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(54) Manufacturing process of composite plates made of magnesium alloys and ceramic foam and composite plates

(57) Process bases on the infiltration of metal melt (matrix) in the pores of ceramic foam (hardening phase). Method of casting, sizing of mould, preheating of ceramic foam or mould, pouring temperature, use of insulating cover and vibrating enable complete filing the pores with metal. For manufacturing of composite plates the gravity casting and vibrating of total system during casting and solidification is used. Such composite plates are used in automotive, aircraft and military industry because composite plates have good mechanical properties, high break-through strength at low density and resistance to cutting.

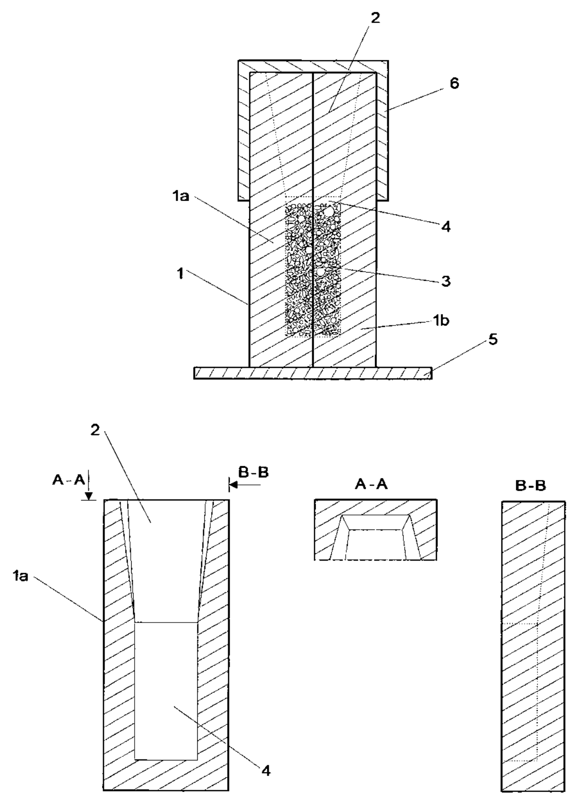

Figure 1

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Description

[0001] The invention is from field of founding and it is related to manufacturing process of metal-matrix composite with magnesium matrix and ceramic foam as hardening phase.

Problem

[0002] The composite is a modern material. It consists of two or more different materials that differ in physical, mechanical and chemical properties. The properties of composite materials depend upon the selection or properties of matrix and hardening phase, form, distribution and orientation of hardening phase, interactions between components on the interface and volume fraction of components. The composites are divided into groups according to the material of matrix: metal-matrix composite (MMC), ceramic-matrix composite (CMC) and polymer-matrix composite (PMC). The metal-matrix composite can be hardened with particles, filaments, flakes, layers, also the interpenetrating phase composite are known where melt infiltrates into pores of hardening phase. The interfaces have important influence on the properties of composites. The primary role of interface is to assure a strong interconnection between matrix and hardening phase and the interface must be mechanically and thermodynamically stable. There are several methods of interconnections and processes on the interfaces that are essential for design and manufacture of composites. The interconnection on the interface occurs with adhesion of constituents that are in close contact during manufacturing. The matrix is usually liquid or it has such a viscosity that behaves similar as liquid. Wetting of hardening phase with matrix is very important for good adhesion and formation of interconnection. The wetting determines extent to which the liquid will spill or spread on the surface of solid body. Good wetting in composites means that the liquid phase must spill over the hardening phase and pours overall surface irrespective of surface roughness and that at the interface may not pin-head blisters remain. The wetting is possible when the viscosity of the matrix is not too large and when the free energy of the system reduces. Strength of bond between liquid and solid phase is determined from the value of contact angle Θ and surface tension liquid $\gamma_{l,g}$ which are measured experimentally. The wetting dependents on more factors, for example, the wetting of ceramic with metal melt depends from: enthalpy of formation of ceramic phase ($-\Delta H$), stoichiometry, electron structure of phases, temperature, time, roughness and crystal structure. The wetting at the contact angle $\Theta = 0°$ is perfect, at $\Theta < 90°$ is good and at $\Theta > 90°$ is not the wetting. The interconnection between matrix and hardening phase forms at the close contact of components of composite when the wetting or the adhesion is present. There are different types of the interconnections: mechanical, electrostatic, chemical, with mutual wettability and solving components and connection of reaction or diffusion.

