(19)

Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

(11) **EP 2 987 875 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
24.02.2016 Bulletin 2016/08

(21) Application number: **14785713.0**

(22) Date of filing: **14.04.2014**

(51) Int Cl.:
C22C 1/02 [(2006.01)]   *B22D 21/04* [(2006.01)]
B22D 27/04 [(2006.01)]   *C22C 23/04* [(2006.01)]
C22C 23/06 [(2006.01)]

(86) International application number:
PCT/JP2014/061105

(87) International publication number:
WO 2014/171549 (23.10.2014 Gazette 2014/43)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME

(30) Priority: **15.04.2013 JP 2013084866**

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(54) **FIRE-RESISTANT MAGNESIUM ALLOY AND PRODUCTION METHOD THEREFOR**

(57)   A method of manufacturing a flame-retardant magnesium alloy having mechanical properties of a long period stacking ordered magnesium alloy and having an ignition temperature of 800°C or more is provided. The method of manufacturing a flame-retardant magnesium alloy comprises a step of melting a flame-retardant magnesium alloy which contains a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg, and a, b and x satisfy formulae 1 to 4 below.

$$(\text{Formula 1}) \quad 0.5 \leq a < 5.0$$

$$(\text{Formula 2}) \quad 0.5 < b < 5.0$$

$$(\text{Formula 3}) \quad 2/3a - 5/6 \leq b$$

$$(\text{Formula 4}) \quad 0 < x \leq 0.5$$

EP 2 987 875 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a flame-retardant magnesium alloy and a method of manufacturing the same.

BACKGROUND ART

[0002] A conventional long period stacking ordered (LPSO) magnesium alloy (refer to, for example, patent literatures 1 to 3) has mechanical properties of high strength and high ductility. The melting and casting temperature of this long period stacking ordered magnesium alloy is 750°C. Since this temperature is close to an ignition temperature, it is dangerous to perform the melting and casting in the air. Therefore, in performing the melting and casting, there has been a necessity of performing an operation thereof under an atmosphere (for example, under an atmosphere of vacuum and an inert gas) in which the combustion of the magnesium alloy is prevented. This increases the cost. In particular, since SF_6 that is used as an inert gas has 23,900 times as high global warming potential as carbon dioxide, SF_6 is harmful to the environment, and thus the utilization needs to be prevented.

PRIOR ART DOCUMENTS

[0003]

Patent literature 1: Japanese Patent No. 3905115
Patent literature 2: Japanese Patent No. 3940154
Patent literature 3: Japanese Patent No. 4139841

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED

[0004] An aspect of the present invention has an object to provide a flame-retardant magnesium alloy having mechanical properties of a long period stacking ordered magnesium alloy and having an ignition temperature of 800°C or more and a method of manufacturing the same.

SOLUTION TO THE PROBLEM

[0005] Hereinafter, various aspects of the present invention will be described.

[1] A method of manufacturing a flame-retardant magnesium alloy comprising a step of melting a flame-retardant magnesium alloy which contains a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg, wherein a, b and x satisfy formulae 1 to 4 below.

$$\text{(Formula 1)} \ 0.5 \leq a < 5.0$$

$$\text{(Formula 2)} \ 0.5 < b < 5.0$$

$$\text{(Formula 3)} \ 2/3a - 5/6 \leq b$$

$$\text{(Formula 4)} \ 0 < x \leq 0.5 \ \text{(preferably,} \ 0.1 \leq x \leq 0.5, \text{ and}$$

$$\text{further preferably,} \ 0.15 \leq x \leq 0.5)$$

[2] A method of manufacturing a flame-retardant magnesium alloy comprising a step of melting a flame-retardant magnesium alloy which contains a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg, wherein

a, b and x satisfy formulae 1 to 4 below.

$$\text{(Formula 1)} \quad 0.25 \leq a \leq 5.0$$

$$\text{(Formula 2)} \quad 0.5 \leq b \leq 5.0$$

$$\text{(Formula 3)} \quad 0.5a \leq b$$

$$\text{(Formula 4)} \quad 0 < x \leq 0.5 \text{ (preferably, } 0.1 \leq x \leq 0.5, \text{ and}$$

$$\text{further preferably, } 0.15 \leq x \leq 0.5)$$

[3] The method of manufacturing a flame-retardant magnesium alloy in [1] or [2] above, wherein the flame-retardant magnesium alloy has an ignition temperature of 800°C or more (preferably, 850°C or more).
[4] The method of manufacturing a flame-retardant magnesium alloy in any one of [1] to [3] above, wherein the flame-retardant magnesium alloy is melted at a temperature of 800°C or less (preferably, 850°C or less).
[5] The method of manufacturing a flame-retardant magnesium alloy in any one of [1] to [4] above, wherein the flame-retardant magnesium alloy is melted, and then the melted flame-retardant magnesium alloy is cast.
[6] The method of manufacturing a flame-retardant magnesium alloy in [5] above, wherein a cooling rate in casting the flame-retardant magnesium alloy is 1000K/second or less (preferably, 100K/second or less).
[7] The method of manufacturing a flame-retardant magnesium alloy in any one of [1] to [6] above, wherein the flame-retardant magnesium alloy contains y atomic% of Al, and y satisfies formula 5 below.

$$\text{(Formula 5)} \quad 0 < y \leq 0.5 \text{ (preferably, } 0.05 \leq y \leq 0.5)$$

[8] The method of manufacturing a flame-retardant magnesium alloy in [1] or [7] above, wherein the flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7 below or formula 7 and formula 8 below.

$$\text{(Formula 6)} \quad 0 \leq c < 2.0$$

$$\text{(Formula 7)} \quad 0.2 \leq b + c \leq 6.0$$

$$\text{(Formula 8)} \quad c/b \leq 1.5$$

[9] The method of manufacturing a flame-retardant magnesium alloy in [2] or [7] above, wherein the flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7 below.

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0.1 \leq b + c \leq 6.0$$

[10] The method of manufacturing a flame-retardant magnesium alloy in [1] or [7] above, wherein the flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 8 and formula 9 below.

$$\text{(Formula 8)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 9)} \quad 0.2 \leq b + c \leq 6.0$$

[11] The method of manufacturing a flame-retardant magnesium alloy in [2] or [7] above, wherein the flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 8 and formula 9 below.

$$\text{(Formula 8)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 9)} \quad 0.1 \leq b + c \leq 6.0$$

[12] The method of manufacturing a flame-retardant magnesium alloy in [1] or [7] above, wherein the flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 or formulae 8 and 9 below.

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0 \leq d < 2.0$$

$$\text{(Formula 8)} \quad 0.2 \leq b + c + d \leq 6.0$$

$$\text{(Formula 9)} \quad d/b \leq 1.5$$

[13] The method of manufacturing a flame-retardant magnesium alloy in [2] or [7] above, wherein the flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 below.

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0 \leq d \leq 3.0$$

$$\text{(Formula 8)} \quad 0.1 \leq b + c + d \leq 6.0$$

[14] The method of manufacturing a flame-retardant magnesium alloy in any one of [1] to [13], wherein the flame-retardant magnesium alloy contains, in total, more than 0 atomic% and not more than 2.5 atomic% of at least one element selected from a group consisting of Th, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V.

[15] A flame-retardant magnesium alloy comprising a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg,
wherein a, b and x satisfy formulae 1 to 4 below, and said alloy comprises a crystalline structure having a long period stacking ordered structural phase.

(Formula 1) 0.5 ≤ a < 5.0

(Formula 2) 0.5 < b < 5.0

(Formula 3) 2/3a − 5/6 ≤ b

(Formula 4) 0 < x ≤ 0.5 (preferably, 0.1 ≤ x ≤ 0.5, and

further preferably, 0.15 ≤ x ≤ 0.5)

[16] A flame-retardant magnesium alloy comprising a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg,
wherein a, b and x satisfy formulae 1 to 4 below, and said alloy comprises a crystalline structure having a long period stacking ordered structural phase.

(Formula 1) 0.25 ≤ a ≤ 5.0

(Formula 2) 0.5 ≤ b ≤ 5.0

(Formula 3) 0.5a ≤ b

(Formula 4) 0 < x ≤ 0.5 (preferably, 0.1 ≤ x ≤ 0.5, and

further preferably, 0.15 ≤ x ≤ 0.5)

[17] In [15] or [16] above, the alloy has an ignition temperature of 800°C or more (preferably, 850°C or more).
[18] In any one of [15] to [17] above, the alloy contains y atomic% of Al, and y satisfies formula 5 below.

(Formula 5) 0 < y ≤ 0.5 (preferably, 0.05 ≤ y ≤ 0.5)

[19] In [15] or [18] above, the alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7 below or formula 7 and formula 8 below.

(Formula 6) 0 ≤ c < 2.0

(Formula 7) 0.2 ≤ b + c ≤ 6.0

(Formula 8) c/b ≤ 1.5

[20] In [16] or [18] above, the alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7.

(Formula 6) 0 ≤ c ≤ 3.0

(Formula 7) $0.1 \leq b + c \leq 6.0$

[21] In [15] or [18] above, the alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 6 and formula 7 below.

(Formula 6) $0 \leq c \leq 3.0$

(Formula 7) $0.2 \leq b + c \leq 6.0$

[22] In [16] or [18] above, the alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 6 and formula 7 below.

(Formula 6) $0 \leq c \leq 3.0$

(Formula 7) $0.1 \leq b + c \leq 6.0$

[23] In [15] or [18] above, the alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 or formulae 8 and 9 below.

(Formula 6) $0 \leq c \leq 3.0$

(Formula 7) $0 \leq d < 2.0$

(Formula 8) $0.2 \leq b + c + d \leq 6.0$

(Formula 9) $d/b \leq 1.5$

[24] In [16] or [18] above, the alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 below.

(Formula 6) $0 \leq c \leq 3.0$

(Formula 7) $0 \leq d \leq 3.0$

(Formula 8) $0.1 \leq b + c + d \leq 6.0$

[25] In any one of [15] to [24] above, the alloy contains, in total, more than 0 atomic% and not more than 2.5 atomic% of at least one element selected from a group consisting of Th, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V.
[26] In any one of [15] to [25] above, the alloy is a cast.

EFFECTS OF THE INVENTION

[0006] An aspect of the present invention is applied, and thus it is possible to provide a flame-retardant magnesium alloy having mechanical properties of a long period stacking ordered magnesium alloy and having an ignition temperature of 800°C or more and a method of manufacturing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007]

Fig. 1 is a graph showing a relationship between the content of Ca, tensile yield strength and elongation when a tensile test is performed on a sample in an Example at room temperature;
Fig. 2 is a graph showing a relationship between the content of Ca, tensile yield strength and elongation when a tensile test is performed on the sample in the Example at a temperature of 523K;
Fig. 3 is a graph showing a relationship between the content of Ca and an ignition temperature on the sample in the Example;
Fig. 4 is a SEM photograph showing the crystalline structure of an extrusion member of an alloy of $Mg_{95.75-X}Zn_2Y_{1.9}L_{0.1}Al_{0.25}Ca_X$ (where X = 0, 0.3, 0.6 and 0.9) in the Example;
Fig. 5 is a SEM photograph and an EDS image showing the crystalline structure of the extrusion member of an alloy of $M_{95.75-X}Zn_2Y_{1.9}La_{0.1}A_{0.25}Ca_X$ (where X = 0.9) in the Example;
Fig. 6 is a graph showing a relationship between the content of Al, tensile yield strength and elongation when a tensile test is performed on a sample in a Comparative Example at room temperature;
Fig. 7 is a graph showing a relationship between the content of Al, tensile strength and elongation when a tensile test is performed on the sample in the Comparative Example at a temperature of 523K;
Fig. 8 is a SEM photograph showing the crystalline structure of an extrusion member of an alloy of $Mg_{96-X}Zn_2Y_{1.9}La_{0.1}Al_X$ (where X = 0.05, 0.1, 0.15, 0.2 and 0.25) in the Comparative Example;
Fig. 9 is a SEM photograph showing the crystalline structure of an extrusion member of an alloy of $Mg_{96-X}Zn_2Y_{1.9}La_{0.1}Al_X$ (where X = 0.3, 0.35, 0.4 and 0.5) in the Comparative Example;
Fig. 10 is an EDS image showing an extrusion member of an alloy of $Mg_{95.7}Zn_2Y_{1.9}La_{0.1}Al_{0.3}$ in the Comparative Example;
Fig. 11 is an EDS image showing an extrusion member of an alloy of $Mg_{95.5}Zn_2Y_{1.9}La_{0.1}Al_{0.5}$ in the Comparative Example;
Fig. 12 is a photograph showing the crystalline structure of an extrusion member of $Mg_{96-X}Zn_2Y_{1.9}La_{0.1}Al_X$ (where X = 0.1, 0.2, 0.3, 0.4 and 0.5) in the Comparative Example;
Fig. 13 is a graph showing the results of a creep test on the extrusion member of the Comparative Example; and
Fig. 14 is a photograph showing the crystalline structure of an extrusion member of $M_{98.4-X}Zn_XY_{1.5}La_{0.1}$ (where X = 0.25, 0.5, 1.0, 1.5 and 2.0).

