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(54) **MAGNESIUM ALLOY**

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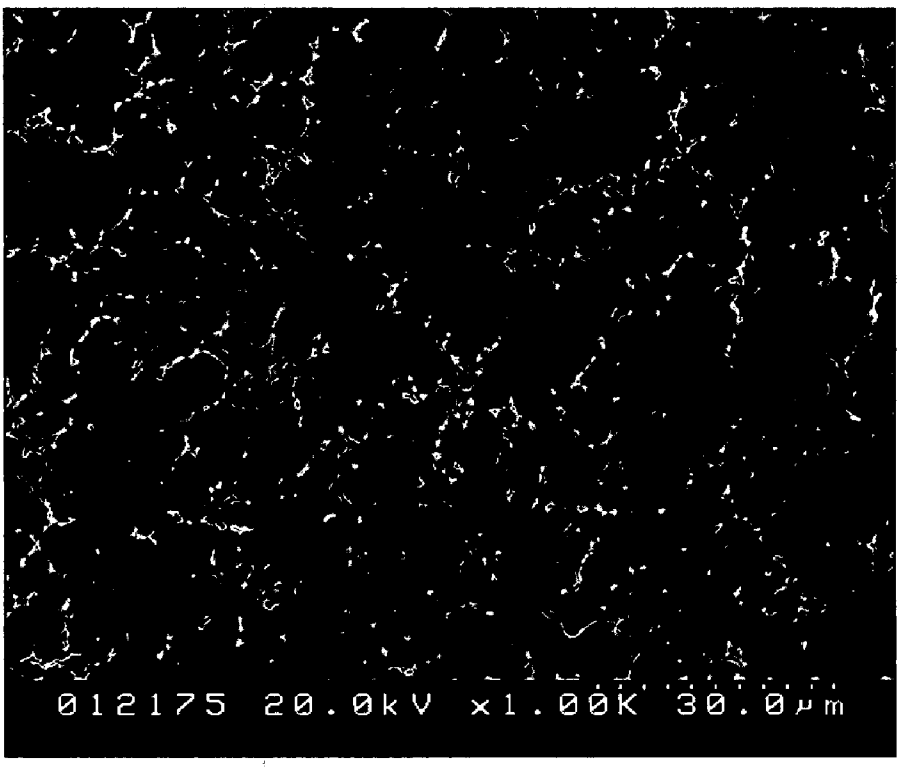
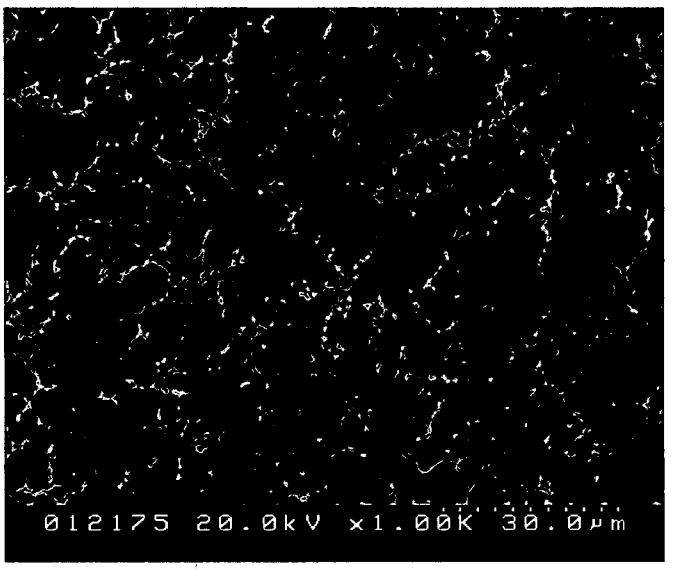
(57) **ABSTRACT**

A magnesium alloy containing 2.0 to 10 at. % zinc, 0.05 to 0.2 at. % zirconium, 0.2 to 1.50 at. % rare earth element, and the balance being magnesium and unavoidable impurities. The Mg—Zn-RE has improved strength, particularly high-temperature strength.



