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(54) METALLURGICAL PROCESS FOR THE PREPARATION OF SEMI-SOLID MAGNESIUM ALLOYS IN A QUASI-LIQUID STATE

(57) An object of the present invention is a metallurgical process for the preparation of a semi-solid magnesium alloy in a quasi-liquid state wherein the alloy is stirred under isothermal conditions by magnetic stirring with permanent magnets and/or by stirring carried out by bubbling nitrogen or argon gas, such that to provide a highly uniform magnesium alloy, or highly-defined objects in terms of shape and details.

Said processes is carried out under safety conditions which do not involve the use of known highly-polluting protective gas.

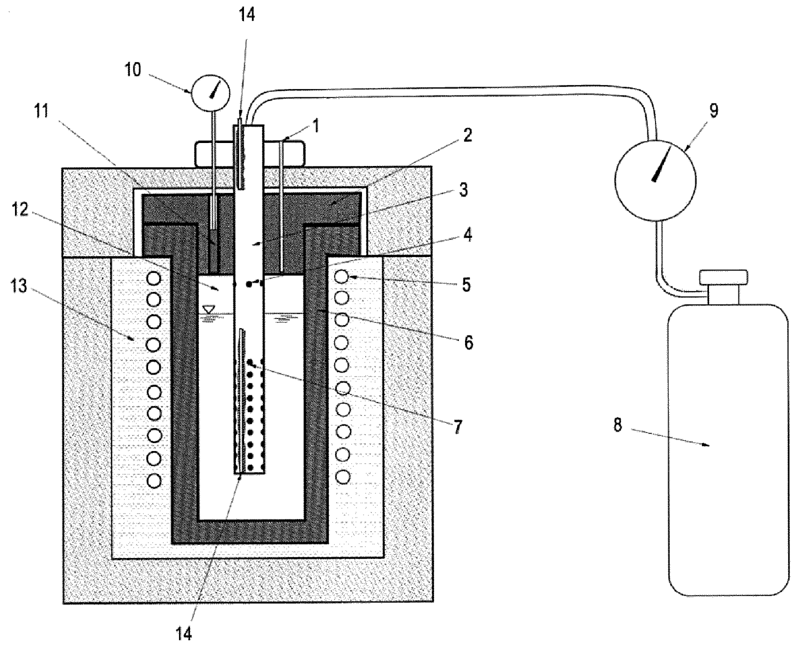

Fig. 1

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Description

TECHNICAL FIELD

[0001] The present invention is in the metallurgic field of the magnesium alloys.

BACKGROUND

[0002] The development of magnesium alloys, which was driven during the last century by the aerospace industry, historically occurred in order to satisfy the needs of the transportation industry, that was seeking advantages on further strategies related to weight reduction, considering the very low specific weight of such alloys.

[0003] The viscosity of magnesium (abbreviated Mg) at the molten state is lower than the viscosity of aluminum alloys, allowing an easier filling of the mold cavities, thus allowing to make castings of particular geometrical complexity, even with thin walls. Compared to aluminum alloys, magnesium in a liquid state also has a reduced chemical compatibility with steel used for manufacturing shell casting molds; this property allows to markedly reduce the phenomena of gradual wear of steel molds due to liquid metal attack. Although such promising characteristic, Mg alloys show significant problems due to the high reactivity of magnesium metal with oxygen. The high affinity of magnesium for the atmosphere oxygen causes high flammability of Mg and alloys thereof which, once flame-triggered, proceed with an incessant exothermic process of self-combustion, fed by the presence of oxygen (abbreviated O_2) and supported by the flame temperature: once the flame is triggered, in the presence of oxygen, the combustion reaction proceeds forming the combustion product magnesium oxide (abbreviated MgO) and releasing heat. The combustion flame rapidly reaches temperatures between 2.000 °K and 4.000 °K, therefore capable of perforating any crucible, even if made of refractory material.

[0004] Due to this problem Mg alloys require the use of special melting plants and trained personnel, increasing the production cost of Mg alloy castings despite the Mg raw material cost is actually similar to the cost of pure aluminum.

[0005] In order to safe control Mg alloys at the molten state therefore it is necessary removing O_2 contacting the metal bath, i.e. the primary trigger source of Mg combustion reaction is to be completely eliminated. That is possible by achieving inert atmospheres with respect to melted Mg. Accordingly, there are several techniques in Mg foundries, which are divided in: a) vacuum melting plants, b) melting plants provided with atmospheres being inert and protective of Mg bath. The inert atmospheres usually used are those mixed SF_6 and CO_2, those based on R-134a freon gas and those based on SO_2. Both SF_6 R-134a freon gas are classified as very high GWP (global warming potential) greenhouse gases, while SO_2 gas, although being a valid alternative to greenhouse gases SF_6 and R-134a from an environmental point of view, requires stringent application protocols due to its high toxicity to the operators.