BEST MODE FOR CARRYING OUT THE INVENTION

[0008] Hereinafter, embodiments and examples of the present invention will be explained in detail using the drawings. However, a person skilled in the art would be able to easily understand that the present invention is not limited to the following explanation but the configuration and details thereof can be changed variously without deviating from the gist and the scope of the present invention. Accordingly, the present invention should not be construed as being limited to the description of the present embodiments shown below.

[0009] With respect to the conditions such as the composition range and the manufacturing process, and the like for generating a long period stacking ordered structural phase in a magnesium alloy according to each of the embodiments described below, the reasons why the upper limit and the lower limit of each of the components are determined and the reasons why the range of each of the conditions of the manufacturing process are determined, are as described in Japanese Patent No. 3905115, Japanese Patent No. 3940154 and Japanese Patent No. 4139841.

<First embodiment>

[0010] A method of manufacturing a flame-retardant magnesium alloy according to an aspect of the present invention will be described.

[0011] An alloy which contains a atomic% of Zn, b atomic% of Y and x atomic% of Ca and in which the remaining part is formed of Mg, and a, b and x satisfy formulae 1 to 4 below is melted and cast at a temperature of 800°C or less (preferably 850°C or less). Since this alloy has an ignition temperature of 800°C or more (preferably 850°C or more) by

containing Ca. In this way, a magnesium alloy cast is made. The cooling rate at the time of casting is 1000K/second or less, and is more preferably 1.00K/second or less.

$$\text{(Formula 1) } 0.5 \leq a < 5.0$$

$$\text{(Formula 2) } 0.5 < b < 5.0$$

$$\text{(Formula 3) } 2/3a - 5/6 \leq b$$

$$\text{(Formula 4) } 0 < x \leq 0.5 \text{ (preferably, } 0.1 \leq x \leq 0.5 \text{ and further preferably, } 0.15 \leq x \leq 0.5)$$

[0012]   Various processes can be used as the process for producing the magnesium alloy cast described above, and for example, high-pressure casting, roll casting, inclined plate casting, continuous casting, thixomolding, die-casting and the like can be used. In addition, a product cut into a predetermined shape from an ingot may be used as the magnesium alloy cast.

[0013]   Then, homogenized heat treatment may be performed on the magnesium alloy cast. Preferably, in the conditions of the heat treatment at this time, the temperature is set at 400 to 550°C, and the treatment time is set at 1 to 1500 minutes (or 24 hours).

[0014]   Then, plastic processing is performed on the magnesium alloy cast. Examples of the methods of performing this plastic processing, that are used, include extrusion, an ECAE (equal-channel-angular-extrusion) processing method, rolling, drawing and forging, processing of repeating these, FSW (friction stir welding) processing and the like.

[0015]   Preferably, when the plastic processing is performed by extrusion, the extrusion temperature is set to 250°C or more and 500°C or less, and the cross-section reduction rate by extrusion is set to 5% or more.

[0016]   The ECAE processing method is a method of rotating the longitudinal direction of the sample by 90° per pass in order to introduce uniform distortion into the sample. Specifically, the ECAE processing method is the following method: a magnesium alloy cast serving as a molding material is forcibly made to enter a molding hole of a molding die where the molding hole whose cross section is in the shape of the letter L is formed, in particular, in a part of the L-shaped molding hole that is bent by 90°, a stress is applied to the magnesium alloy cast and thus a molded member having excellent strength and toughness is obtained. The number of passes of the ECAE is preferably 1 to 8. The number is more preferably 3 to 5. The temperature at the time of processing of the ECAE is preferably 250°C or more and 500°C or less

[0017]   When the plastic processing is performed by rolling, it is preferable that the rolling temperature is set to 250°C or more and 500°C or less, and the rolling reduction rate is set to 5% or more.

[0018]   When the plastic processing is performed by drawing processing, it is preferable that the temperature at which the drawing processing is performed is set to 250°C or more and 500°C or less, and the cross-section reduction rate in the drawing processing is set to 5% or more.

[0019]   When the plastic processing is performed by forging, it is preferable that the temperature at which the forging processing is performed is set to 250°C or more and 500°C or less, and the processing rate in the forging processing is set to 5% or more.

[0020]   In the plastic processing performed on the magnesium alloy cast, it is preferable that the amount of distortion for each processing is 0.002 or more and 4.6 or less, and the total amount of distortion is 15 or less. In the plastic processing, it is preferable that the amount of distortion for each processing is 0.002 or more and 4.6 or less, and the total amount of distortion is 10 or less. The reason why the preferable total amount of distortion is set to 15 or less and the more preferable total amount of distortion is set to 10 or less is because even when the total amount of distortion is increased, the strength of the magnesium alloy is not always increased accordingly and as the total amount of distortion is made larger, the manufacturing cost is increased.

[0021]   Note that the amount of distortion in the ECAE processing is 0. 95 to 1.15/ each processing, and for example, when 16 times of the ECAE processing are performed, the total amount of distortion is $0.95 \times 16 = 15.2$, whereas when 8 times of the ECAE processing are performed, the total amount of distortion is $0.95 \times 8 = 7.6$.

[0022]   In addition, the amount of distortion in the extrusion processing is 0.92/ each processing when the extrusion ratio is 2.5, is 1.39/ each processing when the extrusion ratio is 4, is 2.30/ each processing when the extrusion ratio is

10, is 2.995/ each processing when the extrusion ratio is 20, is 3.91/ each processing when the extrusion ratio is 50, is 4.61/ each processing when the extrusion ratio is 100 and is 6.90/ each processing when the extrusion ratio is 1000.

[0023] The plastic-processed product obtained by performing the plastic processing on the magnesium alloy cast as described above has a crystalline structure of an hcp structure magnesium phase and a long period stacking ordered structural phase at room temperature, the volume fraction of the crystal grains of the long period stacking ordered structure is 5% or more (more preferably 10% or more) and the crystal grain size of the magnesium alloy is 100 nm or more and 500 μm or less. The average grain size of the hcp structure magnesium phase is 2 μm or more, and the average grain size of the long period stacking ordered structural phase is 0.2 μm or more. Within the crystal grain of the long period stacking ordered structural phase, a plurality of random grain boundaries is present, and the average grain size of the crystal grain specified by the random grain boundaries is 0.05 μm or more. The dislocation density is high in the random grain boundary, but the dislocation density is low in the portions of the long period stacking ordered structural phase other than the random grain boundaries. Therefore, the dislocation density of the hcp structure magnesium phase is one or more digits larger than the dislocation density in the portions of the long period stacking ordered structural phase other than the random grain boundaries.

[0024] At least part of the long period stacking ordered structural phase is curved or bent. The plastic-processed product may have at least one type of precipitate selected from a precipitate group consisting of a compound of Mg and a rare-earth element, a compound of Mg and Zn, a compound of Zn and a rare-earth element, and a compound of Mg and Zn and a rare-earth element. The total volume fraction of the precipitate is preferably more than 0% and not more than 40%. Additionally, the plastic-processed product has hcp-Mg. In a plastic-processed product after the plastic processing is performed, both the Vickers hardness and the yield strength are increased as compared with a cast before the plastic processing is performed.

[0025] Heat treatment may be performed on the plastic-processed product after the plastic processing is performed on the magnesium alloy cast. Preferably, in the conditions of the heat treatment, the temperature is set to not less than 200°C and less than 500°C, and the heat treatment time is set at 10 to 1500 minutes (or 24 hours). The reason why the heat treatment temperature is set to less than 500°C is because when the heat treatment temperature is set to 500°C or more, the amount of distortion applied by the plastic processing is cancelled.

[0026] In the plastic-processed product after the heat treatment is performed, both the Vickers hardness and the yield strength are increased as compared with the plastic-processed product before the heat treatment is performed. Furthermore, the plastic-processed product after the heat treatment has, as with the plastic-processed product before the heat treatment, a crystalline structure of an hcp structure magnesium phase and a long period stacking ordered structural phase at room temperature, the volume fraction of the crystal grains of the long period stacking ordered structure becomes 5% or more (more preferably 10% or more), the average grain diameter of the hcp structure magnesium phase is 2 μm or more, and the average grain diameter of the long period stacking ordered structural phase is 0.2 μm or more. Within the crystal grain of the long period stacking ordered structural phase, a plurality of random grain boundaries is present, and the average grain diameter of the crystal grain specified by the random grain boundaries is 0.05 μm or more. The dislocation density is high in the random grain boundary, but the dislocation density is low in the portions of the long period stacking ordered structural phase other than the random grain boundaries. Therefore, the dislocation density of the hcp structure magnesium phase is one or more digits larger than the dislocation density in the portions of the long period stacking ordered structural phase other than the random grain boundaries.

[0027] At least a part of the long period stacking ordered structural phase of the plastic-processed product after the heat treatment is curved or bent. In addition, the plastic-processed product may have at least one type of precipitate selected from a precipitate group consisting of a compound of Mg and a rare-earth element, a compound of Mg and Zn, a compound of Zn and a rare-earth element, and a compound of Mg and Zn and a rare-earth element. The total volume fraction of the precipitate is preferably more than 0% and not more than 40%.

[0028] In the present embodiment, in the processes of melting and casting for manufacturing a magnesium alloy including mechanical properties of high strength and high ductility by having the long period stacking ordered structural phase, it becomes possible to carry out the processes in the air without setting an atmosphere in which combustion is prevented (an inert gas atmosphere having problems in cost and environment) . The reason for this is that it is possible to set the ignition temperature of the magnesium alloy to 800°C or more (preferably 850°C or more) by addition of a small amount of Ca. The addition amount of Ca is 0 atomic% or more and 0.5 atomic% or less (is preferably more than 0.1 atomic% and not more than 0.5 atomic% and is further preferably 0.15 atomic% or more and 0.5 atomic% or less).

[0029] Namely, when Ca is not added, since the temperature of the magnesium alloy at the time of melting is close to the ignition temperature, it is necessary to adopt an atmosphere in which combustion is prevented, whereas it is possible to make the ignition temperature be higher than the temperature at the time of melting by addition of a small amount of Ca, it becomes possible to perform the melting and casting in the air.

[0030] In addition, the magnesium alloy of the present embodiment is an alloy obtained by achieving flame retardance by the increase in the ignition temperature, conventional metal processing facilities may be utilized without being changed, and it is possible to reduce risk of igniting fine powder or cutting chips generated at the time of processing, with the result

that problems related to the environment, the cost and the safety in the processing steps can be solved at the same time.

[0031] Additionally, the magnesium alloy according to the present embodiment can increase the strength by having the long period stacking ordered structural phase, and has a property less likely to be combusted at the time of melting, casting and processing. Namely, it is possible to realize the magnesium alloy that is advantageous both in high strength and flame retardance.

[0032] Furthermore, the range of the application of the magnesium alloy in the present embodiment covers various fields such as an IT field (a smart phone, a notebook computer and the like), a medical field, an automobile field, an airplane field and a railway field.

[0033] Moreover, the range of the composition of the magnesium alloy in the present embodiment will be described below.