Information of so far known salvations and their weaknesses

[0003] Manufacture of metal-matrix composites bases on the different foundry processes or casting processes. The hardening phase is mixed in the melt before casting and then the composite is ready to cast into a mould. The gravity casting, low-pressure casting, pressure casting or other casting processes are used. Further, the metal-matrix composites can be formed hot or cold.

[0004] Manufacturing processes of metal-matrix composites and their properties can be found in the following literature:

1. ASM HANDBOOK, Volume 21, Composites, Volume Chair Daniel B. Miracle and Steven L. Donaldson, ASM International 2001.

2. Choi, H., Alba-Baena, N., Nimityongskul, S., Jones, M., Wood, T., Sahoo, M., Lakes, R., Kou, S., Li, X. Characterization of hot extruded Mg/SiC nanocomposites fabricated by casting, J. Mater. Sci. (2011) 46, str. 2991-2997.

[0005] The most commonly used method of manufacturing metal-matrix composites is based on the mixing particles of different shapes and sizes in the melt and further casting to prepare composite. Thus, manufactured composite materials have higher mechanical properties then the matrix, but at defined content of hardening phase the mechanical properties can be reduced. The problems occur during mixing of hardening phase into the melt or their non-uniform distribution in the composite material.

[0006] Other less used manufacturing process of composite materials is infiltration of the melt into the hardening phase (with) using a squeeze casting, low pressure and pressure casting. At manufacturing of interpenetrating phase composites the hardening phase has defined homogeneous preform that is porous and in that the matrix infiltrates. The homogeneous preform of hardening phase has advantage in the uniform distribution in the composite material, thus composite material has uniform mechanical properties. The composite material, where the melt must infiltrate into pores of hardening phase is in the practice difficult to achieve. Foundry processes that are used for manufacturing such composite materials are casting processes where the melt is pushed into mould by pressure. Low pressure or pressure casting and squeeze casting are used. At low pressure casting the melt is pushed into mould by assistance of gas pressure that operates on the surface of melt, at pressure casting the melt is pushed into mould by injection piston while the squeeze casting is liquid forging. Such casting processes are industrially difficult, require control of a large number of parameters, need the low pressure or pressure machine have and so the manufacturing processes are expensive.

3. Prielipp, H., Knechtel, M., Claussen, N., Streiffer, S. K., Müllejans, H., Rühle, M. R., Rödel, J. R., Mater. Sci. Eng. A 197 (1995), str. 19- 30.

4. Skirl, S., Hoffman, M., Bowman, K., Wiederhorn, S., Roedel, J., Acta Mater. (1998), str. 2493-2499.

5. Lo, J. S. H., Carpenter, G. J. C., Fabrication of SiC-Reinforced AZ91D Magnesium Based Composites, Woodhead Publishing Limited, Gold Coast, Queensland, Australia, 1997, str. 688.

6. Peng, L. M., Cao, J. W., Noda, K., Han, K. S. Mechanical properties of ceramic-metal composites by pressure infiltration of metal into porous ceramics, Materials Science and Engineering A 374 (2004), str. 1-9.

[0007] Scientific papers where magnesium alloys with ceramic foam by squeeze casting process were combined are:

7. Zeschky, J., Lo, J., Höfner, T., in Greil, P. Mg alloy infiltrated Si-O-C ceramic foams, Materials Science and Engineering A 403, 2005, str. 215-221.

8. Zeschky J., Lo J. S. H., Scheffler M., Hoeppel H-W., Arnold M., Greil P., Polysiloxane-derived ceramic foam for the reinforcement of Mg alloy. Zeitschrift für Metallkunde (2002), vol. 93, issue 8, str. 812-818.

9. Zeschky J, Goetz-Neunhoeffer F., Neubauer J., Jason Lo S. H., Kummer B., Scheffler M., Greil P., Preceramic polymer derived cellular ceramics. Composites Science and Technology (2003), vol. 63, issue16, str. 2361-2370.

[0008] Other scientific papers on the theme of production of composite materials with magnesium alloy as matrix and ceramic foam as hardening phase were not found.