[0006] All these problems related to the uncommon technical skills necessary for magnesium melting, the high investment costs for magnesium die casting nowadays relegate magnesium melting to a market niche in the aerospace, military air force and automotive field.

[0007] Together with the above cited magnesium technological barrier limiting the widespread use of magnesium, although it is the lightest metal available in the Earth, when conventional melting processes are used, metallurgic drawbacks exist (e.g. gravity die casting, pressure die casting, centrifugal die casting) for producing fused pieces.

[0008] Starting from ’90s, it was found that the addition of calcium (abbreviated Ca) to magnesium alloy significantly increased the flammability temperature of Mg, as cited by Sakamoto, Mitsuru et al. in "Suppression of ignition and burning of melted Mg alloys by Ca bearing stable oxide film." Journal of Materials Science Letters, 16, (1997): 1048-1050. According to such article, the addition of only 1% by weight of Ca in Mg alloys promotes the melting step and the subsequent casting of Mg alloy in air without using blanket gases. Currently is known that other elements of Mg alloy such as beryllium (abbreviated Be) and Yttrium (abbreviated Y), together with calcium, are common inhibitors of Mg alloy ignition. The phenomenon regulating the higher protection provided by Ca, Be and Y elements present in the Mg bath against oxygen present in the atmosphere, although little known, it is however known; the volume ratio between the volume of Mg oxide (abbreviated MgO) formed by spontaneous reaction of Mg of the bath with air O_2 and the volume of underlying melted Mg is lower than the unity. This implies that, for each mass unity of melted Mg reacting with atmosphere oxygen, a magnesium oxide film not capable of covering the entire melted Mg metal surface, and therefore not capable of operating its action of continuous, stable protective film, and then perfectly oxygen impermeable unlike melted aluminum, is formed. -the result is the presence on the surface of the melted Mg of a film of porous oxide exposing the Mg bath underlying to the oxide film to the oxygen present in the atmosphere, activating the above-mentioned conditions of flame ignition and resulting reaction of exothermic reaction of exothermic combustion between liquid Mg and the oxygen in the atmosphere.

[0009] In particular, Sakamoto demonstrated that the structure of oxide film extending on the Ca-added Mg alloy added is characterized by a very thin and uniform oxide film, which is resistant although the long air expositions of the melted alloy at 973 °K for 60 minutes, confirming that the oxide film formed as Mg alloys with Ca acts as an effective barrier for preventing both oxygen diffusion from air to the melted metal and magnesium volatilization. In the last years, together, not flammable pure-Ca added Mg alloys (and/or with other above-mentioned flame inhibitor elements such as Be and Y) calcium oxide (CaO)-modified magnesium alloys, commercially known as Eco-magnesium alloys (abbreviated Eco-Mg) were developed to be used at low costs similarly to the Mg alloys with Ca as pure alloying element. The use of high-reactive elements with atmosphere oxygen - such as Ca, Be and Y - allow to considerably reduce (theoretically, eliminating) the use of the above-mentioned gases, highly-polluting protective gas even using melting plants closed in protective atmosphere usually used for melting conventional Mg alloys, i.e. without adding the above-mentioned three elements.

DESCRIPTION OF THE DRAWINGS

[0010]

Figure 1 shows a scheme of the apparatus used for the preparation of the magnesium alloy of the present invention, wherein:

- 1 is the hole for the evacuation of air contained in the controlled-atmosphere chamber corresponding to 12;
- 2 is the sealed lid of the crucible corresponding to 6;
- 3 is the adduction tube of N nitrogen-type inert gas;
- 4 are the insufflating holes of nitrogen above the free top surface of the metal bath;
- 5 are the electrical resistances for the thermoregulation and thermostatation of crucible 6 and the metal bath in the crucible;
- 6 is the casting crucible;
- 7 are the holes of nitrogen-type inert gas insufflation below the free top surface of the metal bath for inert gas bubbling and bath mixing;
- 8 is the cylinder use for nitrogen-type inert gas adduction;
- 9 is the flux meter for adjusting of inert gas flow adjustment insufflated through 4 in the O_2- depleted atmosphere chamber 12 and inside the metal bath through 7;
- 10 is the oxygen meter;
- 11 is the detection sensor for monitoring the residual oxygen content present in the atmosphere of the casting chamber 12;
- 12 is the part of casting chamber occupied by oxygen-depleted atmosphere whose content is monitored by 11;
- 13 refractory body of the melting furnace.

Figure 2 shows a micrography of the magnesium alloy prepared according to the process of the invention, by the apparatus of Fig. 1, wherein the globular equiaxed structure is observed.

Figure 3 shows a micrography of the metallurgic structure obtained in the apparatus of Fig.1 above the liquidus temperature of the AZ91D-1.5CaO-type Mg alloy without the bubbling of nitrogen-type inert gas by immersion.

- Comparative.