[0034] When the content of zinc is 5 atomic% or more, in particular, the toughness (or the ductility) tends to be lowered. In addition, when the total content of Y is 5 atomic% or more, in particular, the toughness (or the ductility) tends to be lowered.

[0035] The increases in strength and toughness are remarkable when the content of zinc is 0.5 to 1.5 atomic%. When the content of zinc is near 0.5 atomic% and the content of a rare-earth element is decreased, the strength tends to be lowered, but even in such a range, the strength and the toughness are higher than those in a conventional case. Therefore, the range of the content of zinc in the magnesium alloy of the present embodiment is at the widest range 0.5 atomic% or more and 5.0 atomic% or less.

[0036] Although the Mg-Zn-Y magnesium alloy of the present embodiment has the content in the range described above, impurities to the extent of not affecting the properties of the alloy may be contained.

[0037] Note that the magnesium alloy of the present embodiment may further contain y atomic% of Al, and y satisfies formula 5 below, preferably satisfies formula 51 below, further preferably satisfies formula 52 or formula 53 below and more preferably satisfies formula 54 or formula 55 below. The upper limit of the content of Al is set to less than 0.35 atomic% (preferably 0.3 atomic% or less), and thus it is possible to maintain high strength at high temperature.

$$\text{(Formula 5)} \quad 0 < y \leq 0.5$$

$$\text{(Formula 51)} \quad 0.05 \leq y \leq 0.5$$

$$\text{(Formula 52)} \quad 0 < y < 0.35$$

$$\text{(Formula 53)} \quad 0.05 \leq y < 0.35$$

$$\text{(Formula 54)} \quad 0 < y \leq 0.3$$

$$\text{(Formula 55)} \quad 0.05 \leq y \leq 0.3$$

[0038] In addition, the magnesium alloy of the present embodiment may contain, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c preferably satisfies formula 6 and formula 7 below or formula 7 and formula 8 below.

$$\text{(Formula 6)} \quad 0 \leq c < 2.0$$

$$\text{(Formula 7)} \quad 0.2 \leq b + c \leq 6.0$$

$$\text{(Formula 8)} \quad c/b \leq 1.5$$

[0039] Mm (misch metal) is a mixture or an alloy of a plurality of rare-earth elements each containing Ce and La as the main components, and is a residue after Sm, Nd and the like which are useful rare-earth elements are removed by being refined from ores, and its composition depends on the compositions of the ores before refinement.

[0040] The main reason why the upper limit of the content of La and the like is set to 2.0 atomic% is because there is almost no solid solubility limit of La and the like. Additionally, the reason why La and the like are contained is because an effect of miniaturizing crystal grains and an effect of precipitating an intermetallic compound are obtained.

[0041] Furthermore, the magnesium alloy of the present embodiment may contain, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c preferably satisfies formula 8 and formula 9 below.

$$\text{(Formula 8)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 9)} \quad 0.2 \leq b + c \leq 6.0$$

[0042] The reason why the upper limit of the content of Yb and the like is set to 3.0 atomic% is because the solid solubility limit of Yb and the like is low. In addition, the reason why Yb and the like are contained is because an effect of miniaturizing crystal grains and an effect of precipitating an intermetallic compound are obtained.

[0043] Moreover, the magnesium alloy of the present embodiment may contain, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, may contain, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d preferably satisfy formulae 6 to 8 or formulae 8 and 9 below.

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0 \leq d < 2.0$$

$$\text{(Formula 8)} \quad 0.2 \leq b + c + d \leq 6.0$$

$$\text{(Formula 9)} \quad d/b \leq 1.5$$

[0044] The reason why the total content of Y, Yb and the like and La and the like is set to 6.0 atomic% or less is because, when the total content exceeds 6%, the weight of the magnesium alloy is increased, the cost of raw materials is increased and furthermore, the toughness is lowered. In addition, the reason why Yb and the like and La and the like are contained is because an effect of miniaturizing crystal grains and an effect of precipitating an intermetallic compound are obtained. Additionally, the reason why formula 9 above is preferably satisfied is because when d/b is made greater than 1.5 times, the effect of formation of the long period stacking ordered structural phase is reduced and the weight of the magnesium alloy is increased.

[0045] Furthermore, the magnesium alloy of the present embodiment preferably contains, in total, more than 0 atomic% and not more than 2.5 atomic% of at least one element selected from a group consisting of Th, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V. When Th and the like are added, it is possible to improve the other qualities while maintaining high strength and high toughness. The addition of Th and the like is effective for, for example, corrosion resistance, grain miniaturization and the like.

[0046] Moreover, when the magnesium alloy obtained by adding more than 0 atomic% and not more than 2.5 atomic% of Zr is melted and cast, in the magnesium alloy cast, the precipitation of a compound such as $Mg_3Zn_3RE_2$ is reduced, the formation of the long period stacking ordered structural phase is facilitated and the crystalline structure is miniaturized. Therefore, plastic processing such as extrusion is easily performed on this magnesium alloy cast, and the plastic-processed product on which the plastic processing is performed has a larger amount of long period stacking ordered structural phases and a more miniaturized crystalline structure than a plastic-processed product of the magnesium alloy to which Zr is not added. The plastic-processed product has a large amount of long period stacking ordered structural phases, and thus it is possible to enhance strength and toughness.

<Second embodiment>

[0047] A method of manufacturing a flame-retardant magnesium alloy according to one aspect of the present invention will be described. Note that, in the method of manufacturing a flame-retardant magnesium alloy according to the second embodiment, the description of the same parts as in the method of manufacturing a flame-retardant magnesium alloy according to the first embodiment will be omitted as much as possible.

[0048] An alloy which contains a atomic% of Zn, b atomic% of Y and x atomic% of Ca and in which the remaining part is formed of Mg and a, b and x satisfy formulae 1 to 4 below is melted and cast at a temperature of 800°C or less (preferably 850°C or less). Since this alloy has an ignition temperature of 800°C or more (preferably 850°C or more) by containing Ca. In this way, a magnesium alloy cast is formed. As the magnesium alloy cast, a product cut into a predetermined shape from an ingot is used.

$$\text{(Formula 1)} \quad 0.25 \le a \le 5.0$$

$$\text{(Formula 2)} \quad 0.5 \le b \le 5.0$$

$$\text{(Formula 3)} \quad 0.5a \le b$$

$$\text{(Formula 4)} \quad 0 < x \le 0.5 \text{ (preferably, } 0.1 \le x \le 0.5 \text{ and}$$

$$\text{further preferably, } 0.15 \le x \le 0.5)$$

[0049] Next, a plurality of chip-shaped casts having a size of several mm square or less is produced by cutting the magnesium alloy cast.

[0050] Then, the chip-shaped casts may be preliminarily molded using a compression means or a means of a plastic processing method, and thus may be subjected to homogenized heat treatment. Preferably, in the conditions of the heat treatment at this time, the temperature is set to 400 to 550°C, and the treatment time is set to 1 to 1500 minutes (or 24 hours). In addition, heat treatment may be performed on the preliminarily molded product at a temperature of 150 to 450°C for 1 to 1500 minutes (or 24 hours).

[0051] The chip-shaped cast is generally used as, for example, the raw material of thixotropic mold.

[0052] Note that a mixture of the chip-shaped cast and ceramic particles may be preliminarily molded using a compression means or a means of a plastic processing method, and thus may be subjected to homogenized heat treatment. Furthermore, before the chip-shaped cast is preliminarily molded, the cast may be additionally subjected to strong distortion processing.

[0053] Subsequently, plastic processing is performed on the chip-shaped cast, and thus the chip-shaped cast is solidified and molded. Various methods can be used as the method of performing the plastic processing in the same way as in the first embodiment. Note that, before the chip-shaped cast is solidified and molded, repetition processing including: mechanical alloying such as a ball mill, a stamp mill, or a high-energy ball mill; or bulk mechanical alloying may be added. In addition, after the solidification and molding, plastic processing or blasting processing may further be added. Furthermore, the magnesium alloy cast may be complexed with intermetallic compound particles, ceramic particles, fibers or the like, or the cut product may be mixed with ceramic particles, fibers or the like.

[0054] The plastic-processed product obtained by performing the plastic processing as described above has, at room temperature, a crystalline structure of the hcp structure magnesium phase and the long period stacking ordered structural phase. At least a part of the long period stacking ordered structural phase is curved or bent. With regard to the plastic-processed product after the plastic processing is performed, both the Vickers hardness and the yield strength are increased as compared with the cast before the plastic processing is performed.

[0055] The total amount of distortion when the plastic processing is performed on the chip-shaped cast is preferably 15 or less, and is more preferably 10 or less. The amount of distortion for each processing is preferably 0.002 or more and 4.6 or less.

[0056] Note that the total amount of distortion here is the total amount of distortion that is not cancelled by heat treatment such as annealing, and means the total amount of distortion when the plastic processing is performed after the chip-shaped cast is preliminarily molded. Namely, distortion that is cancelled by performing heat treatment in the middle of the manufacturing process is not counted as the total amount of distortion, and the amount of distortion until

the chip-shaped cast is preliminarily molded is not counted as the total amount of distortion.

[0057] Heat treatment may be performed on the plastic-processed product after the plastic processing is performed on the chip-shaped cast. Preferably, in the conditions of the heat treatment, the temperature is set to not less than 200°C and less than 500°C, and the heat treatment time is set to 10 to 1500 minutes (or 24 hours). The reason why the heat treatment temperature is set to less than 500°C is because, when the heat treatment temperature is set to 500°C or more, the amount of distortion applied by the plastic processing is cancelled.

[0058] In the plastic-processed product after the heat treatment is performed, both the Vickers hardness and the yield strength are increased as compared with the plastic-processed product before the heat treatment is performed. In addition, the plastic-processed product after the heat treatment has, as with the plastic-processed product before the heat treatment, a crystalline structure of an hcp structure magnesium phase and a long period stacking ordered structural phase at room temperature. At least a part of the long period stacking ordered structural phase is curved or bent.

[0059] Also in the present embodiment, the same effects as in the first embodiment can be obtained.

[0060] In addition, in the present embodiment, the chip-shaped cast is produced by cutting the cast, and thus the structure is miniaturized, with the result that, as compared with the first embodiment, it becomes possible to produce, for example, the plastic-processed product having high strength, high ductility and high toughness. Additionally, in the magnesium alloy of the present embodiment, even when the concentrations of zinc and a rare-earth element are lower than in the magnesium alloy of the first embodiment, it is possible to obtain the properties of high strength and high toughness.

[0061] Furthermore, when the content of zinc is less than 0.25 atomic% or the content of Y is less than 0.5 atomic%, at least one of strength and toughness is insufficient. Therefore, the lower limit of the content of zinc is set to 0.25 atomic%, and the lower limit of the total content of the rare-earth element is set to 0.5 atomic%. The reason why the lower limit of the content of zinc can be as low as one half of that in the first embodiment is because the application to the chip-shaped cast is carried out.

[0062] Moreover, although the Mg-Zn-Y magnesium alloy of the present embodiment has the content in the range described above, impurities to the extent of not affecting the properties of the alloy may be contained.

[0063] Note that the magnesium alloy of the present embodiment may contain, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c preferably satisfies formula 6 and formula 7 below.

$$(\text{Formula 6})\ 0 \le c \le 3.0$$

$$(\text{Formula 7})\ 0.1 \le b + c \le 6.0$$

[0064] In addition, the magnesium alloy of the present embodiment may contain, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c preferably satisfies formula 8 and formula 9 below.

$$(\text{Formula 8})\ 0 \le c \le 3.0$$

$$(\text{Formula 9})\ 0.1 \le b + c \le 6.0$$

[0065] Additionally, the magnesium alloy of the present embodiment may contain, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, may contain, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d preferably satisfy formulae 6 to 8 below.

$$(\text{Formula 6})\ 0 \le c \le 3.0$$

$$(\text{Formula 7})\ 0 \le d \le 3.0$$

$$(\text{Formula 8})\ 0.1 \le b + c + d \le 6.0$$

Examples

<First Example>

(Production of sample)

[0066] The alloy components of samples in a first Example include $Mg_{95.75-X}Zn_2Y_{1.9}La_{0.1}Al_{0.25}Ca_X$ (where X = 0 to 1.05) . An ingot of a magnesium alloy having these alloy components was melted using a high frequency melting furnace in the atmosphere, and cast members each having a shape of $\phi 32 \times 7$ 0 mm were produced by being cut from the ingot. These cast members were extruded under conditions of a temperature of 350°C, an extrusion ratio of 10 and an extrusion rate of 2.5 mm/second.

