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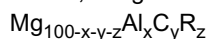
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Remarks:
Amended claims in accordance with Rule 137(2) EPC.

(54) **Magnesium-aluminum based alloy with grain refiner**

(57) The present invention relates to magnesium-aluminum based alloys having a small grain size and to a method of their production. The alloys are particularly useful in casting applications. The alloys comprise a grain refiner, the grain refiner having the chemical formula:



wherein R is an element selected from the group consisting of silicon, calcium, strontium or a rare earth element, x is from 10 to 60 At.%, y is from 5 to 50 At.%, and z is from 0 to 20 At.%, provided that x+y+z is less than 100 At.%.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to magnesium-aluminum based alloys having a small grain size and to a method of their production. The alloys are particularly useful in casting applications.

[0002] Magnesium alloy developments have traditionally been driven by aerospace industry requirements for light-weight materials to operate under increasingly demanding conditions. Magnesium alloys have always been attractive to designers due to their low density, only two thirds that of aluminium. This has been a major factor in the widespread use of magnesium alloy castings and wrought products.

10 **[0003]** A further requirement in recent years has been for superior corrosion performance and dramatic improvements have been demonstrated for new magnesium alloys. Improvements in mechanical properties and corrosion resistance have led to greater interest in magnesium alloys for aerospace and speciality application.

15 BACKGROUND OF THE INVENTION

[0004] Suitability of magnesium alloys is generally improved with smaller grain size. A small grain size generally accounts for improved mechanical properties and structural uniformity of magnesium alloys, resulting in better machinability, good resistance to hot tearing and superior extrudability. Numerous components are produced by extrusion, rolling or forging from cast billets. Thus, a small grain size of magnesium alloys in casting is important not only for the service performance of as-cast products but also for the components which are necessary for performing the secondary processing.

20 **[0005]** Generally magnesium alloys can be classified into two broad groups: aluminum free and aluminum bearing magnesium alloys. Aluminum-free alloys mainly refer to those containing zinc or grain refined by zirconium such as ZE41, ZK60, WE43 and EZ33. In these alloys, the grain sizes can be controlled and reduced by adding zirconium. The exceptional grain-refining ability of zirconium does not function in aluminum bearing alloys such as AM50, AM60, and AZ91, as aluminum and zirconium can readily interact to form stable intermetallic phases, which are unfortunately ineffective as nucleants for magnesium grains. Therefore, a suitable grain refiner for magnesium-aluminum alloys is still desirable.

30 STATE OF THE ART

[0006] Various approaches to decrease the grain size of magnesium-aluminum alloys have been explored.

35 **[0007]** In the superheating method, the magnesium alloys are heated to around 150 to 250°C above their melting point, maintained at that temperature for 5 to 15 minutes, and then rapidly cooled to the casting temperature. The grain refining mechanism was suggested to be a heterogeneous nucleation by an Al-Mn-Fe compound. Some basic features have to be observed during the superheating method. Firstly, a specific temperature range above the pouring temperature is required to maximize the grain refining effect. Secondly, rapid cooling from the overheating temperature to the pouring temperature and the short holding time are also crucial requirements to produce fine grains. Because of the high temperature, the energy costs of this method are comparatively high, and there is also the expense involved in preventing oxidation of the melt and in casting ladle checking and maintenance procedures.

40 **[0008]** Carbon inoculation is another major and effective grain refining approach developed to date for magnesium-aluminum based alloys. The key step of this process is the introduction of carbon into the molten magnesium. The grain refining mechanism is said to be heterogeneous nucleation by aluminum carbide (Al_4C_3) produced by carbon in the compound reacting with aluminum in the melt. In commercial processes C_7Cl_6 was added as a grain refiner, but this is no longer allowed because it produces harmful gases. Also, the inorganic carbon, such as graphite, carbon and wax were investigated as a grain refiner. However, their effects on the grain refinement are limited.

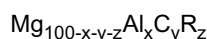
45 **[0009]** In the Elfinal method ferric chloride is added to a melt at around 760°C, and the melt is at this temperature maintained for 30 to 60 minutes, giving rise to the formation of an Al-Mn-Fe compound that was said to produce the grain refinement. It has been reported that in order to obtain a pronounced refinement effect, the manganese content has to be above a critical value. The problem with this method is the deterioration of corrosion resistance caused by a localized battery effect of the Fe and Mn.