DESCRIPTION OF THE INVENTION

[0011] The process of the present invention allows to solve the limits related to magnesium melting and its alloys reducing as much as possible the melting temperature and the temperature at which the product is poured. All of this is achieved by preparing a semi-solid magnesium alloy near to the alloy liquidus temperature, i.e. in a quasi-liquid state, using an oxygen-lean atmosphere and a particular stirring system that, together with the above-mentioned conditions, allows to avoid the Mg flame ignition.

[0012] Furthermore, the process involves a step wherein, under isothermal conditions, the semi-solid magnesium alloy is subjected to stirring for a certain time, with particular stirring systems which allow to obtain an highly-homogeneous alloy, a high-pourability globular equiaxed microstructure and having a reduce volume contraction at the terminal stage of complete solidification, allowing to obtain complex-shape castings and in the absence of porosity and/or shrinkage cavities typical of solidified castings from liquid conditions.

[0013] The invention is also described according to preferred embodiments and the claims, whose definitions are integral part of the present description.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Object of the present invention is a metallurgical process for the preparation of a semi-solid magnesium alloy comprising calcium and/or calcium oxide (CaO) (hereinafter Mg alloy with Ca and/or CaO) semi-solid near to the liquidus temperature, but within the range of solidification of the metal alloy, i.e. under conditions of quasi-liquid semi-solid mass.

[0015] Such metallurgical process for the preparation of a semi-solid magnesium alloy in a quasi-liquid state comprises the following steps:

a) loading an apparatus with melted magnesium alloy comprising calcium and/or calcium oxide,
b) achieving an atmosphere with an oxygen content not higher than 10% mol. inside said apparatus,
c) cooling the melted magnesium alloy of step b) until a semi-solid magnesium alloy in a quasi-liquid state is formed,
d) maintaining the semi-solid magnesium alloy in a quasi-liquid state of step c) under isothermal conditions at the temperature obtained by step c), stirring for at least 20 seconds by electromagnetic stirring and/or magnetic stirring with permanent magnets and/or by stirring carried out by bubbling nitrogen or

argon gas.

e) discharging the semi-solid magnesium alloy in a quasi-liquid state from the apparatus.

[0016] According to a preferred embodiment, the metallurgical process comprises the following steps:

a) loading an apparatus with magnesium alloy comprising calcium and/or calcium oxide under conditions of complete melting, i.e. at a temperature higher than the alloy liquidus temperature;

b) inside said apparatus, which is top closed with a sealed lid and provided with at least one insufflation lance of inert gas such as nitrogen or argon, achieving an atmosphere with an oxygen content in dry atmosphere not higher than 10% mol. by insufflation of inert gas of nitrogen or argon;

c) measuring the bath temperature by means of a submerged thermal probe, thermoadjusting the apparatus in order to thermostate the above-mentioned magnesium alloy to a process temperature in a thermal range between 5°C and 15°C below the temperature bath complete melting, this latter referred as liquidus temperature;

d) maintaining the magnesium alloy comprising Ca and/or CaO under isothermal conditions within the above-mentioned range of *near-to-liquidus* semi-solid process described in previous point c) and stirring the mass for a time of at least 20 seconds by electromagnetic stirring and/or magnetic stirring with permanent magnets and/or by bubbling inert gas such as nitrogen or argon, preferably below the free top surface of the bath;

e) discharging the semi-solid magnesium alloy in a quasi-liquid state from the apparatus of preparation.

[0017] According to an alternative embodiment, the process can involve a variant wherein the steps a) and b) are reversed.

[0018] Therefore, the process of the present invention allows the preparation of magnesium alloys comprising Ca and/or CaO under semi-solid conditions avoiding the adoption of conventional highly-polluting protective gases (such as SF_6, SO_2, R134a) which, in the conventional processes, on a precautionary basis, however are necessary although the alloys are Ca- or CaO-added since, during the stirring step carried out mechanically, the oxide film stabilized in a static melting stage would continuously removed thus causing the trigger of incipient flame also on Mg alloys containing Ca/CaO, thus making the preparation of the semi-solid mass unfeasible even for these alloys in free atmosphere.

[0019] The fact of operating the specific stirring magnetically and/or electromagnetically and/or by bubbling of inert gas of the semi-solid magnesium alloy comprising Ca and/or CaO in combination with an atmosphere with an oxygen content not higher than 10% mol. allows to completely avoid the trigger and the subsequent combustion of said magnesium alloy.

[0020] Furthermore, the fact of operating such specific stirring of the above-cited alloy in a semi-solid state under isothermal conditions, together with the fact that said stirring is carried out by electromagnetic stirring and/or permanent magnets and/or bubbling of nitrogen or argon gas, i.e. it is a stirring wherein no mechanical shearing is applied, instead, under isothermal conditions, the end of solid nucleus enucleation with globular-like equiaxed growth is promoted, allowing to prepare an alloy characterized at the same time by:

a) globular equiaxed microstructure, i.e. not dendritic (see Fig. 2),

b) a low volume contraction for the terminal stage of solidification, where this latter property allowing the production of melted casting in the absence of hot tearing and/or shrinkage cavities (micro/macro shrinkage cavities).