[0009] It was also found a US Patent.

10. US Patent. Method to produce ceramic reinforced or ceramic-metal matrix composite articles. Patent Number: 5, 67, 271. Date of Patent: Dec. 1, 1992.

[0010] However this patent is based on the pressure filtration to infiltrate a reinforcing organic or inorganic network with ceramic particles. It is different from our case, where no pressure is needed and the infiltration is achieved using vibration.

Description of new salvation

MANUFACTURING PROCESS OF COMPOSITE PLATES FROM MAGNESIUM ALLOYS AND CERAMIC FOAM AND COMPOSITE PLATES

[0011] The invention is a new manufacturing process of composite panels from magnesium alloys hardened with ceramic foam by gravity casting process.

[0012] Previously known solutions of production of composite panels from magnesium alloys hardened with ceramic foam SiC - AlO_3 - SiO_2 with different porosity did not include the manufacturing process of gravity casting.

[0013] The basic components are casting of magnesium alloys with different alloying elements and ceramic foams with different open porosity.

[0014] Different casting magnesium alloys that contain different concentrations of alloying elements: aluminium, beryllium, calcium, lithium, manganese, silicon, silver, zinc, zirconium, rare earth, etc. are used as matrix. Key characteristics of casting magnesium alloys with different alloying elements are low density about 1.7 g/cm^3 and good mechanical properties.

[0015] Ceramic foam with open porosity has low density and high hardness is used as hardening phase. This ceramic foam is commercial accessible and is used for filtration of melt because it is stable up to temperature of 1700 °C. Material for manufacturing of ceramic foam is based on SiC - Al_2O_3 - SiO_2 with density of about 2.6 g/cm^3.

[0016] For new procedure, three types of ceramic foams with different sizes and distribution of pores are used:

- 10 pores on distance of 25.4 mm,
- 20 pores on distance of 25.4 mm and
- 30 pores on distance of 25.4 mm.

[0017] Mould (1) (Figure 1) with properly sized of getting system (2) is first made that the metal-static pressure is achieved that the melt can fill all pores of ceramic foam (3). The mould consists of two parts (1a, 1b) with mould cavities (4) that represent geometry of casting after combining. Tool steel or grey cast iron are used for mould manufacturing. Wall thickness of mould is 1- to 2-times of casting thickness, sides of getting system and of mould cavity have foundry inclination from 1 to 3 °. The mould is coated before the casting to prevent reactions between melt and mould. In the mould prepared this way the ceramic foam is inserted and then the mould is closed. That the melt can fill all pores of ceramic, the mould or ceramic foam must be preheated to certain temperature. The preheated temperature depends on size and distribution pores of ceramic foam and is from 450 °C to 700 °C. During heating of ceramic foam the melt of magnesium alloy is prepared by induction furnace. At preparation of melt it is necessary to consider that magnesium has very large affinity to oxygen, therefore the magnesium alloys are protected by protective gas between melting to prevent the ignition of magnesium alloys or the melt is prepared in the vacuum induction melting furnace. The pouring temperature of magnesium alloys is from 650 °C to 750 °C and depends on type and amount of alloying elements. When the ceramic foam and the mould are heated to a suitable temperature, the mould with ceramic foam is taken out of the furnace, placed on the vibration plate (5) and the melt of magnesium alloys is gravity cast through the ingate or inlet channel. When the mould cavity and gating system are filled with melt, the insulation cover (6) is placed on top of the mould, which acts as a feeder. During the casting, the mould vibrates so that the caught air from the pores of ceramic foam and the mould cavity is eliminated. The vibration plate is metallic therefore, it transfers the heat from the bottom of mould very well and thus enables the directional solidification.

[0018] New manufacturing process enables easy production of composite plates. The invention is suitable for industrial manufacturing of metal-matrix composites because the casting process is simple and inexpensive comparing with other casting methods. Such composite plates are used in automotive, aircraft and military industry because composite plates have good mechanical properties, high break-through strength at low density and resistance to cutting.