50 **[0010]** The above methods are described e.g. in Y.C. Lee et al. Metallurgical and Materials Transactions, Vol. 31A, 2000, pages 2805-2906.

55 **[0011]** In summary, there are still no satisfying approaches to refine the grain of as-cast magnesium-aluminum alloys. Therefore, it is an objective of the present invention to provide an improved method of grain refining of magnesium-aluminum based alloys.

SUMMARY OF THE INVENTION

[0012] In a first aspect, the present invention provides a magnesium-aluminum alloy comprising a grain refiner, the grain refiner having the chemical formula:

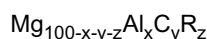


wherein R is an element selected from the group consisting of silicon, calcium, strontium or a rare earth element, x is from 10 to 60 At.%, y is from 5 to 50 At.%, and z is from 0 to 20 At.%, provided that x+y+z is less than 100 At.%. Preferably, x is from 20 to 50 At.%; further preferably y is from 10 to 35 At.%; and further preferably z is from 1 to 20 At.%.
10

[0013] Preferably, the rare earth element is selected from the group consisting of lanthanum, cerium, neodymium, samarium, europium and rare earth mischmetal.

[0014] The magnesium-aluminum alloy preferably comprises the grain refiner in an added amount of 0.1 to 2% by weight of the initial weight of the alloy. The magnesium-aluminum alloy can be any conventional alloy comprising magnesium and aluminum. Preferably, the magnesium-aluminum alloy is selected from the group consisting of magnesium-aluminum-zinc alloys and magnesium-aluminum-manganese alloys, more preferably, the alloy is selected from the group consisting of AM50, AM60, AM201, AZ10, AZ31, AZ63, AZ80 and AZ91.
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[0015] In a second aspect, the present invention provides a method for producing a magnesium-aluminum alloy having fine grain, which comprises melting an alloy comprising magnesium and aluminum under a protective gas atmosphere, adding to the molten magnesium-aluminum alloy a grain refiner having the chemical formula:
20



wherein R is an element selected from the group consisting of silicon, calcium, strontium or a rare earth element, x is from 10 to 60 At.%, y is from 5 to 50 At.%, and z is from 0 to 20 At.%, provided that x+y+z is less than 100 At.%, and allowing the alloy to solidify. Preferably, the rare earth element is selected from the group consisting of lanthanum, cerium, neodymium, samarium, europium and rare earth mischmetal.
25

[0016] The magnesium-aluminum alloy preferably comprises the grain refiner in an added amount of 0.1 to 2% by weight of the initial weight of the alloy. The magnesium-aluminum alloy can be any conventional alloy comprising magnesium and aluminum. Preferably, the magnesium-aluminum alloy is selected from the group consisting of magnesium-aluminum-zinc alloys and magnesium-aluminum-manganese alloys, more preferably, the alloy is selected from the group consisting of AM50, AM60, AM201, AZ10, AZ31, AZ63, AZ80, AZ91, AE44, AE42, AJ53, AS41 and AS42.
30

[0017] Preferably, the molten magnesium-aluminum alloy comprising the grain refiner is cast prior to allowing the alloy to solidify. Preferably the protective gas comprises an inert gas such as a noble gas, e.g. helium or argon. More preferably the protective gas is a mixture of argon and SF₆.
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[0018] The grain refiner is preferably prepared by high energy milling, which is an effective method for preparing the desired grain refiner, which has a comparatively high melting point, by solid phase reaction.

[0019] The grain refiner can be added to the melt of magnesium-aluminum alloy in a similar fashion to zirconium in aluminum-free magnesium alloys. Then the prepared refiner is added in the melt of magnesium alloys as nucleants.
40

[0020] When preparing the grain refiner by high energy milling, the following processing parameters should preferably be observed:

Preferably the milling rate is between 600 and 1300 rpm, more preferably between 800 and 1100 rpm.