[0021] Therefore, the novelty introduced by the metallurgical process object of the present invention relates to the double and joint action performed on the metal bath including stirring the bath without mechanical action of mixing simultaneously to the thermostatation of the bath itself which is maintained under isothermal condition at a temperature selected within the heat range as identified at point c) above, thus differently from what reported in the know art typically describing a not mechanical stirring which is instead performed by a continuous and gradual cooling of the semi-solid bath. As also well defined in the experimental section, the metallurgical effect provided by the above joint action of stirring and isothermal conditions maintainment is promoting the development of semi-globular shapes of the solid germs in suspension in the liquid mass which are already typical of semi-solid metallurgic processes in the presence of bath stirring, but in addition - and typically - the metallurgical process object of the present invention enhances the globularization effect due to the stirring action through the isothermal condition, that itself is the semi-liquid condition causing the equiaxed grows of the first germs of solid. A further advantage consists in making the semi-globular morphology of the solid germs under quasi-liquid conditions, therefore at a very low viscosity and with higher heat capacity of the mass to be poured than what usually occurs in the semi-solid phase casting process known in literature (the process object of the present invention allow to achieve a higher castability and processability of the semi-liquid mass).

[0022] Such benefits affect the manufacturing of objects made of magnesium alloy having complex shapes with, if required, thin walls being free of defects.

[0023] In other terms, the above-described specific process using stirring modes performed under isothermal conditions and in O_2-lean atmosphere and in the absence of mechanical stirring (i.e. carried out by electromagnets and/or by permanent magnets and/or by stirring carried out by bubbling nitrogen or argon gas) spontaneously result in the homogeneous formation of solidification nuclei with their subsequent equiaxed-type growth, such that to eliminate the above-mentioned lacks typical of conventional solidification (i.e. from 100% liquid conditions).

[0024] Therefore, the metal objects or pieces made of magnesium alloy manufactured according to the process of the invention have higher shape-definition and profile-precision with respect to both those obtained by the current "full-liquid" processes and those obtainable in the case a mechanical stirring is performed in the process of the present invention (see Fig. 2 and 3 comparison, particularly the lower micro-defects present in figure 2). The semi-solid magnesium alloy in a quasi-liquid state can have a solid fraction content ranging between about 0% and about 20%.

[0025] The quasi-liquid semi-solid magnesium alloy is a magnesium alloy non-flammable under certain conditions, i.e. a magnesium alloy known to be non-flammable, such as Mg-alloys comprising Ca and/or CaO (and, in substitution or in addition to Ca as anti-flammability, also Be and/or Y elements) and it can further comprise other elements usually used in foundry Mg-alloys.

[0026] The quasi-liquid semi-solid magnesium alloy must comprise Ca and/or calcium oxide and can optionally comprise other components, such as Be, Y and/or aluminum.

[0027] The semi-solid magnesium alloy in a quasi-liquid state comprises calcium and/or calcium oxide, and according to a preferred embodiment, the semi-solid magnesium alloy in a quasi-liquid state can further comprise aluminum.

[0028] The aluminum improves the mechanical properties in the aluminum alloys, but reducing the time of alloy self-combustion trigger in air.

[0029] According to a more preferred embodiment, the semi-solid magnesium alloy in a quasi-liquid state comprises calcium and/or calcium oxide in an amount ranging between 1% and 2 % by weight, i.e. weight-on-weight, and aluminum ranging between 2% and 9% by weight.

[0030] In step b), an atmosphere with an oxygen content lower than 10% mol. is achieved inside the apparatus. For this purpose, the apparatus is hermetically sealed and provided with a closed heated thermoregulation chamber, provided with at least one inlet channel to insufflate inert gas such as, for example, nitrogen or argon, and with an outlet channel to remove the air of the atmosphere containing oxygen to reduce O_2 concentration in the apparatus atmosphere below 10% mol. before the beginning of the semi-solid mass stirring.

[0031] The term 10% mol. means the oxygen content in dry atmosphere as oxygen moles with respect to the total moles. The oxygen content in dry atmosphere, means water-free atmosphere, steam or moisture. According to a preferred embodiment, the atmosphere has an oxygen content ranging between 0.1 and 10% mol., more preferably between 0.1% and 5% mol..

[0032] Optionally, the outlet channel can be connected with a vacuum pump to accelerate oxygen evacuation from the apparatus.

[0033] The quantification of the maximum oxygen content, that into the atmosphere of the closed apparatus in must be lower than 10% mol. can be carried out on the leaving gas effluent by the conventional oxygen-content detectors currently available on the market.

[0034] Step a) of loading the apparatus with melted magnesium alloy can be carried out by simple pouring of the melted Ca and/or CaO-added magnesium alloy prepared in another furnace through an opening, closeable, of the apparatus. Preferably, but not necessarily, the loading is carried out by a closable inlet mouth, maintaining open the inert gas inlet inside the apparatus chamber, such that the loading occurs under protective atmosphere, and in countercurrent.

