, the casting produces a clear metallic sound, typical for gravity die castings. The outer surface of the sample has a low surface roughness and is slightly glossy.

Example 3

[0018] A ceramic mould of a conical shape based on Molochite as a filler and with the LUDOX® PX30 binder is baked at a temperature of 950° C. for 3 hours and then cooled to a temperature of 700° C., held at this temperature for 20 minutes and poured at a temperature of 1450° C. with liquid chromium-molybdenum cast iron, containing in weight per-

cent: 3.35 C, 0.53 Si, 92 Mn, 9.5 Cr, 0.14 Ni, 1.53 Mo, rest Fe. Then, after 15 seconds, the mould with liquid cast iron is immersed at a speed of 5 mm/s in an aqueous solution of the liquid THERMISOL QZS 700 polymer at a concentration of 19.14 volume percent and at a temperature of 50° C.

[0019] The directional cooling has resulted in improved compactness: the average density of casting $\rho = 7.51 \text{ g/cm}^3$, while the average hardness value is equal to 664 HV. For comparison, the properties of casting made in a sand mould are: $\rho = 7.45 \text{ g/cm}^3$, and the average hardness value equal to 547 HV. The accelerated crystallisation and cooling favour the spheroidisation of primary and eutectic carbides in a ferritic matrix.

Example 4

[0020] A ceramic mould made of aluminosilicate filler called Molochite and the LUDOX® PX30 binder based on colloidal silica is baked for 3 hours at 900° C. Then the mould is cooled to room temperature and then heated to 400° C. The mould is held at this temperature for 30 minutes and poured with the liquid AC- AlSi7Mg0.3 alloy at a temperature of 710-740° C. After 15 seconds, the mould poured with the liquid alloy is immersed at an average speed of about 5 mm/s in a tank filled with a polymer coolant, which is a 20 percent aqueous solution of POLIHARTENOL-E8 at room temperature.

[0021] The microstructure of the resulting casting is more refined than the micro-structure of casting solidifying in a self-supported ceramic mould at a temperature of 400° C. The overall quality of the outer surface of casting has been very good in both cases: it has low surface roughness, and is bright and glossy. The casting made by the method according to the invention is more compact, with no internal defects and, compared with the casting made by a traditional technique, depending on wall thickness, has a higher density of from 0.01 to 0.04 g/cm^3 . Faster crystallisation has reduced the α_{Al} dendrites of the aluminium solid solution; particularly visible is the effect of undercooling-related modification of the ($\alpha_{Al} + \beta_{Si}$) eutectic. It has also been observed that in hypoeutectic silumins of the AC- AlSi7Mg0.3 type, the DAS or SDAS parameters, i.e. the interdendritic spacing of I- and II-order, better correlate with the solidification rate than the grain size. In casting made from an AlSi7Mg0.3 alloy by the method according to the invention, the average dendrite arm spacing is 40 μm . The increased solidification rate in casting made according to the invention is reflected in an increase of the mechanical properties: $R_m = 280 \text{ MPa}$, $R_{p0.2} = 235 \text{ MPa}$, $A_5 = 4.0\%$, while, for example, in the casting solidifying in a traditional ceramic mould at room temperature, the average dendrite arm spacing is 47 μm , and mechanical properties assume the following values: $R_m = 245 \text{ MPa}$, $R_{p0.2} = 195 \text{ MPa}$, $A_5 = 2.5\%$.

Example 5

[0022] Three ceramic moulds based on Molochite with the LUDOX® PX30 type binder are baked at a temperature of 900° C. for 2.5 hours and then are cooled to 500° C., held at this temperature for 15 minutes and are next poured with liquid copper alloy of the BA1044, B555, or M059 type, according to PN-91/H-87026, overheated by 100-150° C. above the initial melting point. After 30 seconds since the end of the mould cavity filling, the mould is immersed at a speed of 8.5 mm/s in a polymer coolant based on POLI-

HARTENOL-E8, at a concentration of 15-25 volume percent H₂O, at a temperature of 35° C.

[0023] The outer surface of copper alloy castings is characterised by low surface roughness and is glossy, especially in the case of BA1044 aluminium bronze. Rapid directional solidification of copper alloy castings reduces in the microstructure both the grain size and SDAS. For example, in B555 alloy, these distances were reduced: from 33 µm—for castings made by the method according to the invention, to 26 µm for castings undergoing free cooling in a self-supported molochite mould at a temperature of about 500° C. Cooling conditions had a significant effect on the hardness of copper alloy castings, and while HV of the BA1044 alloy in a self-supported mould was 232 units, it increased to 253 in casting solidifying directionally in the mould placed in a liquid polymer medium. After rapid directional solidification, a general increase was observed in the strength parameters R_m and $R_{p0.2}$, in ductility A_5 , and in hardness HV of the examined copper alloys. Additional increase in the mechanical properties is possible after adjustment of the basic chemical composition, and the application of modification-refining and heat treatment.

1. A method for producing investment castings, in ceramic moulds, from alloys based on Al, Mg, Cu, Zn and Fe, comprising:

baking a ceramic mould at a temperature of 800-1000° C. for 2-4 hours;

cooling said mould to a temperature of 20-950° C., and holding said mould at this temperature for 10-40 minutes;

pouring into said mould a liquid alloy overheated by from 50 to 200° C. above the initial melting point and after a lapse of 10-100 seconds; and

immersing said mould at a fixed or variable speed in a liquid cooling medium, the said liquid cooling medium being a 1-99 volume percent aqueous solution of liquid polymer at a temperature of 15-80° C.

2. A method for producing investment castings according to claim 1, characterised in that the liquid polymer is a polymer of the PAG, or PVP, or ACR, or PEO type.

3. A method for producing investment castings according to claim 1, characterised in that the ceramic moulds made of aluminosilicate or high alumina refractories, especially based on synthetic sand, for example Molochite, are used.

4. The method according to claim 1, further comprising: pouring an aluminum alloy into said mould.

5. The method according to claim 1, further comprising: pouring a magnesium alloy into said mould.

6. The method according to claim 1, further comprising: pouring a copper alloy into said mould.

7. The method according to claim 1, further comprising: pouring an iron alloy into said mould.

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