[0021] During the milling the protective gas atmosphere is preferably continuously or intermittently renewed in order to prevent oxidation of magnesium and/or aluminum during the milling process. If the protective gas atmosphere is renewed intermittently, renewing of the atmosphere preferably takes place at least 3 times, more preferably at least 5 times during the milling process.
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[0022] Preferably a mill ball made of zirconium oxide or high strength steel is used during the milling process in order to decrease the harmful effects caused by iron. In a ball mill, the ratio of ball to powder preferably lies between 5:1 and 10:1, more preferably between 6:1 and 8:1. The milling time is preferably chosen to be between 4 hours and 8 hours, more preferably between 5 hours and 7 hours. The dwell time before starting the milling process is preferably chosen to be between 1 hour and 4 hours, more preferably between 1 hour and 3 hours.
50

[0023] When preparing the grain refiner by high energy milling the materials shall preferably be used in form of their powders. The particle sizes of materials used to prepare the grain refiner by high energy milling is preferably between 100 μm and 400 μm, more preferably between 250 μm and 350 μm. Materials used to prepare the grain refiner preferably have a purity of from 99 % to 99.999%, more preferably between 99.9% and 99.99%.
55

[0024] It is preferred that the grain refiner is milled to a particle sizes of between 0.1 nm and 50 nm, more preferably

between 0.1 nm and 10 nm.

[0025] The grain refiner according to the present invention is particularly effective for cast magnesium-aluminum alloys. This includes e.g. gravity-cast magnesium-aluminum based alloys, die casting magnesium-aluminum based alloys, semi solid casting magnesium-aluminum based alloys, rheocasting magnesium-aluminum based alloys and continuous casting magnesium-aluminum based alloys.

[0026] In the method for producing a magnesium-aluminum alloy having fine grain the temperature of the molten alloy is preferably 720°C or higher in order to avoid the segregation of the nanoparticles of the grain refiner. The more elevated the temperature, the shorter the time it takes to achieve the grain refinement. However, since too high a temperature can result in ignition of the molten material, a temperature of the melt between 720°C and 760°C is preferable, most preferably around 750°C.

[0027] The content of grain refiner added in cast magnesium-aluminum based alloys is preferably between 0.1 and 2% by weight, more preferably between 0.5 and 1.5% by weight. When the content of its addition is below 0.1% by weight, the effect of grain refinement may not be sufficient. When the content of its addition is higher than 2% by weight, the residual grain refiner may influence the properties of magnesium alloys.

[0028] The melt is preferably stirred in order to obtain homogeneously distributed alloys. The stirring speeds are preferably between 150 rpm and 300 rpm, more preferably between 150 and 250 rpm. The stirring time is preferably between 10 min and 60 min, more preferably between 20 min and 40 min.

[0029] The dwell time after the addition of grain refiner is advantageous for the grain refinement of cast magnesium-aluminum based alloys. The dwell time should preferably be between 10 min and 90 min, more preferably between 30 min and 60 min.

[0030] Examples of the present invention will now be described. However, it is to be understood that the invention is not limited to the examples described below.

BRIEF DESCRIPTION OF THE FIGURES

[0031]

FIGS. 1(a)-(c) are optical microstructures showing the grain refining efficiency of as-received powders when added to magnesium-3 wt.% aluminum alloy at 750°C. FIG 1(a) is magnesium-3 wt.% aluminum alloy. FIG. 1(b) is magnesium-3 wt.% aluminum alloy containing 1 wt. % grain refiner $Mg_{0.3}Al_{0.4}C_{0.15}Ca_{0.15}$ with milling time for 20 hours. The stirring time is 30 minutes during melting. FIG. 1(c) is magnesium-3 wt. % aluminum alloy containing 1 wt.% grain refiner $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ with milling time for 20 hours. The stirring time is 30 minutes during melting.

FIG.2 are optical microstructures showing the grain refining efficiency of as-received powders when added to magnesium-3 wt.% aluminum alloy at 750°C. FIG. 2(a) is magnesium-3 wt.% aluminum alloy containing 0.5 wt.% $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ grain refiner with milling time for 20 hours. FIG. 2(b) is magnesium-3 wt.% aluminum alloy containing 0.8 wt.% $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ grain refiner with milling time for 20 hours.