(Tensile test)

[0067] In the extrusion member after the extrusion processing, tensile yield strength and elongation were measured at room temperature with a tensile test, and the results thereof are shown in Fig. 1. In Fig. 1, ■ represents the tensile yield strength, and ● represents the elongation.
[0068] In the extrusion member, tensile yield strength and elongation were measured at a temperature of 523K with a tensile test, and the results thereof are shown in Fig. 2. In Fig. 2, ■ represents the tensile yield strength, and ● represents the elongation.

(Measurement of ignition temperature)

[0069] The ignition temperature of each of the cast members was measured. A measurement method is as follows.
[0070] After the ingot of each of the cast members was processed with a lathe in the shape of a chip, a chip of 0.5 g having a given size was put into an electric furnace and the ignition temperature was measured under heating (100K/min).
[0071] The results of the measurement performed as described above are shown in Fig. 3.
[0072] In Fig. 3, when the content of Ca was 0 .15 to 0.6 atomic%, the ignition temperature of the magnesium alloy shown was 850°C or more. In other words, the content of Ca is set to more than 0 atomic% and less than 0.75 atomic% (preferably set to not less than 0.1 atomic% and less than 0.75 atomic%), and thus the ignition temperature of 800°C or more can be expected.
[0073] On the other hand, the ignition temperature of a composition to which Ca is not added, for example, an alloy of $Mg_{95.75}Zn_2Y_{1.9}La_{0.1}Al_{0.25}$ is approximately 775°C, and this ignition temperature is close to 750°C which is the temperature at the time of melting and casting of this alloy. Therefore, when this alloy is melted, it is necessary to use an atmosphere of an inert gas. However, as with the sample of the present Example, when the ignition temperature is 800°C or more or 850°C or more, it becomes possible to perform melting processing even without the use of an inert gas since the ignition temperature is sufficiently higher than the melting point of the alloy.
[0074] It was confirmed from Figs . 1 and 2 that when the content of Ca exceeds 0.5 atomic%, the tensile strength at room temperature and the tensile strength at a high temperature (523K) are significantly lowered. Therefore, the addition range of Ca having an ignition temperature of 800°C or more or 850°C or more while having excellent mechanical properties of the long period stacking ordered magnesium alloy is more than 0 atomic% and not more than 0.5 atomic% (preferably, 0.1 to 0.5 atomic%) by addition of Ca to the long period stacking ordered magnesium alloy.

(Crystalline structure of extrusion member)

[0075] The structure observation of the extrusion member subjected to the extrusion processing was made by SEM and EDS. The results thereof are shown in Figs. 4 and 5.

[Comparative Example]

(Production of sample)

[0076] The alloy components of samples in a Comparative Example include $Mg_{96-X}Zn_2Y_{1.9}La_{0.1}Al_X$ (where X = 0 to 0.5). An ingot of a magnesium alloy having these alloy components was melted using a high frequency melting furnace in an atmosphere of Ar, and cast members each having a shape of $\phi 32 \times 70$ mm were produced by being cut from the ingot. These cast members were extruded under conditions of a temperature of 350°C, an extrusion ratio of 10 and an extrusion rate of 2.5 mm/second.

(Tensile test)

[0077] In the extrusion member after the extrusion processing, tensile strength and elongation were measured at room temperature with a tensile test, and the results thereof are shown in Fig. 6. In Fig. 6, ■ represents the tensile strength (σ_{UTS}), ▲ represents a yield strength ($\sigma_{0.2}$) and ● represents the elongation (%).

[0078] In the extrusion member, tensile yield strength and elongation were measured at a temperature of 523K with a tensile test, and the results thereof are shown in Fig. 7. In Fig. 7, ■ represents the tensile strength (σ_{UTS}), ▲ represents a yield strength ($\sigma_{0.2}$) and ● represents the elongation (%).

[0079] It was confirmed from Fig. 7 that when the content of Al exceeds 0.3 atomic%, the tensile strength at high temperature (523K) is lowered. Therefore, the content of Al is set to less than 0.35 atomic% (preferably set to 0.3 atomic% or less), and thus it is possible to maintain high strength at high temperature.

(Crystalline structure of extrusion member)

[0080] The structure observation of the extrusion member on which the extrusion processing was performed was made by SEM and EDS. The results thereof are shown in Figs. 8 to 12.

[0081] Furthermore, in the same method as in the Comparative Example, a sample of the extrusion member of $Mg_{98.4-X}Zn_XY_{1.5}La_{0.1}$ (where X = 0.25, 0.5, 1.0, 1.5 and 2.0) was produced, and the structure observation thereof was performed. The results thereof are shown in Fig. 14.

(Creep test)

[0082] A creep test was performed on a sample of the extrusion member. The alloy components of the samples include $Mg_{96-X}Zn_2Y_{1.9}La_{0.1}Al_X$ (where X = 0, 0.05, 0.15 and 0.25). In addition, in the same method as in the Comparative Example, a sample of the extrusion member of the alloy of $Mg_{96}Zn_2Y_2$ was produced, and a creep test was performed. The condition of the creep test was 200°C and 150 MPa. The results thereof are shown in Fig. 13.

<Second Example>

(Production of sample)

[0083] The alloy components of samples in a second Example are as shown in Table 1. An ingot of a magnesium alloy having these alloy components was melted using a high frequency melting furnace in the atmosphere, and cast members each having a shape of $\phi 32 \times 70$ mm were produced by being cut from the ingot. These cast members were extruded under conditions of a temperature of 350°C, an extrusion ratio of 10 and an extrusion rate of 2.5 mm/second.

(Measurement of ignition temperature)

[0084] The ignition temperature of the cast member was measured. A measurement method is as follows.

[0085] After the ingot of the cast member was processed with a lathe in the shape of a chip, a chip of 0.5 g having a given size was put into an electric furnace and the ignition temperature was measured under heating (100K/min).

[0086] The results of the measurement performed as described above are shown in Fig. 1.

[0087] It is found from Table 1 that it was possible to increase the ignition temperature by containing Ca in the magnesium alloy.

[Table 1]

Number	Alloy Components	Ignition temperature °C
1	$Mg_{95.7}Zn_2Y_2Ca_{0.3}$	832
2	$Mg_{95.55}Zn_2Y_{1.9}Al_{0.25}Ca_{0.3}$	870
3	$Mg_{95.7}Zn_2Y_{1.9}SM_{0.1}Ca_{0.3}$	832
4	$Mg_{95.7}Zn_2Y_{1.9}Nd_{0.1}Ca_{0.3}$	829
5	$Mg_{95.7}Zn_2Y_{1.9}La_{0.1}Ca_{0.3}$	878
6	$Mg_{95.7}Zn_2Y_{1.9}Ce_{0.1}Ca_{0.3}$	869

(continued)

Number	Alloy Components	Ignition temperature °C
7	$Mg_{95.7}Zn_2Y_{1.9}Gd_{0.1}Ca_{0.3}$	862
8	$Mg_{95.6}Zn_2Y_{1.9}Gd_{0.1}Sm_{0.1}Ca_{0.3}$	842
9	$Mg_{95.6}Zn_2Y_{1.9}La_{0.1}Nd_{0.1}Ca_{0.3}$	850
10	$Mg_{95.6}Zn_2Y_{1.9}Ce_{0.1}Yb_{0.1}Ca_{0.3}$	891
11	$Mg_{95.45}Zn_2Y_{1.9}La_{0.1}A_{0.25}Ca_{0.3}$	936
12	$Mg_{95.6}Zn_2Y_{1.9}\,La_{0.1}Al_{0.15}Ca_{0.15}$	865
13	$Mg_{95.3}Zn_2Y_{1.9}\,La_{0.1}Al_{0.25}Ca_{0.45}$	906
14	$Mg_{95.4}Zn_2Y_{1.9}La_{0.1}Nd_{0.2}Zr_{0.2}Ca_{0.3}$	853
15	$M_{95.45}Zn_2Y_{1.9}Gd_{0.1}Al_{0.25}Ca_{0.3}$	910

Claims

1. A method of manufacturing a flame-retardant magnesium alloy comprising a step of melting a flame-retardant magnesium alloy which contains a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg, wherein a, b and x satisfy formulae 1 to 4 below,

$$(Formula\ 1)\ \ 0.5 \leq a < 5.0$$

$$(Formula\ 2)\ \ 0.5 < b < 5.0$$

$$(Formula\ 3)\ \ 2/3a - 5/6 \leq b$$

$$(Formula\ 4)\ \ 0 < x \leq 0.5.$$

2. A method of manufacturing a flame-retardant magnesium alloy comprising a step of melting a flame-retardant magnesium alloy which contains a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg, wherein a, b and x satisfy formulae 1 to 4 below,

$$(Formula\ 1)\ \ 0.25 \leq a \leq 5.0$$

$$(Formula\ 2)\ \ 0.5 \leq b \leq 5.0$$

$$(Formula\ 3)\ \ 0.5a \leq b$$

$$(Formula\ 4)\ \ 0 < x \leq 0.5.$$

3. The method of manufacturing a flame-retardant magnesium alloy according to claim 1 or 2, wherein said flame-retardant magnesium alloy has an ignition temperature of 800°C or more.

4. The method of manufacturing a flame-retardant magnesium alloy according to any one of claims 1 to 3,

wherein said flame-retardant magnesium alloy is melted at a temperature of 800°C or less.

5. The method of manufacturing a flame-retardant magnesium alloy according to any one of claims 1 to 4,
wherein said flame-retardant magnesium alloy is melted, and then the melted flame-retardant magnesium alloy is cast.

6. The method of manufacturing a flame-retardant magnesium alloy according to claim 5,
wherein a cooling rate in casting said flame-retardant magnesium alloy is 1000k/second or less.

7. The method of manufacturing a flame-retardant magnesium alloy according to any one of claims 1 to 6,
wherein said flame-retardant magnesium alloy contains y atomic% of Al, and y satisfies formula 5 below,

$$\text{(Formula 5)} \ 0 < y \leq 0.5.$$

8. The method of manufacturing a flame-retardant magnesium alloy according to claim 1 or 7,
wherein said flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7 below or formula 7 and formula 8 below,

$$\text{(Formula 6)} \ 0 \leq c < 2.0$$

$$\text{(Formula 7)} \ 0.2 \leq b + c \leq 6.0$$

$$\text{(Formula 8)} \ c/b \leq 1.5.$$

9. The method of manufacturing a flame-retardant magnesium alloy according to claim 2 or 7,
wherein said flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7 below,

$$\text{(Formula 6)} \ 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \ 0.1 \leq b + c \leq 6.0.$$

10. The method of manufacturing a flame-retardant magnesium alloy according to claim 1 or 7,
wherein said flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 8 and formula 9 below,

$$\text{(Formula 8)} \ 0 \leq c \leq 3.0$$

$$\text{(Formula 9)} \ 0.2 \leq b + c \leq 6.0.$$

11. The method of manufacturing a flame-retardant magnesium alloy according to claim 2 or 7,
wherein said flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 8 and formula 9 below,

$$\text{(Formula 8)} \ 0 \leq c \leq 3.0$$

(Formula 9) $0.1 \le b + c \le 6.0.$

12. The method of manufacturing a flame-retardant magnesium alloy according to claim 1 or 7,
    wherein said flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from
    a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group
    consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 or formulae 8 and 9 below,

(Formula 6) $0 \le c \le 3.0$

(Formula 7) $0 \le d < 2.0$

(Formula 8) $0.2 \le b + c + d \le 6.0$

(Formula 9) $d/b \le 1.5.$

13. The method of manufacturing a flame-retardant magnesium alloy according to claim 2 or 7,
    wherein said flame-retardant magnesium alloy contains, in total, c atomic% of at least one element selected from
    a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group
    consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 below,

(Formula 6) $0 \le c \le 3.0$

(Formula 7) $0 \le d \le 3.0$

(Formula 8) $0.1 \le b + c + d \le 6.0.$

14. The method of manufacturing a flame-retardant magnesium alloy according to any one of claims 1 to 13,
    wherein said flame-retardant magnesium alloy contains, in total, more than 0 atomic% and not more than 2.5 atomic%
    of at least one element selected from a group consisting of Th, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba,
    Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V.