[0035] In step d), the apparatus chamber is thermoregulated to get the temperature of the melted Ca and/or CaO-added magnesium alloy to a value such that a semi-solid magnesium alloy in a quasi-liquid state is made. The temperature at which the apparatus is set is a temperature below the one at which the alloy passes into a liquid state, but above the minimum temperature wherein the chemical composition of the alloy can locally vary due to the solidification, even partial, of one or more of its constituents; said minimum temperature depends on the composition of the magnesium alloy considered and it must be set such not more than 20% of solid fraction is present in the semi-solid magnesium alloy in a quasi-liquid state.

[0036] The temperature of the magnesium alloy can be controlled by a thermocouple submersed in the alloy itself.

[0037] According to a preferred embodiment, in step c) the melted magnesium alloy is cooled until a temperature within a ranged between 5°C and 15 °C, preferably between 5°C and 10°C, below the *liquidus* temperature (i.e. specific temperature of solidification beginning during the cooling of the overheated liquid) so as to make a semi-solid Ca and/or CaO-added magnesium alloy in a quasi-liquid state.

[0038] According to a more preferred embodiment in step c) the melted magnesium alloy is cooled until a temperature ranging between 570 °C and 610°C, even more preferably 580-595 °C.

[0039] In step c), the apparatus chamber is thermoregulated to maintain the magnesium alloy in a such isothermal temperature condition, below the temperature wherein the alloy passes into a liquid state, but above the minimum temperature for which the subsequent and essential step of isothermal stirring described at point d) makes the nucleation conditions of solid germs and the equiaxed growth thereof without the need of mechanically breaking of dendrites, which are conventional solidification structures.

[0040] The temperature of step d) is the same with respect to the temperature obtained to the end of step c).

[0041] According to a preferred embodiment, in step d) the isothermal condition is obtained by a constant temperature which is comprised in a temperature range set between 5° and 15°C below the temperature of liquidus of the specific alloy treated.

[0042] According to a preferred embodiment, in step d) the isothermal condition is carried out by a constant temperature ranging between 570°C and 610°C, more preferably between 580 °C and 600 °C, even more preferably between 580-595 °C.

[0043] In step d), the stirring under isothermal conditions is carried out for at least 20 seconds, preferably for a time ranging between 20 seconds and 30 minutes, more preferably between 60 seconds and 20 minutes, even more preferably between 60 seconds and 500 seconds.

[0044] In step d) the stirring can be carried out by electromagnetic stirring and/or by magnetic stirring with permanent magnets and/or by stirring carried out by bubbling nitrogen or argon gas.

[0045] According to a preferred embodiment, in step d) the stirring can be carried out by magnetic stirring with rotating permanent magnets.

[0046] According to a preferred embodiment, in step d) the stirring can be carried out by bubbling of nitrogen or argon gas. Such embodiment is preferred since nitrogen or argon gas resulting in the stirring of the magnesium alloy forms or contributes to the atmosphere formation with a maximum oxygen content equal to 10% mol. Therefore, in step d) the bubbling of nitrogen or argon gas is preferred, since it allows to maintain an atmosphere as defined in step b).

[0047] The bubbling of gaseous nitrogen or argon can be carried out by an apparatus having a drilled surface inside it from which nitrogen or argon are allowed to leaves.

[0048] Alternatively and preferentially, nitrogen, argon or other inert gases are bubbled below the free top surface of the metal bath through porous septa. According to a preferred embodiment, the bubbling of nitrogen or argon is carried out through a graphite tube or other inert ceramic material in Mg-bath at the presence, on the end-part thereof, of small holes (diameter < 0.5mm). The inert gas, collected from a classic cylinder or a gas line present in loco, flows inside the tube.

[0049] According to an even more preferred embodiment, in step d) the stirring can be carried out both by bubbling of nitrogen or argon gas and by magnetic stirring with rotating permanent magnets.

[0050] In step d) the stirring can be carried out by magnetic stirring with rotating permanent magnets. Such stirring is carried out through the rotation of permanent magnets around or partially around the external part of the apparatus wherein the magnesium alloy is prepared. Therefore, the magnetic stirring with rotating permanent magnets does not involve any physical contact between the magnesium alloy and the stirring system. The electromagnetic stirring, the magnetic stirring and the stirring carried out by bubbling of nitrogen or argon gas, allow to carry out the stirring action under isothermal conditions thus avoiding the use of mechanical stirrer whose integration inside the apparatus would cause several mechanical problems on one side, and subjecting the semi-solid magnesium alloy to shearing, which provides, as already said, worse results in terms of magnesium alloy homogeneity, on the other side. In fact, the stirring system through which carrying out step d) allows to avoid the use of complex mechanical architecture of the apparatus for the preparation of semi-solid magnesium alloys and provide a product with the best homogeneity i.e. less defects.