FIG. 2(c) is magnesium-3 wt.% aluminum alloy containing 1 wt. % $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ grain refiner with milling time for 20 hours.

FIG. 3 shows the relationship between average grain sizes of magnesium-3 wt.% aluminum alloys and the content of $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ grain refiner with milling time for 20 hours.

The smallest grain is obtained when adding 1.5 wt.% grain refiner.

FIG. 4 shows the relationship between average grain sizes of magnesium-3 wt.% aluminum alloys and the milling time of $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ grain refiner. The content of $Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15}$ is 1.0 wt%. The smallest grain is observed in the alloy when the grain refiner was milled for 20 hours.

FIG. 5 shows average grain sizes of magnesium-3wt.% aluminum alloys by adding the different contents of $Mg_{0.3}Al_{0.4}C_{0.15}Ca_{0.15}$ grain refiner with milling time for 20 hours.

EXAMPLE 1

Preparation of grain refiner:

[0032] In this example, the compositions of powder before milling are shown in Table 1, in which the unit is "atom %".

TABLE 1

Compositions	Mg	Al	C	RE
Before milling	30	40	15	15
Milled 5 h	28	42	16	14
Milled 10 h	27	43	15	15
Milled 15 h	26	43	15	16
Milled 20 h	26	43	14	17

[0033] A cylindrical steel pot was used to prepare the grain refiner. In order to prevent the powder from oxidation at high temperatures during the milling process, pure argon was used to clean the atmosphere for 5 times. The milling speed was 1000 rpm. A zirconium oxide ball was selected, and the ratio of ball to powder was 8:1. The milling time was 5-20 hours (see Table 1). In order to keep the reaction among the different powder continuously, the dwell time between two millings was 2 hours. During the milling process, the crucible canopy was not opened. The compositions of samples after milled for different time are listed in Table 1.

[0034] Refining process of magnesium-aluminum alloy:

In this example, magnesium-3 wt.% aluminum alloy was selected to investigate the role of the new grain refiner. 700 grams of pure magnesium preheated at 400 °C was melted at 750 °C in the steel crucible. Mixed gas of SF₆ and argon was used as protective gas. Preheated 300 grams of pure aluminum were added into the melt. Then, it took 15 minutes to stir the melt. Grain refiners with a size of below 20 nm were added into the liquid. The addition of grain refiners into the melt was repeated three times. After adding the grain refiner, the melt was further stirred for 30 minutes. Then, the alloys were cast after dwelling for 30 minutes. An optical microscope was used to observe the morphology of grain of the cast alloys. The average grain size in each case was measured.

[0035] FIGS. 1(a)-(c) are optical microstructures showing the grain refining ability of as-received powders after they were added to magnesium-3wt.% aluminum alloy at 750 °C. It can be found that the grain size decreases with the addition of different grain refiners.

[0036] FIG. 2 are optical microstructures showing the grain refining efficiency of as-received powders after they were added to magnesium-3 wt.% aluminum alloy at 750°C. The grain size reduces with increasing the content of grain refiners. The detailed values are shown in FIG. 3. The smallest value of grain size is obtained when adding 1.5 wt.% grain refiner. The smallest average grain size is 67 μm.

[0037] FIG 4 shows the relationship between the average grain size of magnesium-3 wt.% aluminum alloys and the milling time of Mg_{0.3}Al_{0.4}C_{0.15}RE_{0.15} grain refiner. The smallest grain size is observed in the alloy by adding the grain refiner with milling time for 20 hours.

EXAMPLE 2

Preparation of grain refiner:

[0038] In this example, the compositions of powder before milling are shown in Table 2, in which the unit is "atom %".

TABLE 2

Compositions	Mg	Al	C	Ca
Before milling	30	40	15	15
Milled 5 h	28	42	15	15
Milled 10 h	27	43	15	15
Milled 15 h	26	43	15	15
Milled 20 h	26	43	14	16

[0039] A cylindrical steel pot was used to prepare the grain refiner. In order to prevent the powder from oxidation at

high temperature during the milling process, the pure argon was used to clean the atmosphere for 5 times. The milling speed was 1000 rpm. A zirconium oxide ball was selected, and the ratio of ball to powder was 8:1. The milling time was 5-20 hours (see Table 2). In order to keep the reaction among the different powders continuously, the dwell time between two milling was 2 hours. During the milling process, the crucible canopy should not be opened. The compositions of samples after milled for different time are also listed in Table 2.