Claims

1. Manufacturing process of the composite plates from magnesium alloys and ceramic foam comprehends and **characterized in,**
   using a steel mould (1) with appropriate gating system (2) and mould cavity (4) in which ceramic foam (3) is inserted and so prepared mould is preheated before gravity casting and is placed on the vibration plate (5), which during casting and solidification vibrates the total system and after the casting insulation cover (6) is placed on top of the mould that is in the gating system last solidification range.

2. Process according to claim 1 is **characterized in that** as matrix the magnesium alloys with alloying elements; aluminium, beryllium, calcium, lithium, manganese, silicon, silver, zinc, zirconium, rare earth are used and as hardening phase the ceramic foam (3) from SiC - Al_2O_3 - SiO_2 with porosity 10 pores on distance of 25.4 mm, 20 pores on distance of 25.4 mm and 30 pores on distance of 25.4 mm is used.

3. Process according to claim 1 is **characterized in that** the mould (1) with the ceramic foam (3) is preheated to temperature from 450 °C to 700 °C depending of dimensions ceramic foam further size and distribution of the pores in the ceramic foam.

4. Process according to claim 1 is **characterized in that** the magnesium alloy is molten in the induction furnace and is protected by inert gas or is molten in the vacuum melting furnace that reaction with oxygen is protected and that the melt is heated on the pouring temperature which is from 650 °C to 750 °C and depends on the type and amount of alloying elements.

5. Process according to claim 1 is **characterized in that** the mould (1) with the ceramic foam (3) is placed on the steel vibration plate (5) before the casting, the vibration plate during the gravity casting of the magnesium alloy together with the mould vibrates and enables that the melt fills all pores of the ceramic foam and so prevents retention of air in the composite material.

6. Process according to claim 1 is **characterized in that** the mould (1) is placed on the steel vibration plate (5) and this enables good removal of heat and directional solidification and after the casting insulation cover (6) is placed on top of the mould and enables that the gating system (2) acts as feeder.

7. The composite plates are **characterized in that** the composite plates are manufactured at this process from claims of 1 to 6.