15. A flame-retardant magnesium alloy comprising a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg,
    wherein a, b and x satisfy formulae 1 to 4 below, and said alloy comprises a crystalline structure having a long period
    stacking ordered structural phase,

(Formula 1) $0.5 \le a < 5.0$

(Formula 2) $0.5 < b < 5.0$

(Formula 3) $2/3a - 5/6 \le b$

(Formula 4) $0 < x \le 0.5.$

16. A flame-retardant magnesium alloy comprising a atomic% of Zn, b atomic% of Y, x atomic% of Ca and a residue of Mg,

wherein a, b and x satisfy formulae 1 to 4 below, and said alloy comprises a crystalline structure having a long period stacking ordered structural phase,

$$\text{(Formula 1)} \quad 0.25 \le a \le 5.0$$

$$\text{(Formula 2)} \quad 0.5 \le b \le 5.0$$

$$\text{(Formula 3)} \quad 0.5a \le b$$

$$\text{(Formula 4)} \quad 0 < x \le 0.5.$$

17. The flame-retardant magnesium alloy according to claim 15 or 16,
wherein said alloy has an ignition temperature of 800°C or more.

18. The flame-retardant magnesium alloy according to any one of claims 15 to 17,
wherein said alloy contains y atomic% of Al, and y satisfies formula 5 below,

$$\text{(Formula 5)} \quad 0 < y \le 0.5.$$

19. The flame-retardant magnesium alloy according to claim 15 or 18,
wherein said alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7 below or formula 7 and formula 8 below,

$$\text{(Formula 6)} \quad 0 \le c < 2.0$$

$$\text{(Formula 7)} \quad 0.2 \le b + c \le 6.0$$

$$\text{(Formula 8)} \quad c/b \le 1.5.$$

20. The flame-retardant magnesium alloy according to claim 16 or 18,
wherein said alloy contains, in total, c atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c satisfies formula 6 and formula 7,

$$\text{(Formula 6)} \quad 0 \le c \le 3.0$$

$$\text{(Formula 7)} \quad 0.1 \le b + c \le 6.0.$$

21. The flame-retardant magnesium alloy according to claim 15 or 18,
wherein said alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 6 and formula 7 below,

$$\text{(Formula 6)} \quad 0 \le c \le 3.0$$

$$\text{(Formula 7)} \quad 0.2 \leq b + c \leq 6.0.$$

22. The flame-retardant magnesium alloy according to claim 16 or 18,
    wherein said alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, and c satisfies formula 6 and formula 7 below,

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0.1 \leq b + c \leq 6.0.$$

23. The flame-retardant magnesium alloy according to claim 15 or 18,
    wherein said alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 or formulae 8 and 9 below,

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0 \leq d < 2.0$$

$$\text{(Formula 8)} \quad 0.2 \leq b + c + d \leq 6.0$$

$$\text{(Formula 9)} \quad d/b \leq 1.5.$$

24. The flame-retardant magnesium alloy according to claim 16 or 18,
    wherein said alloy contains, in total, c atomic% of at least one element selected from a group consisting of Yb, Tb, Sm and Nd, contains, in total, d atomic% of at least one element selected from a group consisting of La, Ce, Pr, Eu, Mm and Gd, and c and d satisfy formulae 6 to 8 below,

$$\text{(Formula 6)} \quad 0 \leq c \leq 3.0$$

$$\text{(Formula 7)} \quad 0 \leq d \leq 3.0$$

$$\text{(Formula 8)} \quad 0.1 \leq b + c + d \leq 6.0.$$

25. The flame-retardant magnesium alloy according to any one of claims 15 to 24,
    wherein said alloy contains, in total, more than 0 atomic% and not more than 2.5 atomic% of at least one element selected from a group consisting of Th, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V.

26. The flame-retardant magnesium alloy according to any one of claims 15 to 25,
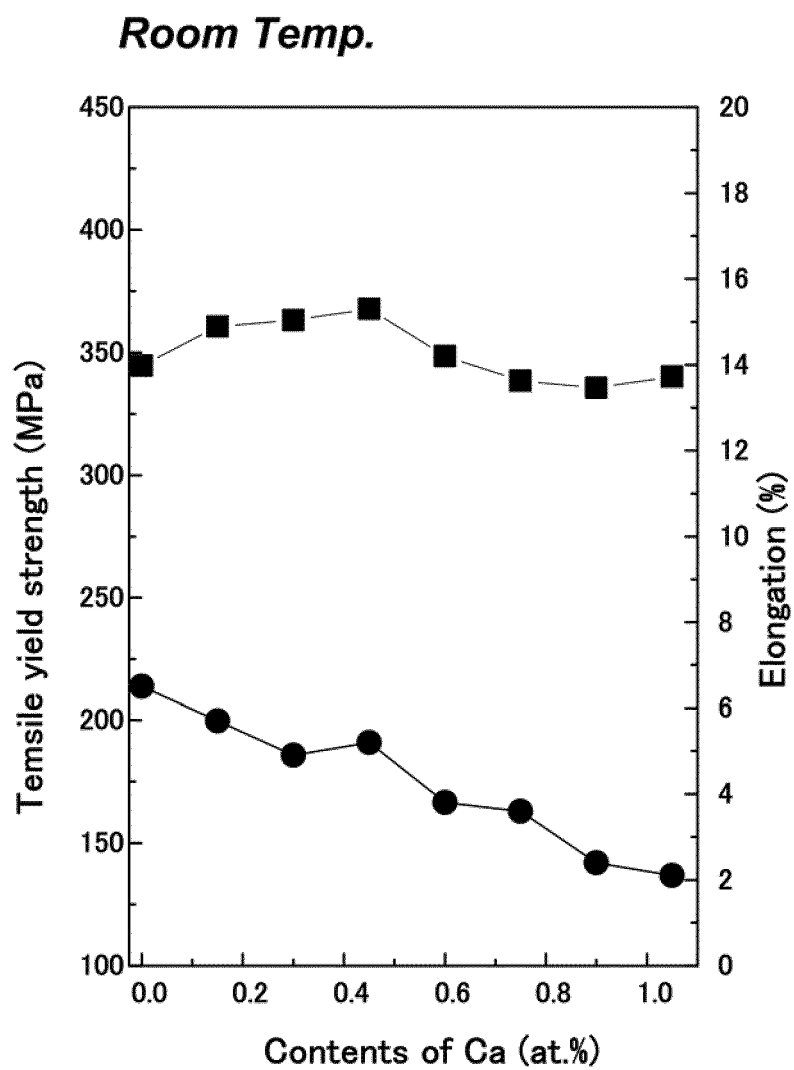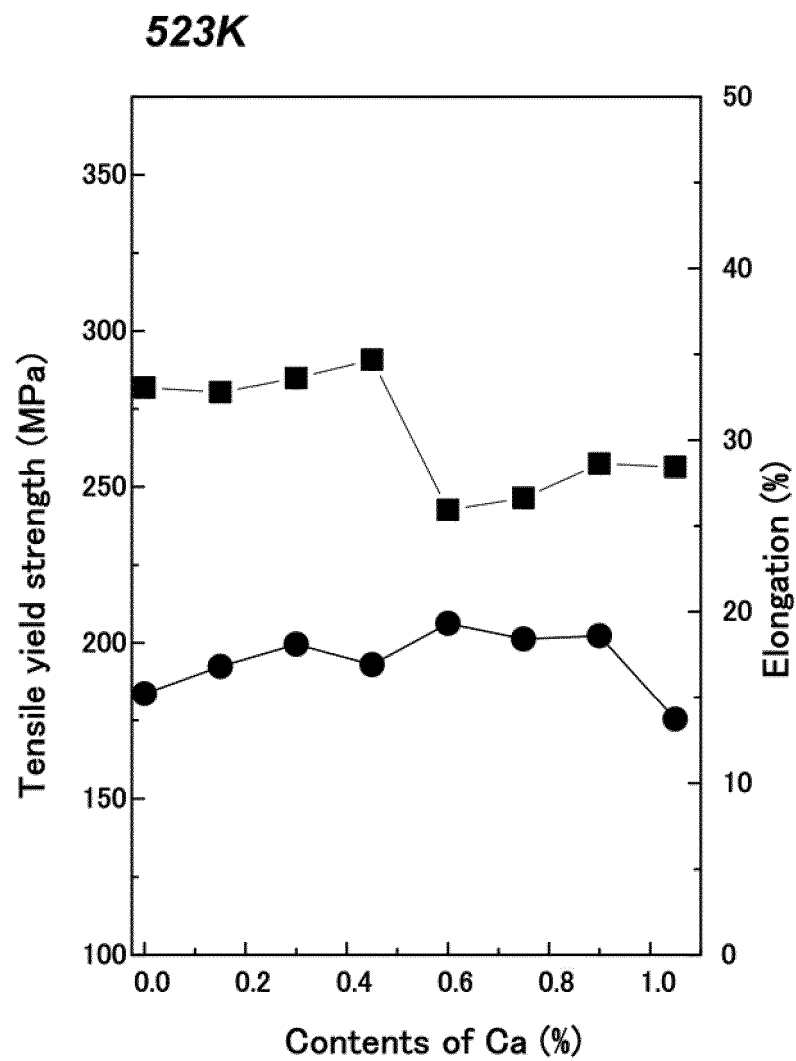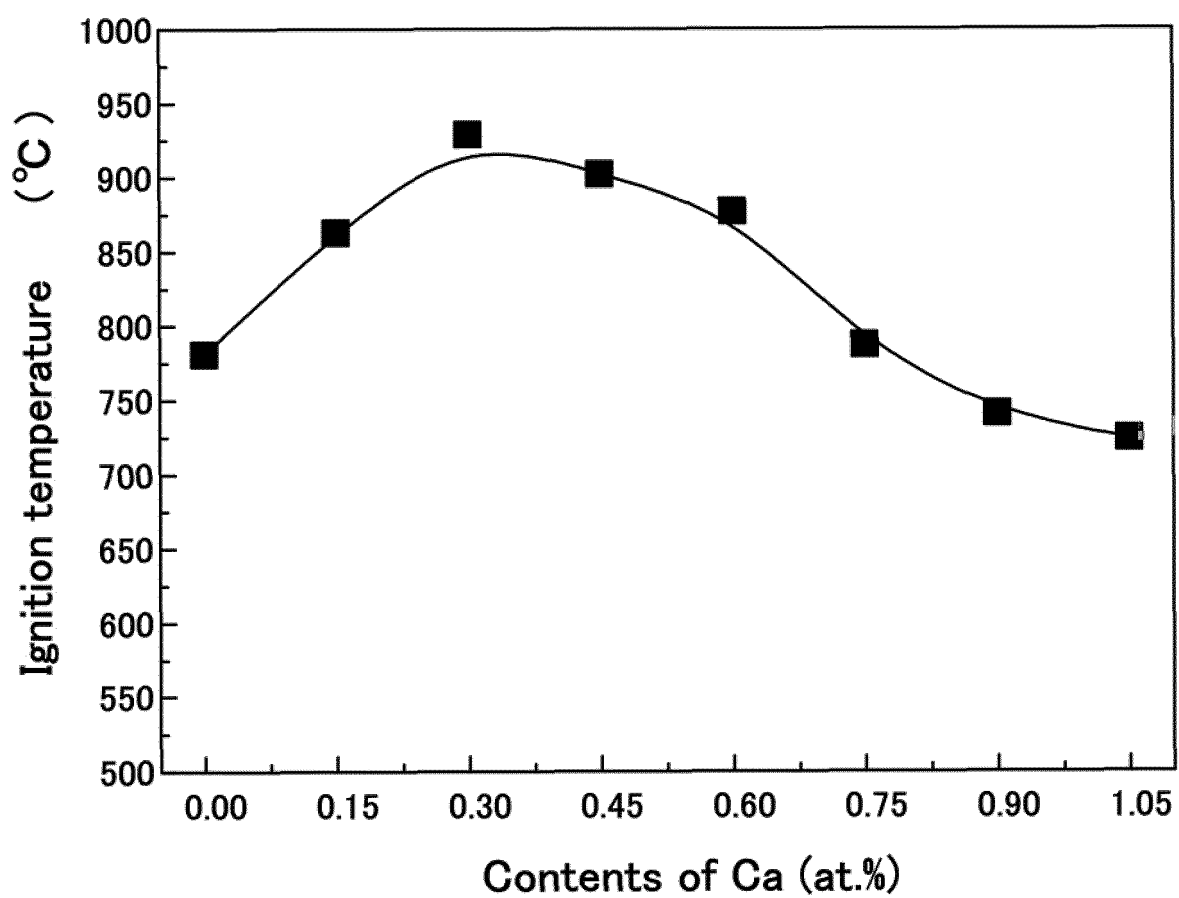   wherein said alloy is a cast.