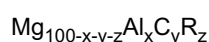
[0040] Refining process of magnesium-aluminum alloy:

In this example, magnesium-3 wt.% aluminum alloy was selected to investigate the role of the new grain refiner. 700 grams of pure magnesium preheated at 400°C was melted at 750°C in the steel crucible. Mixed gas of SF₆ and argon was used as protective gas. Preheated 300 grams of pure aluminum were added into the melt of magnesium alloy. Then, it took 15 minutes to stir the liquid. Grain refiners with a size of below 20 nm were added into the liquid. The addition of grain refiners into the melt was repeated three times. After adding the grain refiner, the melt was further stirred for 30 minutes. Then, the alloys were cast after dwelling for 30 minutes. An optical microscope was used to observe the morphology of grains of the cast alloys. The average grain size in each case was measured.

[0041] The typical microstructure of magnesium-3 wt.% aluminum alloy with the addition of grain refiner Mg_{0.3}Al_{0.4}C_{0.15}Ca_{0.15} is shown in FIG. 1(b). Compared with the magnesium-3 wt.% aluminum alloy, the grain is largely refined after the addition of this refiner. FIG. 5 shows the average grain size as a function of the content of grain refiner Mg_{0.3}Al_{0.4}C_{0.15}Ca_{0.15} added to magnesium-3 wt.% aluminum alloy. The grain size decreases with increasing the content of refiner. After adding more than 1 wt.% refiners, the grain size tends to be stable.

Claims

1. A magnesium-aluminum alloy comprising a grain refiner, the grain refiner having the chemical formula:



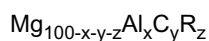
wherein R is an element selected from the group consisting of silicon, calcium, strontium or a rare earth element, x is from 10 to 60 At.%, y is from 5 to 50 At.%, and z is from 0 to 20 At.%, provided that x+y+z is less than 100 At.%.

2. The magnesium-aluminum alloy according to claim 1, which comprises the grain refiner in an added amount of 0.1 to 2% by weight of the initial weight of the alloy.
3. The magnesium-aluminum alloy according to any of the previous claims, wherein the rare earth element is selected from the group consisting of lanthanum, cerium, neodymium, samarium, europium and rare earth mischmetal.
4. The magnesium-aluminum alloy according to any of the previous claims, wherein the magnesium-aluminum alloy is selected from the group consisting of magnesium-aluminum-zinc alloys and magnesium-aluminum-manganese alloys.
5. The magnesium-aluminum alloy according to claim 4, wherein the alloy is selected from the group consisting of AM50, AM60, AM201, AZ10, AZ31, AZ63, AZ80, AZ91, AE44, AE42, AJ53, AS41 and AS42.
6. A method for producing a magnesium-aluminum alloy having fine grain, which comprises melting an alloy comprising magnesium and aluminum under a protective gas atmosphere, adding to the molten magnesium-aluminum alloy a grain refiner according to any of claims 1 to 6, and allowing the alloy to solidify.
7. The method of claim 6, wherein the molten magnesium-aluminum alloy comprising the grain refiner is cast prior to allowing the alloy to solidify.
8. The method of any of claims 6 or 7, wherein the protective gas comprises argon.
9. The method of claim 6, wherein the protective gas further comprises SF₆.
10. The method according to any of claims 6 to 9, wherein the grain refiner is used in the form of a milled powder having a particle size of less than 50 nm.

11. The method according to any of claims 6 to 10, wherein the molten magnesium-aluminum alloy is stirred between 10 minutes and 60 minutes after adding the grain refiner.

5 **Amended claims in accordance with Rule 137(2) EPC.**

1. A grain refiner for use in a magnesium aluminum alloy having the chemical formula:



10 wherein R is an element selected from the group consisting of silicon, calcium or strontium, x is from 10 to 60 At.%, y is from 10 to 35 At.%, and z is from 1 to 20 At.%, provided that x+y+z is less than 100 At.%.