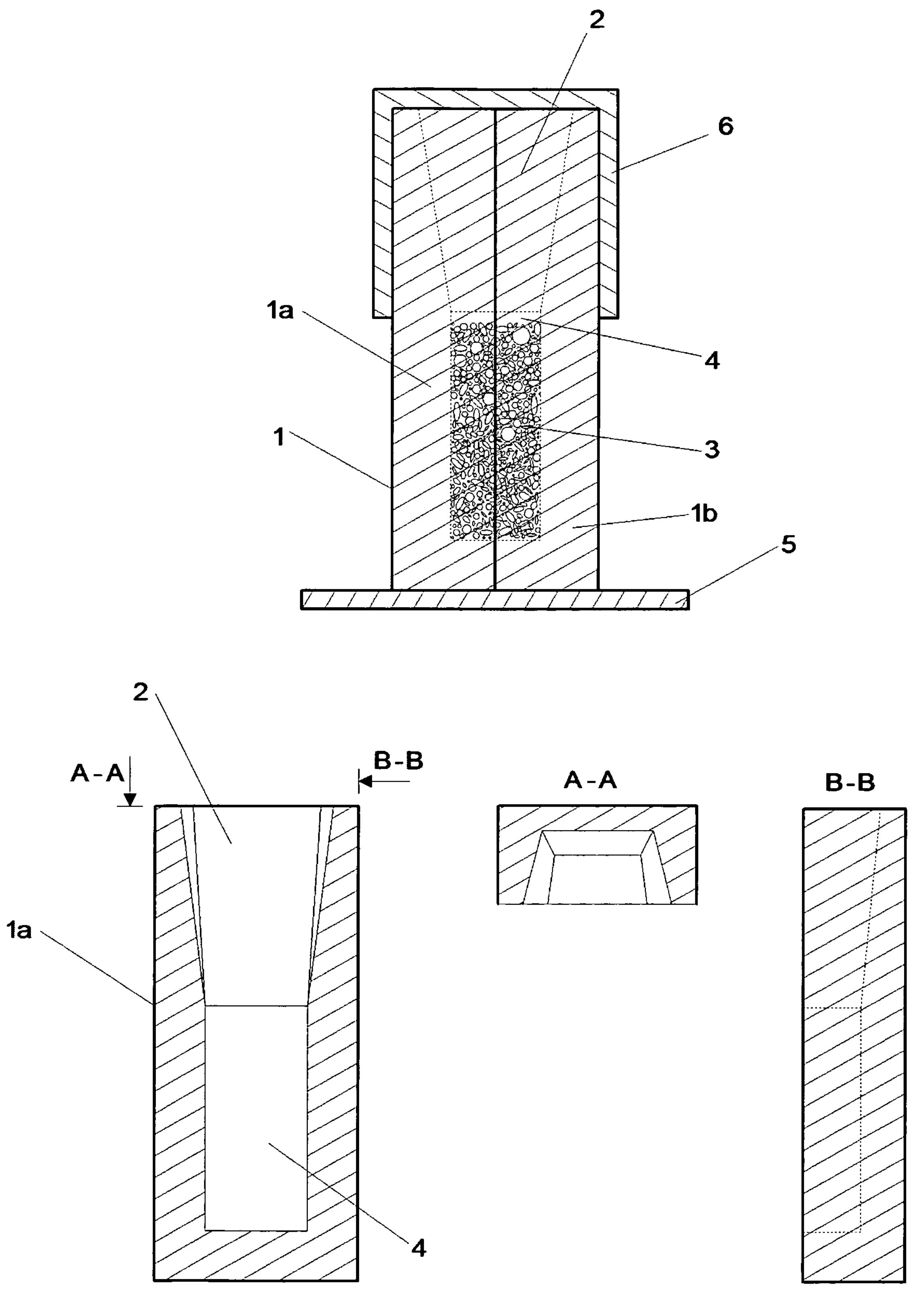

Figure 1

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 567271 A **[0009]**

Non-patent literature cited in the description

- Composites. **CHAIR DANIEL ; B. MIRACLE ; STEVEN L. DONALDSON.** ASM HANDBOOK. ASM International, 2001, vol. 21 **[0004]**
- **CHOI, H. ; ALBA-BAENA, N. ; NIMITYONGSKUL, S. ; JONES, M. ; WOOD, T. ; SAHOO, M. ; LAKES, R. ; KOU, S. ; LI, X.** Characterization of hot extruded Mg/SiC nanocomposites fabricated by casting. *J. Mater. Sci.,* 2011, vol. 46, 2991-2997 **[0004]**
- **PRIELIPP, H. ; KNECHTEL, M. ; CLAUSSEN, N. ; STREIFFER, S. K. ; MÜLLEJANS, H. ; RÜHLE, M. R. ; RÖDEL, J. R.** *Mater. Sci. Eng. A,* 1995, vol. 197, 19-30 **[0006]**
- **SKIRL, S. ; HOFFMAN, M. ; BOWMAN, K. ; WIEDERHORN, S. ; ROEDEL, J.** *Acta Mater.,* 1998, 2493-2499 **[0006]**
- **LO, J. S. H. ; CARPENTER, G. J. C.** Fabrication of SiC-Reinforced AZ91D Magnesium Based Composites. Woodhead Publishing Limited, 1997, 688 **[0006]**
- **PENG, L. M. ; CAO, J. W. ; NODA, K. ; HAN, K. S.** Mechanical properties of ceramic-metal composites by pressure infiltration of metal into porous ceramics. *Materials Science and Engineering,* 2004, vol. A 374, 1-9 **[0006]**
- **ZESCHKY, J. ; LO, J. ; HÖFNER, T. ; GREIL, P.** Mg alloy infiltrated Si-O-C ceramic foams. *Materials Science and Engineering A,* 2005, vol. 403, 215-221 **[0007]**
- **ZESCHKY J. ; LO J. S. H. ; SCHEFFLER M. ; HOEPPEL H-W. ; ARNOLD M. ; GREIL P.** Polysiloxane-derived ceramic foam for the reinforcement of Mg alloy. *Zeitschrift für Metallkunde,* 2002, vol. 93 (8), 812-818 **[0007]**
- **ZESCHKY J ; GOETZ-NEUNHOEFFER F. ; NEUBAUER J. ; JASON LO S. H. ; KUMMER B. ; SCHEFFLER M. ; GREIL P.** Preceramic polymer derived cellular ceramics. *Composites Science and Technology,* 2003, vol. 63 (16), 2361-2370 **[0007]**