FIG. 1

Room Temp.
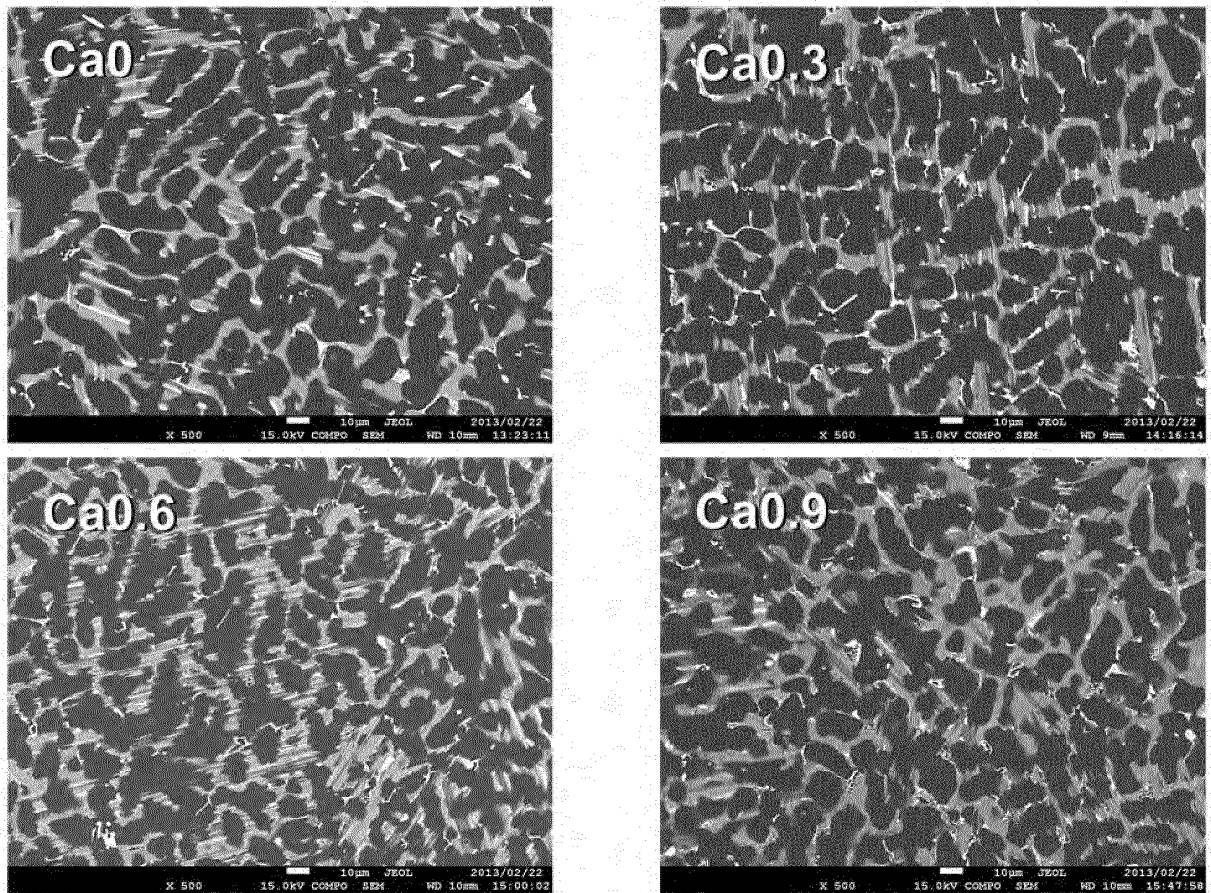
FIG. 2

523K

FIG. 3

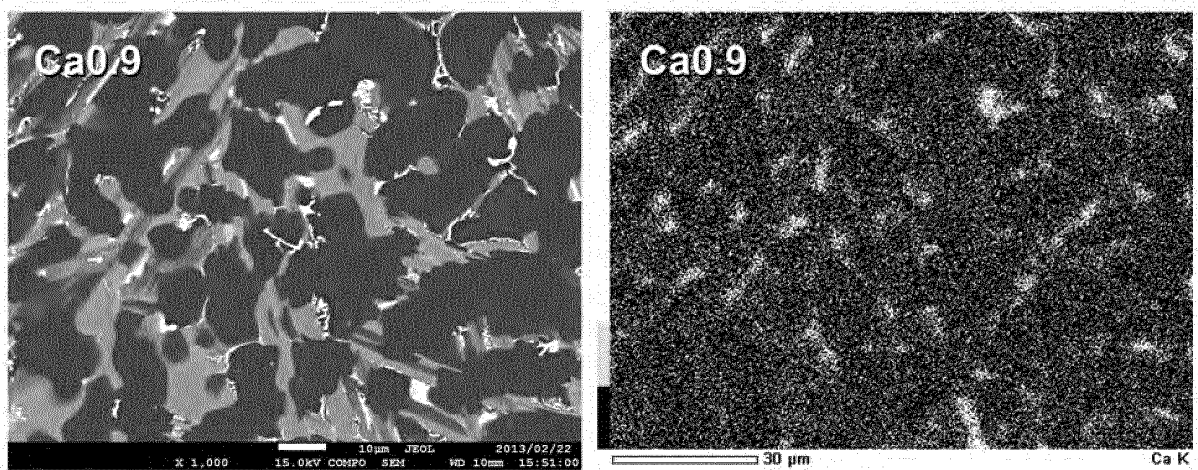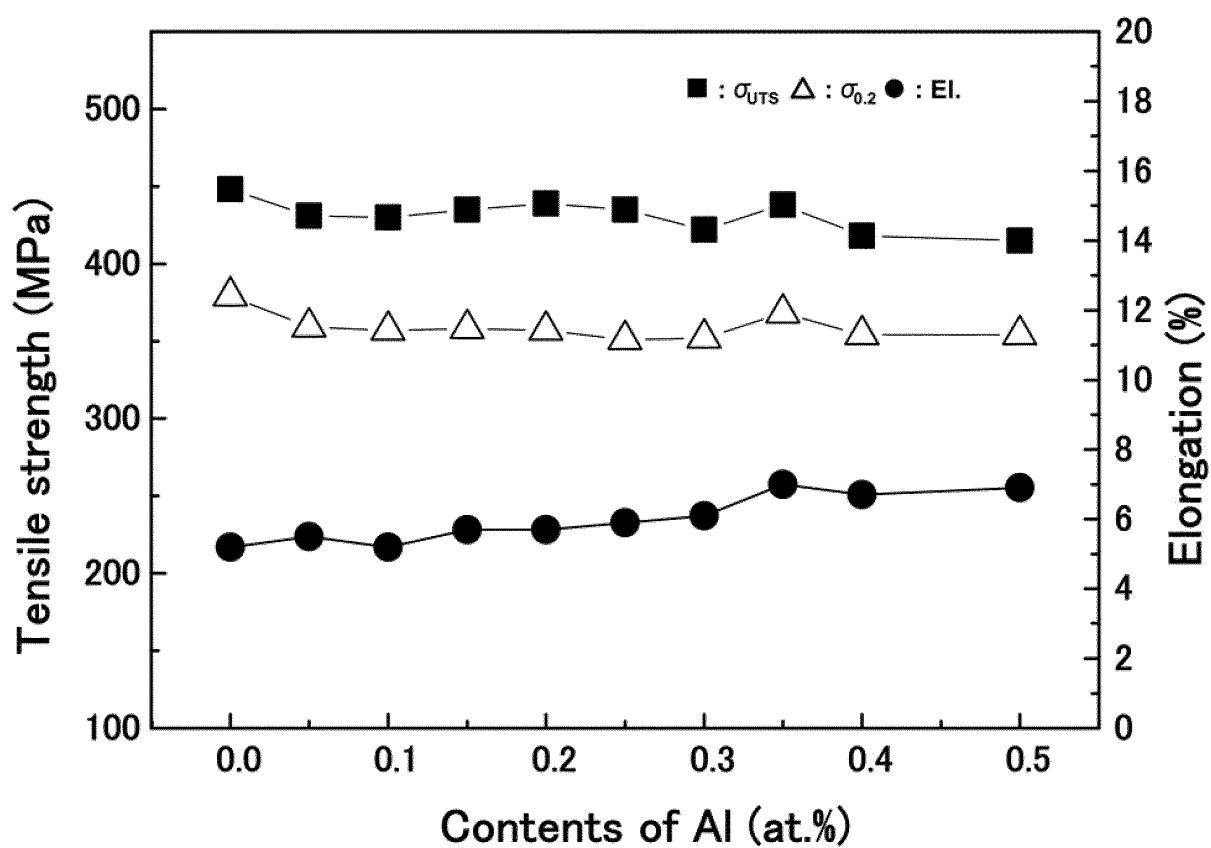# FIG. 4