[0051] The step e) of discharging the semi-solid alloy in a quasi-liquid state from the apparatus can be carried out by pouring the content of the apparatus into another apparatus, for example in an injector or in a press.

[0052] Another object is a process for the preparation of objects consisting of magnesium alloy comprising the following steps:

1) preparing the magnesium alloy comprising calcium and/or calcium oxide in a liquid state;
2) preparing the semi-solid magnesium alloy comprising calcium and/or calcium oxide in a quasi-liquid state according to the process described above;
3) filling an injector with the semi-solid magnesium alloy in a quasi-liquid state of step 2) and injecting it into the mold of a press;
4) molding the object by the press;
5) discharging the object from the press.

[0053] Considering the characteristics given to the semi-solid magnesium alloy in a quasi-liquid state according to the process described above, the present process provides objects with high shapes definition and, then consequently, of the shapes details.

[0054] According to a preferred embodiment, in step 3) the filling of the injector with the semi-solid magnesium alloy in a quasi-liquid state is performed under an atmosphere with an oxygen content not higher than 10% mol..

EXPERIMENTAL SECTION

[0055] An apparatus as in the scheme reported in Fig.1 consisting of a crucible made of graphite which is closed by a sealed lid made of graphite having three openings, one for introducing the drilled tube at two different heights to provide the double function of oxygen atmosphere-depletion in the melting chamber (4) and of bubbling (7) chamber of the inert gas below the top free top surface of the metal bath, the second for the housing for the detection sensor (11) of oxygen percentage in the atmosphere of the chamber (12), the third opening - closable by a seal valve - used for the evacuation O_2-rich air, i.e. for the depletion of O_2 content in the atmosphere of chamber (4) was filled with 450 g of alloy of the AZ91D series added with 1.5%CaO. The cited alloy is commercially available.

[0056] The crucible was then closed with the sealed lid (2). Therefore, the valve of flux meter (9) was opened (9) for insufflating nitrogen inert gas and simultaneously the seal valve (1) was opened for evacuation of oxygen-rich atmosphere. By checking through the oxygen detection sensor (10, 11) O_2-content in the atmosphere present in the melting chamber (12), the maximum O_2 amount was obtained, as described in the present invention. Therefore, the heat unit (5) was actuated for the alloy melting at a temperature of 610 °C.

[0057] The thermocouple (14) inserted for contact with the bath though a hole directly arranged inside the nitrogen insufflating tube submerged in the metal bath allows to measure the actual bath temperature to be maintained within 10 °C below the liquidus temperature of the specific alloy used (in the specific case, the liquefaction temperature, also named liquidus, was equal to 597.6 °C).

[0058] During the entire bubbling step of 20 minutes, the bath was thermostated at a temperature of 590 °C to thermostat the bath at the temperature of 590 °C. At the end of the thermostated mixing at 590 °C by nitrogen insufflating, the mass was poured into a graphite mold pre-heated at 300 °C, for manufacturing cast specimens.

[0059] The cast specimens were sectioned by metallographic sample cut-off machine, smoothed and polished for the optical microscopic observation, for the validation of the globular equiaxed structure in Fig.2.

Claims

1. Metallurgical process for the preparation of a semi-solid magnesium alloy in a quasi-liquid state comprising the following steps:

a) loading an apparatus with melted magnesium alloy comprising calcium and/or calcium oxide,
b) achieving an atmosphere with an oxygen content not higher than 10% mol. inside said apparatus,
c) cooling the melted magnesium alloy of step b) until a semi-solid magnesium alloy in a quasi-liquid state is formed,
d) maintaining the semi-solid magnesium alloy in a quasi-liquid state of step c) under isothermal conditions at the temperature obtained by step c), stirring for at least 20 seconds by electromagnetic stirring and/or magnetic stirring with permanent magnets and/or by stirring carried out by bubbling nitrogen or argon gas,
e) discharging the semi-solid magnesium alloy in a quasi-liquid state from the apparatus.

2. Process according to claim 1, wherein the semi-solid magnesium alloy in a quasi-liquid state comprises a solid fraction content ranging between 0% and 20%.

3. Process according to any one of the claims from 1 to 2, wherein the semi-solid magnesium alloy in a quasi-liquid state comprises aluminum.

4. Process according to claim 3, wherein the semi-solid magnesium alloy in a quasi-liquid state comprises calcium and/or calcium oxide in an amount between 1% and 5% by weight and aluminum in an amount between 2% and 9% by weight.

5. Process according to any one of the claims from 1 to 4, wherein the steps a) and b) are reversed.

6. Process according to any one of the claims from 1 to 5, wherein in step d) the isothermal condition is obtained by a constant temperature which is comprised in a temperature range set between 5°C and 15 °C below the temperature of liquidus of the specific alloy treated.

7. Process according to any one of the claims from 1 to 6, wherein in step d) the time is between 60 and 500 seconds.

8. Process according to any one of the claims from 1 to 7, wherein in step d) the bubbling of nitrogen or argon gas allows to maintain an atmosphere with a maximum oxygen content equal to 10% mol. inside the apparatus.