- 15 **2.** A method for producing a magnesium-aluminum alloy having fine grain, which comprises melting an alloy comprising magnesium and aluminum under a protective gas atmosphere, adding to the molten magnesium-aluminum alloy a grain refiner according to claim 1, and allowing the alloy to solidify.

- 20 **3.** The method of claim 2, wherein the molten magnesium-aluminum alloy comprising the grain refiner is cast prior to allowing the alloy to solidify.

- 4.** The method of any of claims 2 or 3, wherein the protective gas comprises argon.

- 5.** The method of claim 4, wherein the protective gas further comprises SF₆.

- 25 **6.** The method according to any of claims 2 to 5, wherein the grain refiner is used in the form of a milled powder having a particle size of less than 50 nm.

- 7.** The method according to any of claims 2 to 6, wherein the molten magnesium-aluminum alloy is stirred between 10 minutes and 60 minutes after adding the grain refiner.

- 30 **8.** The method of any of claims 2 to 7, wherein the magnesium aluminum alloy is selected from the group consisting of magnesium-aluminum-zinc alloys and magnesium-aluminum-manganese alloys.

- 35 **9.** The method of claim 8, wherein the magnesium aluminum alloy is selected from the group consisting of AM50, AM60, AM201, AZ10, AZ31, AZ63, AZ80, AZ91, AE44, AE42, AJ53, AS41 and AS42.

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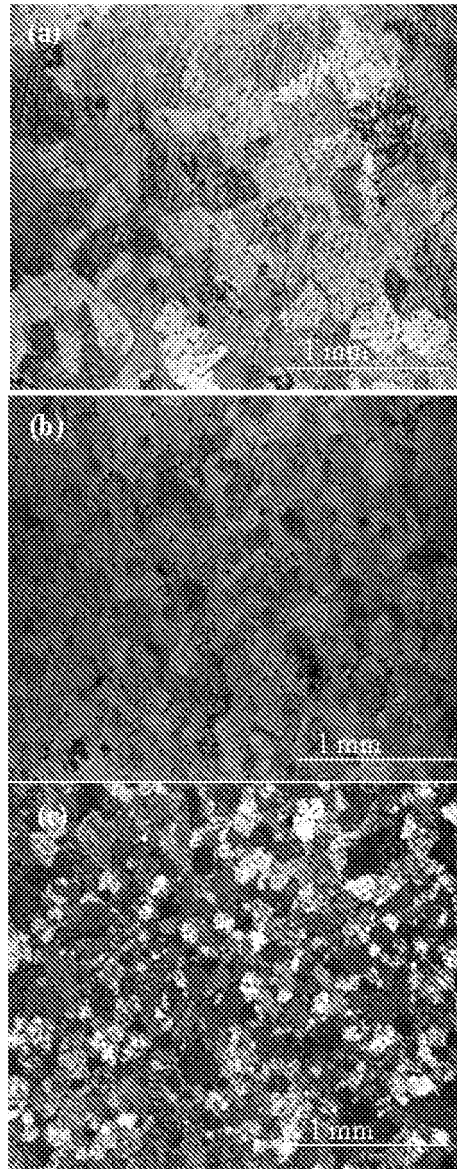