FIG. 5

FIG. 6

❖ *at room temperature*

FIG. 7
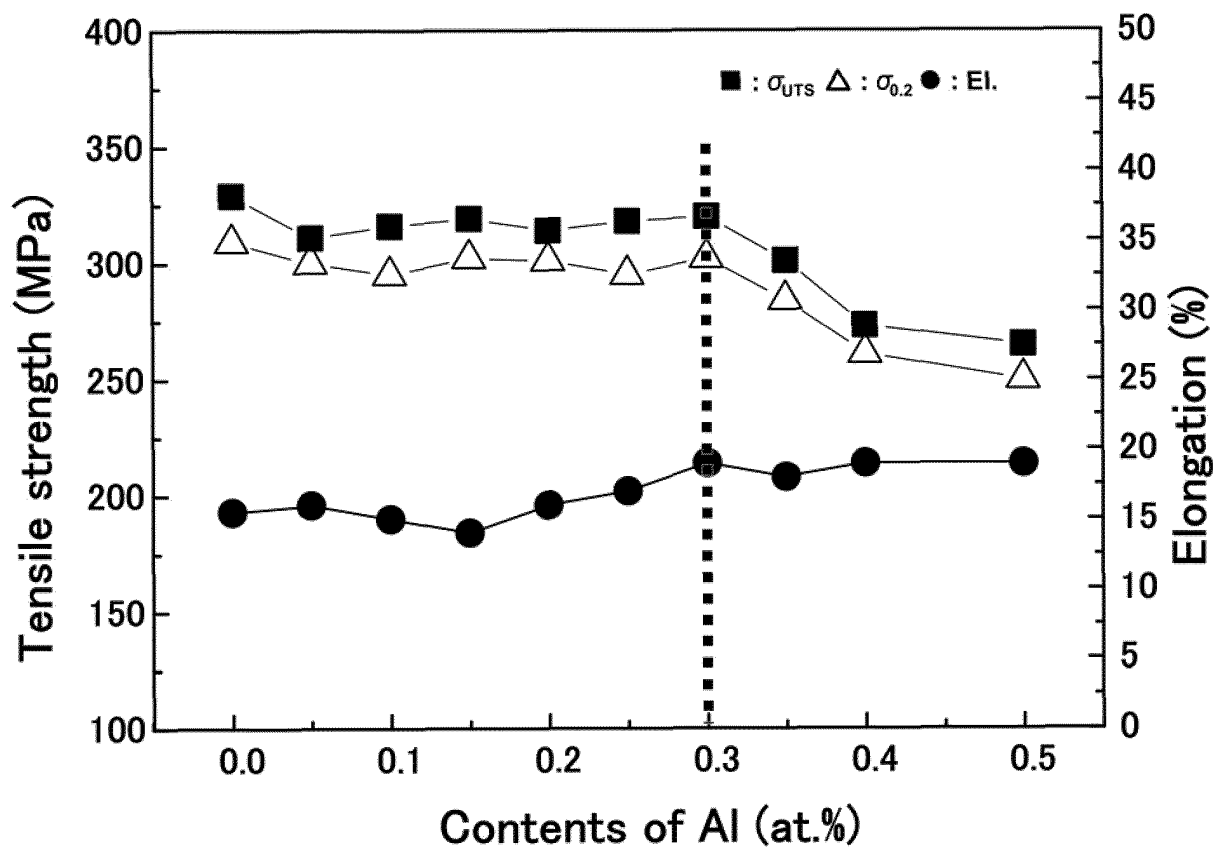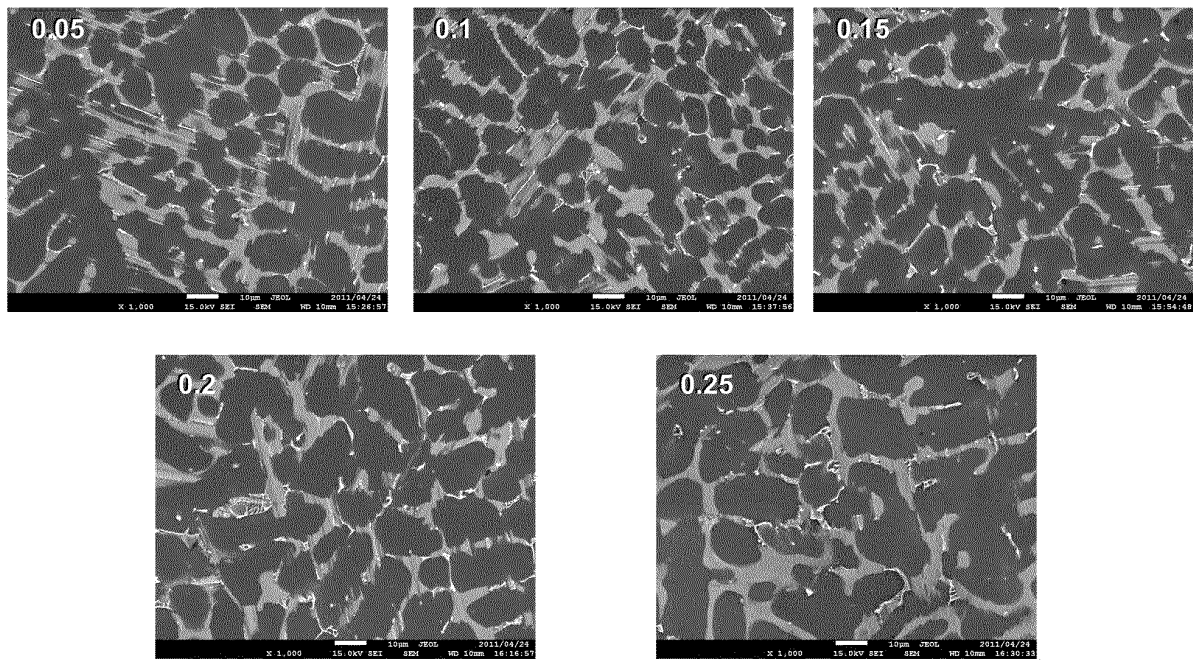
❖ *at elevated temperature (523K)*
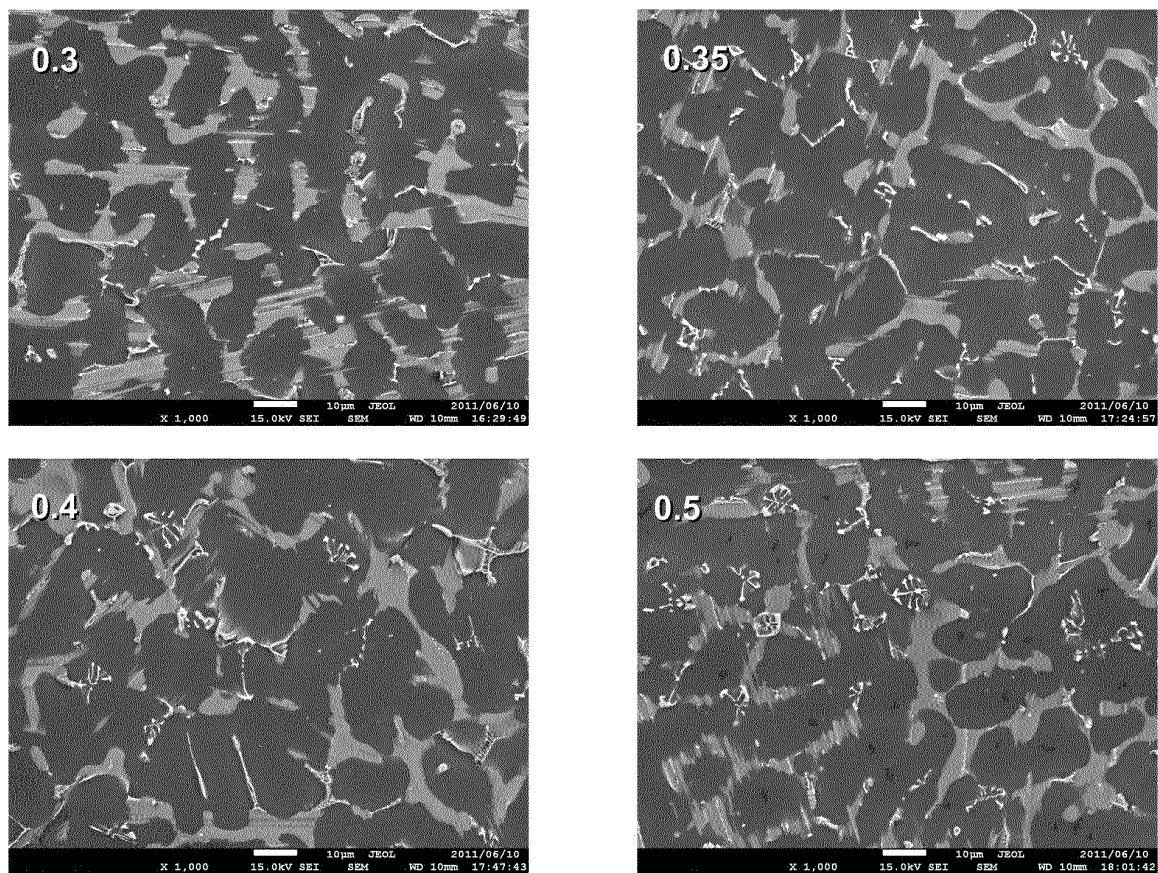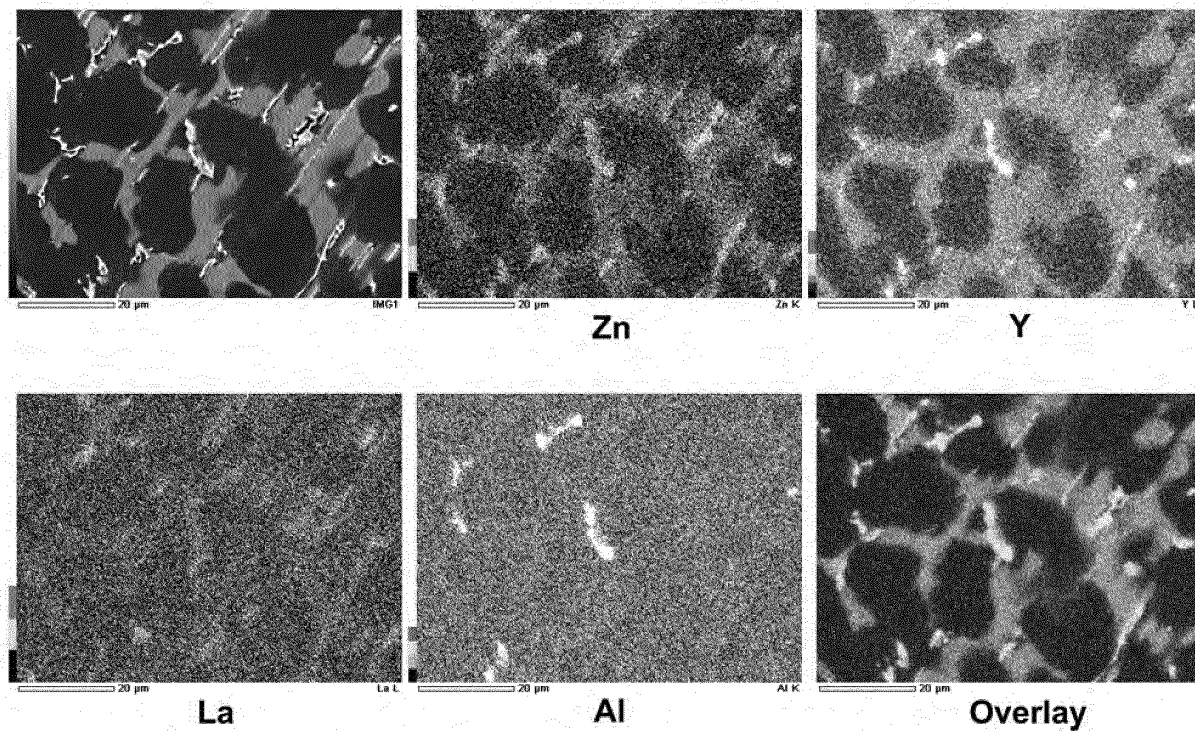
FIG. 8