9. Process for the preparation of objects consisting of magnesium alloy comprising the following steps:

1) preparation of the magnesium alloy comprising calcium and/or calcium oxide in a liquid state;
2) preparation of the semi-solid magnesium alloy in a quasi-liquid state comprising calcium and/or calcium oxide according to the process of any one of the claims from 1 to 8;
3) filling an injector with the semi-solid magnesium alloy in a quasi-liquid state of step 2) and injecting it into the mold of a press;
4) molding the object by the press;
5) discharging the object from the press.

10. Process according to claim 9, wherein the step 3) of filling the injector with the semi-solid magnesium alloy in a quasi-liquid state is performed under an atmosphere with an oxygen content not higher than 10% mol..

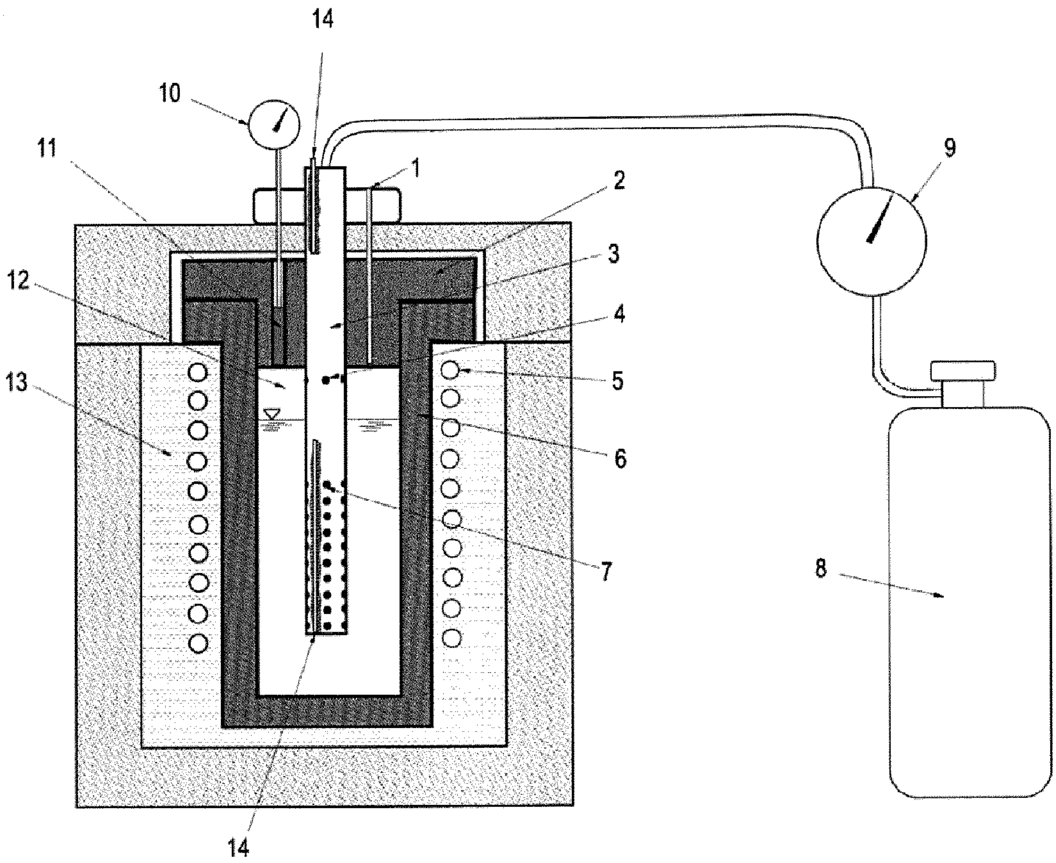

Fig. 1

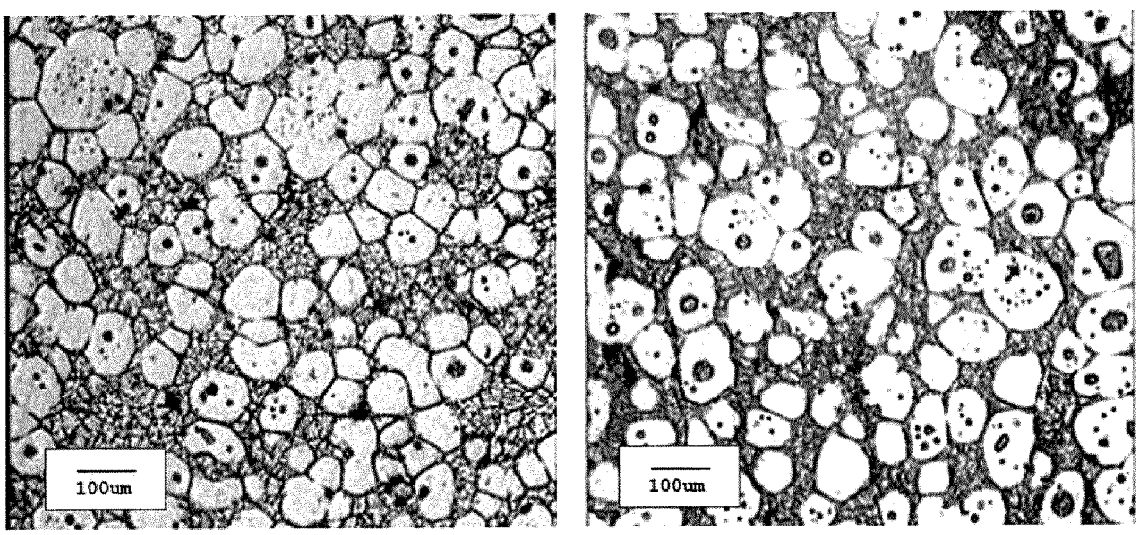

Fig. 2

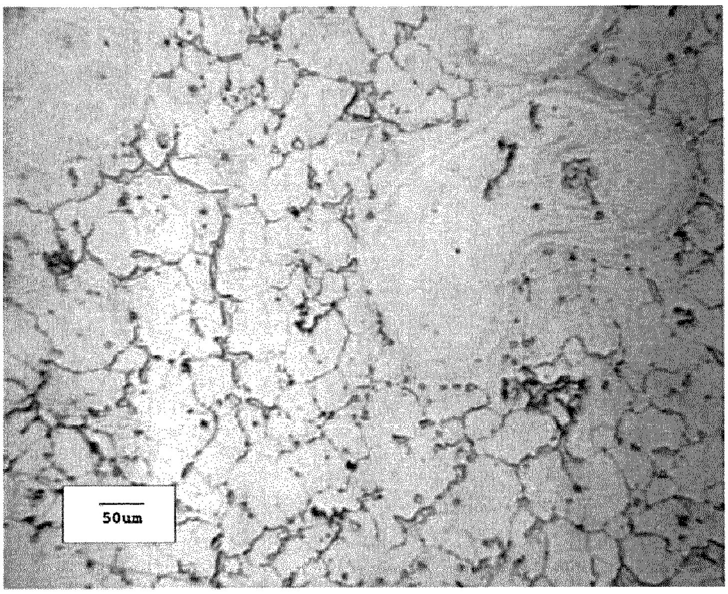

Fig. 3

Europäisches Patentamt
European Patent Office
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EUROPEAN SEARCH REPORT

Application Number
EP 20 20 8196

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	JIMEI MAO ET AL: "Semi-solid slurry preparation, rheo-die casting and rheo-squeeze casting of an AZ91-2Ca-1.5Ce ignition-proof magnesium alloy by gas-bubbling process", JOURNAL OF MATERIALS RESEARCH, vol. 32, no. 3, 20 January 2017 (2017-01-20), pages 677-686, XP055706913, US ISSN: 0884-2914, DOI: 10.1557/jmr.2016.517 * abstract * * Section II. Experimental Procedure, part A. Materials and Sample preparation * -----	1-10	INV. C22C23/00 B22D17/00