FIG. 1

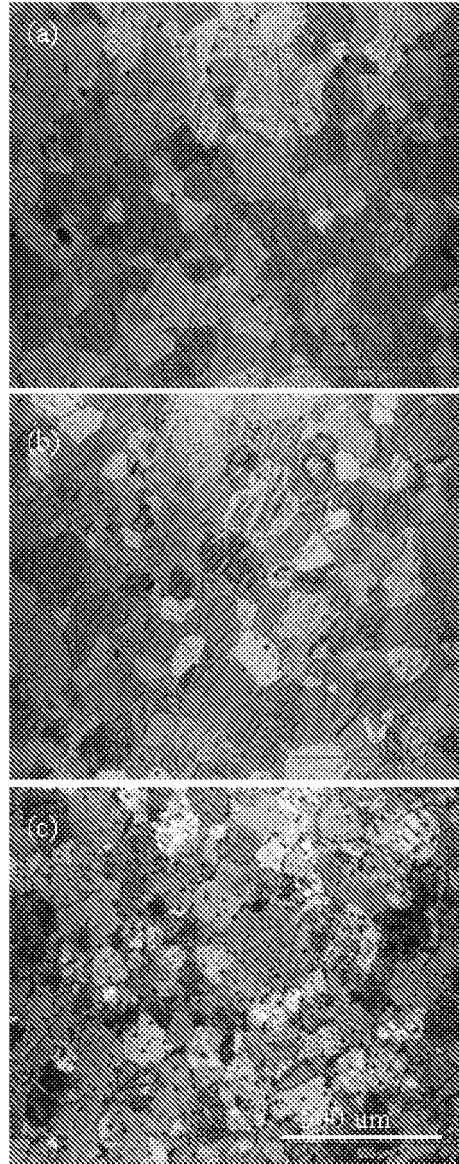


FIG. 2

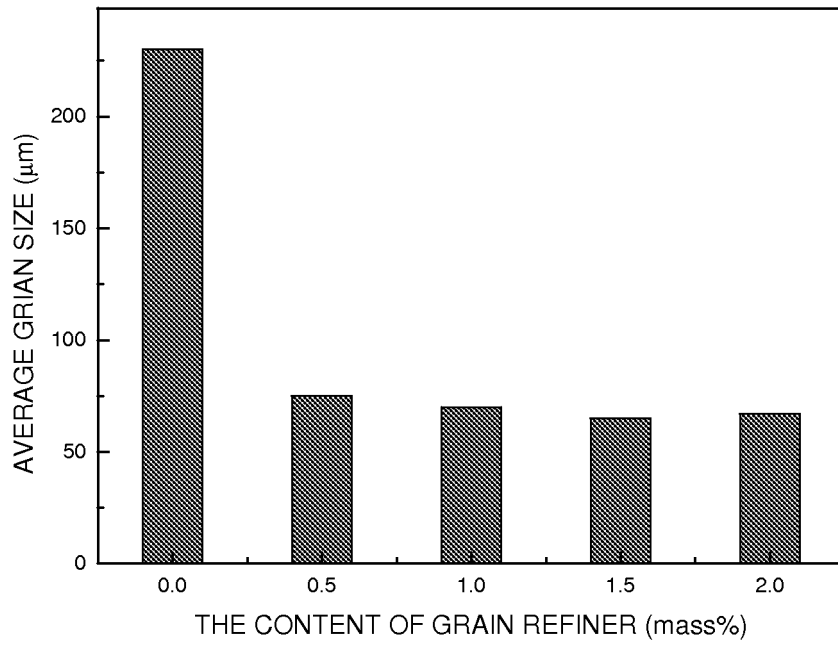


FIG. 3

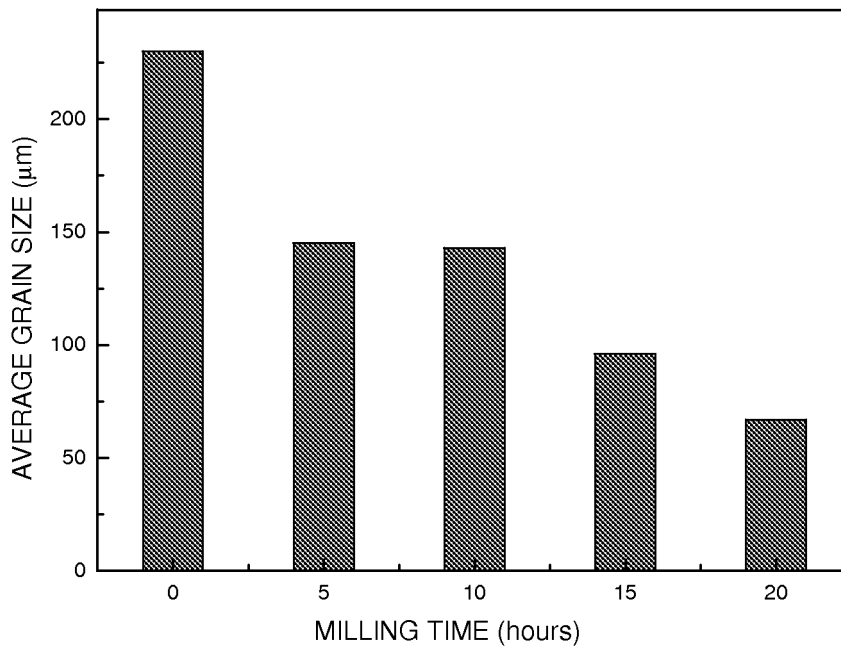


FIG. 4

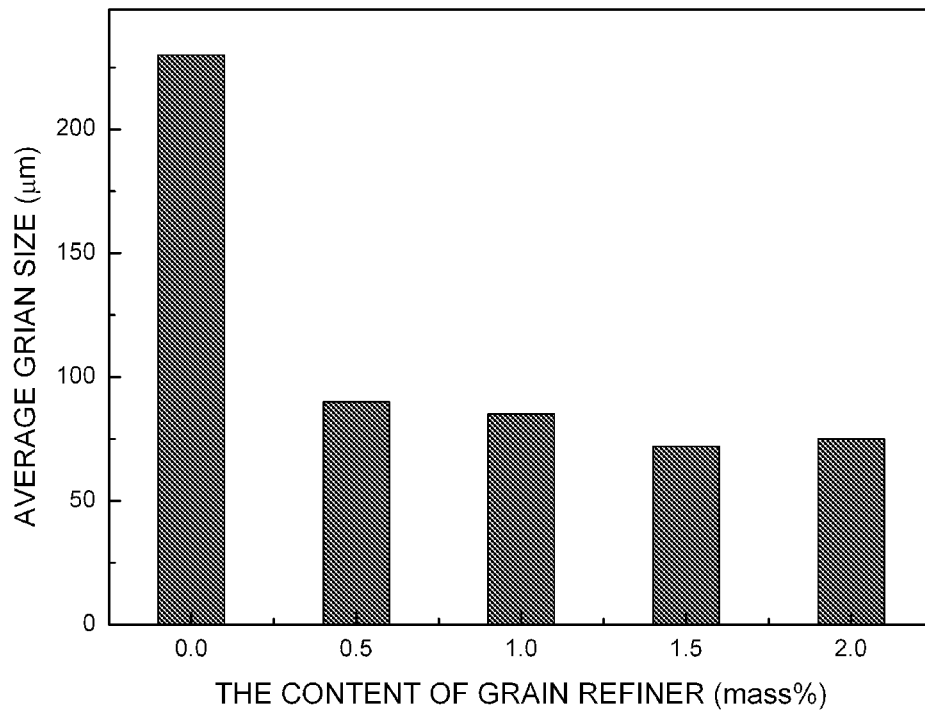


FIG. 5



EUROPEAN SEARCH REPORT

Application Number
EP 11 15 2825

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	CN 101 774 013 A (UNIV SOUTH CHINA TECH) 14 July 2010 (2010-07-14) * EP0DOC abstract * * paragraph [0029] - paragraph [0031] * * paragraph [0058] - paragraph [0074] * * claims * -----	1-11	INV. C22C1/03 C22C23/02 B22D27/20
X	CN 101 135 013 A (UNIV WUHAN TECH [CN]) 5 March 2008 (2008-03-05) * EPODOC abstract * * page 4, line 31 - line 35 * * page 5, line 16 - line 28 * * page 6; examples 1-3 * * claims * -----	1-11	
X	CN 1 410 566 A (UNIV SHANDONG [CN]) 16 April 2003 (2003-04-16) * EPODOC abstract * * claims * -----	1-11	
A	US 2007/181226 A1 (ZENG XIAOQIN [CN] ET AL) 9 August 2007 (2007-08-09) * the whole document * -----	1-11	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC) C22C B22D
Place of search Munich		Date of completion of the search 4 November 2011	Examiner Patton, Guy
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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04-11-2011

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- **Y.C. LEE et al.** *Metallurgical and Materials Transactions*, 2000, vol. 31A, 2805-2906 **[0010]**