FIG. 9

FIG. 10

Zn

Y

La

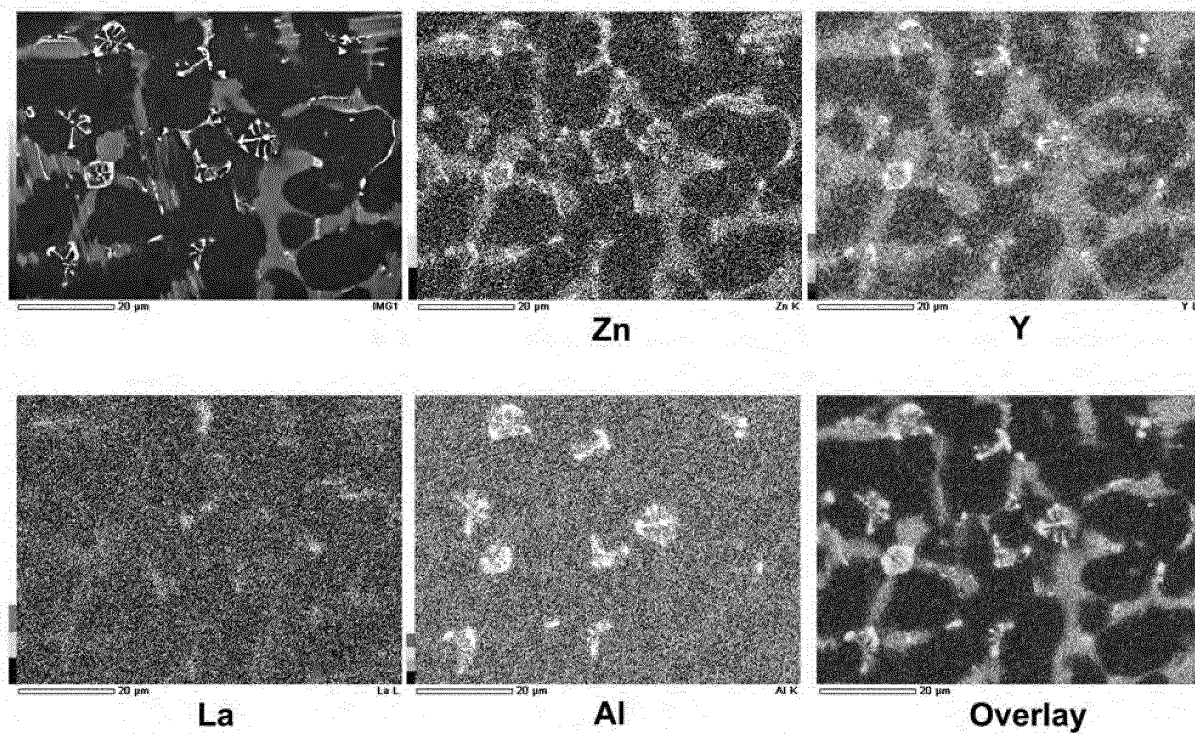Al

Overlay

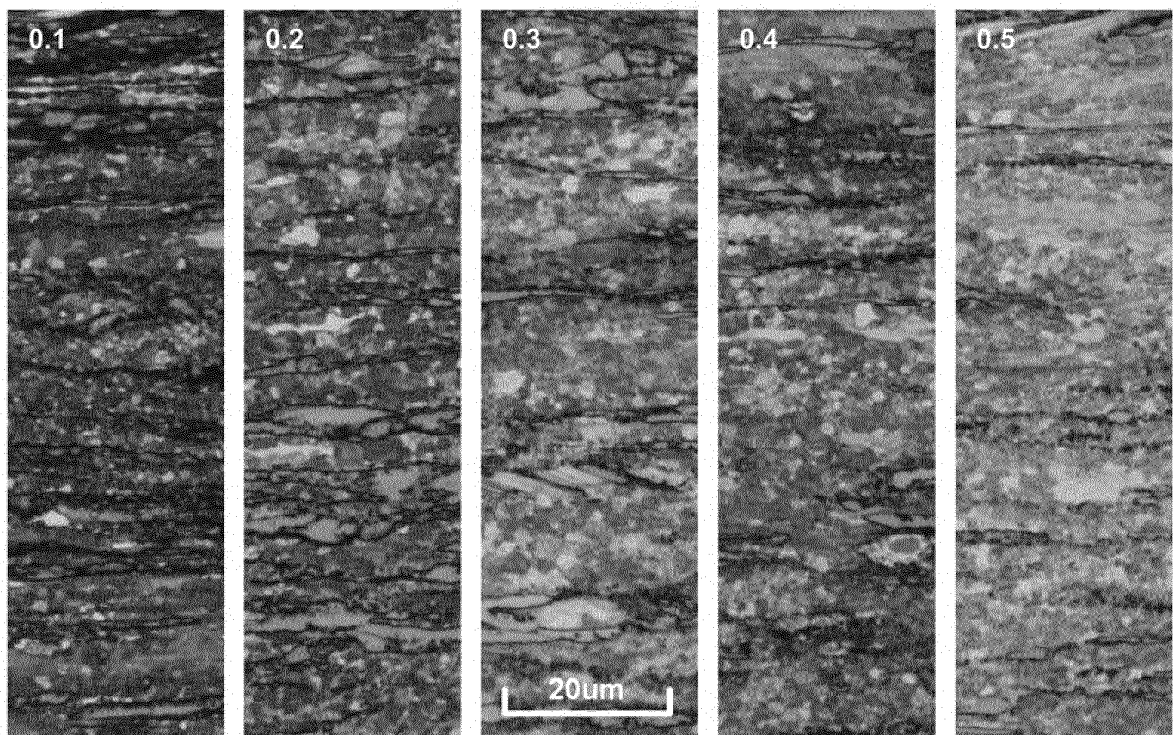## FIG. 11

Zn

Y

La

Al

Overlay

FIG. 12

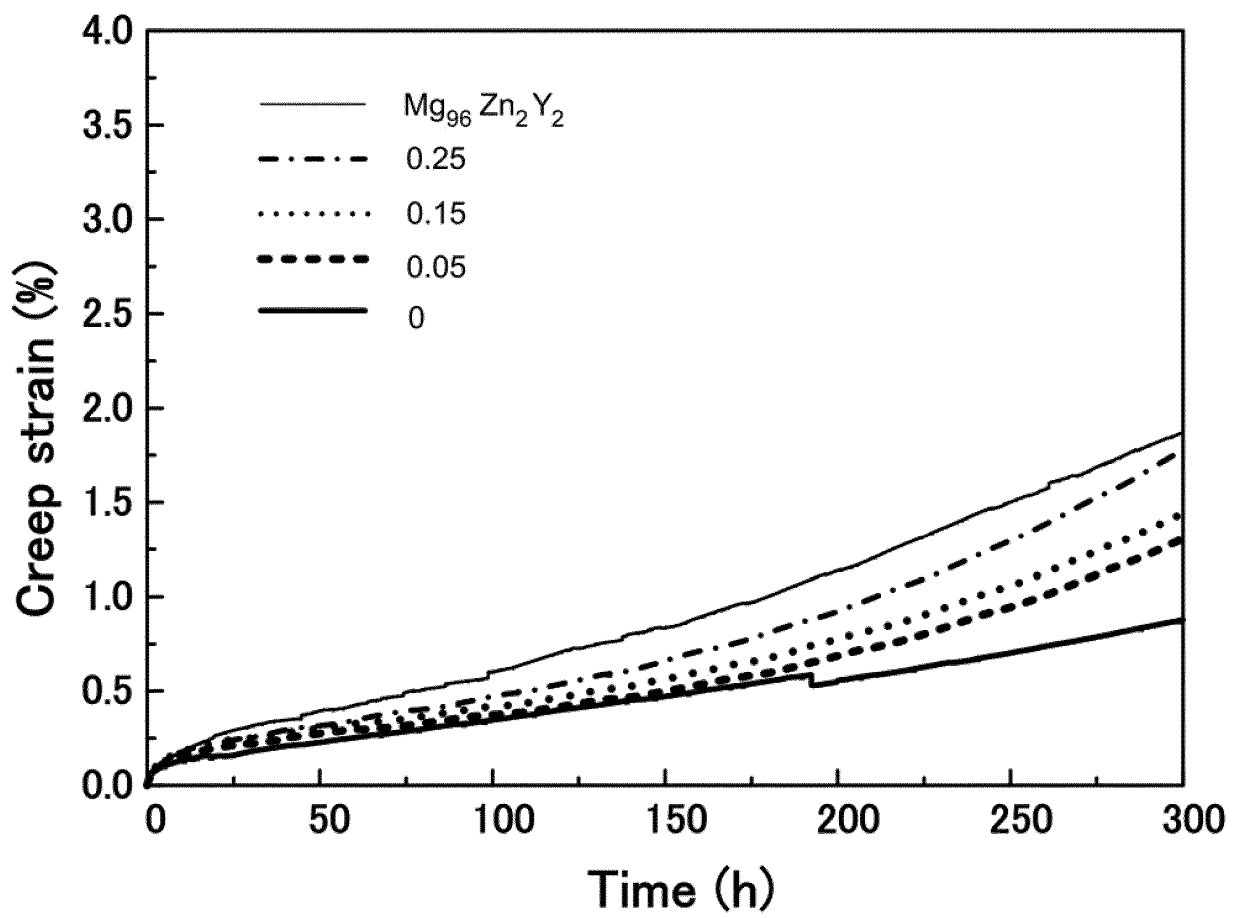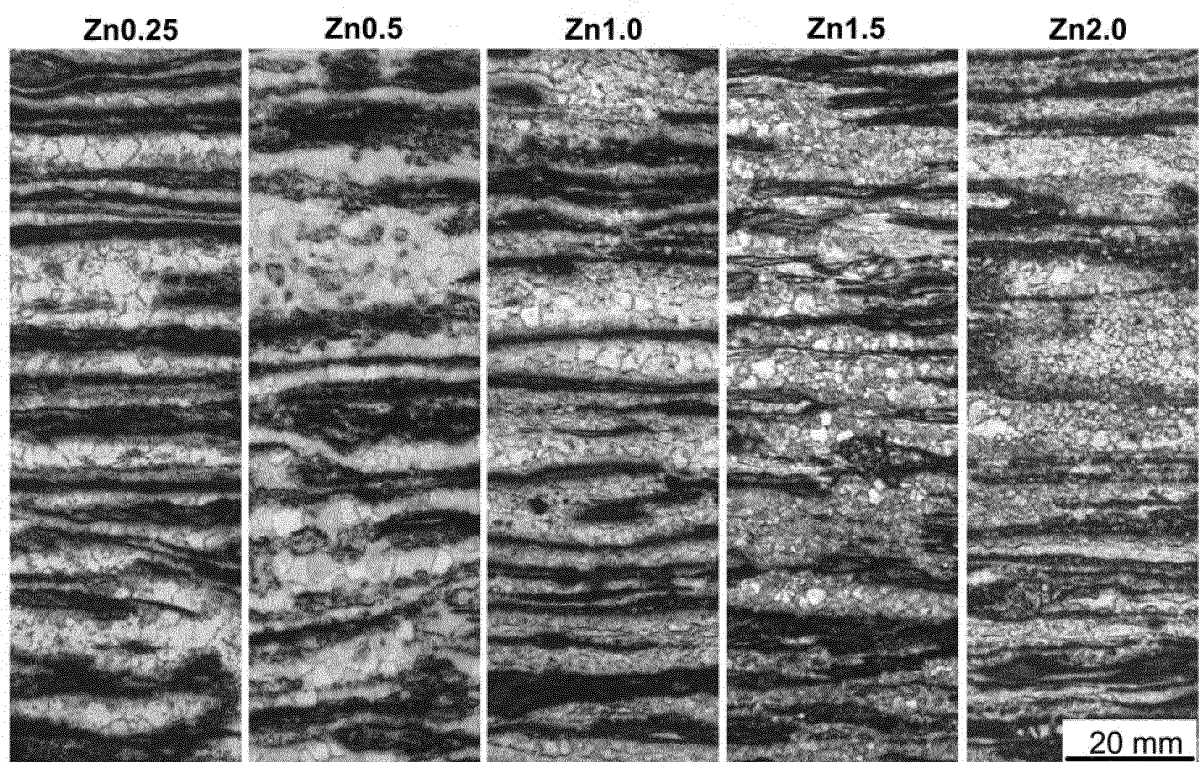# FIG. 13

❖ *Creep conditions: 200℃, 150MPa*

FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/061105

A. CLASSIFICATION OF SUBJECT MATTER
C22C1/02(2006.01)i, *B22D21/04*(2006.01)i, *B22D27/04*(2006.01)i, *C22C23/04*
(2006.01)i, *C22C23/06*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C1/00-49/14, B22D21/04, B22D27/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922–1996	Jitsuyo Shinan Toroku Koho	1996–2014
Kokai Jitsuyo Shinan Koho	1971–2014	Toroku Jitsuyo Shinan Koho	1994–2014

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2008-231536 A (Honda Motor Co., Ltd.), 02 October 2008 (02.10.2008), claims; paragraph [0028] (Family: none)	1-26
Y	JP 2000-109963 A (Director General, Agency of Industrial Science and Technology), 18 April 2000 (18.04.2000), claims; paragraph [0002] (Family: none)	1-26

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 July, 2014 (14.07.14)	22 July, 2014 (22.07.14)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2014/061105

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-16655 A (Sumitomo Electric Industries, Ltd.), 19 January 2006 (19.01.2006), claims; paragraph [0014] (Family: none)	7,18
Y	JP 2008-536008 A (Cast Centre Pty Ltd.), 04 September 2008 (04.09.2008), claims; paragraph [0009] & US 2009/0136380 A1 & US 2010/0061880 A1 & EP 1866452 A & WO 2006/105594 A1 & CA 2603858 A & CN 101189354 A & AU 2006230799 A	7,18
A	US 2003/0129074 A1 (Boris Bronfin et al.), 10 July 2003 (10.07.2003), & EP 1329530 A1 & DE 60200928 D & CA 2415729 A & AT 273400 T & IL 147561 D0	1-26

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- JP 3905115 B **[0003] [0009]**
- JP 3940154 B **[0003] [0009]**
- JP 4139841 B **[0003] [0009]**