A	YING ZOU ET AL: "A New Casting Technique of Agitating Semi-Solid Magnesium Alloy Using a Gas Blowing Method", FOUNDRY, vol. 57, no. 3, 31 March 2008 (2008-03-31), pages 215-218, XP055707494, * abstract * * Section 1.1 Experiment material * * table 2 * -----	1-10	TECHNICAL FIELDS SEARCHED (IPC) C22C B22D
A	JIA XU ET AL: "Effects of rotating gas bubble stirring treatment on the microstructures of semi-solid AZ91-2Ca alloy", JOURNAL OF MAGNESIUM AND ALLOYS, vol. 1, no. 3, 12 September 2013 (2013-09-12), pages 217-223, XP055707485, * abstract * ----- -/--	1-10	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	22 January 2021	Rosciano, Fabio

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 20 20 8196

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	HUANG GUOJIE ET AL: "Influence of Stirring Processing Parameter on Grain Density of Semi-Solid AZ91 Magnesium Alloy", CHINESE JOURNAL OF RARE METALS, vol. 31, no. 5, 31 October 2007 (2007-10-31), pages 606-609, XP055707491, * abstract * -----	1-10	
A	HA N FU-YIN ET AL: "Effect of Electro-magnetic Stirring on Microstructure of Semisolid Magnesium Alloy AZ91D", FOUNDRY TECHNOLOGY, vol. 26, no. 6, 30 June 2006 (2006-06-30), pages 497-507, XP055707497, * abstract * -----	1-10	
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- **SAKAMOTO, MITSURU et al.** Suppression of ignition and burning of melted Mg alloys by Ca bearing stable oxide film. *Journal of Materials Science Letters,* 1997, vol. 16, 1048-1050 **[0008]**