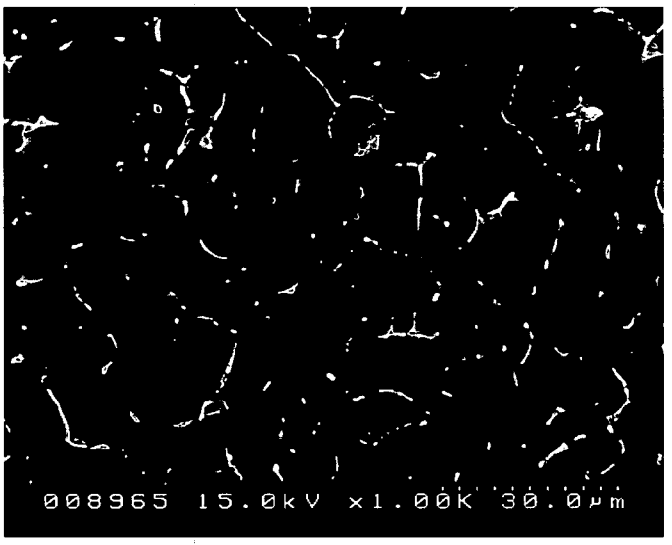
Mg−6Zn−0. 1Zr−0. 9Y (EXAMPLE 1)

Fig. 1A



Mg−6Zn−0. 1Zr−0. 9Y (EXAMPLE 1)

Fig. 1B



Mg−3Zn−0. 5Y (COMPARATIVE EXAMPLE)

Fig. 2

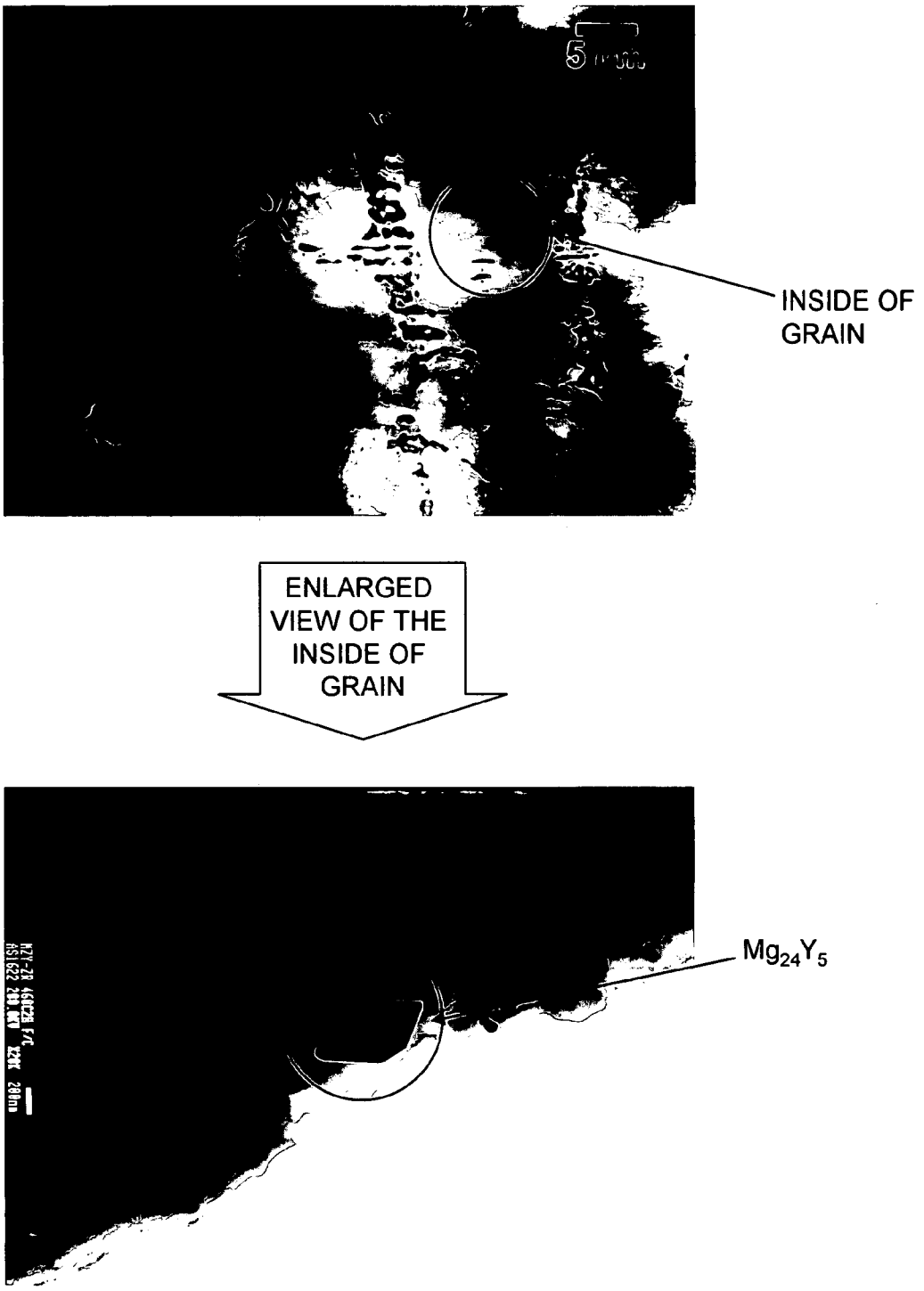
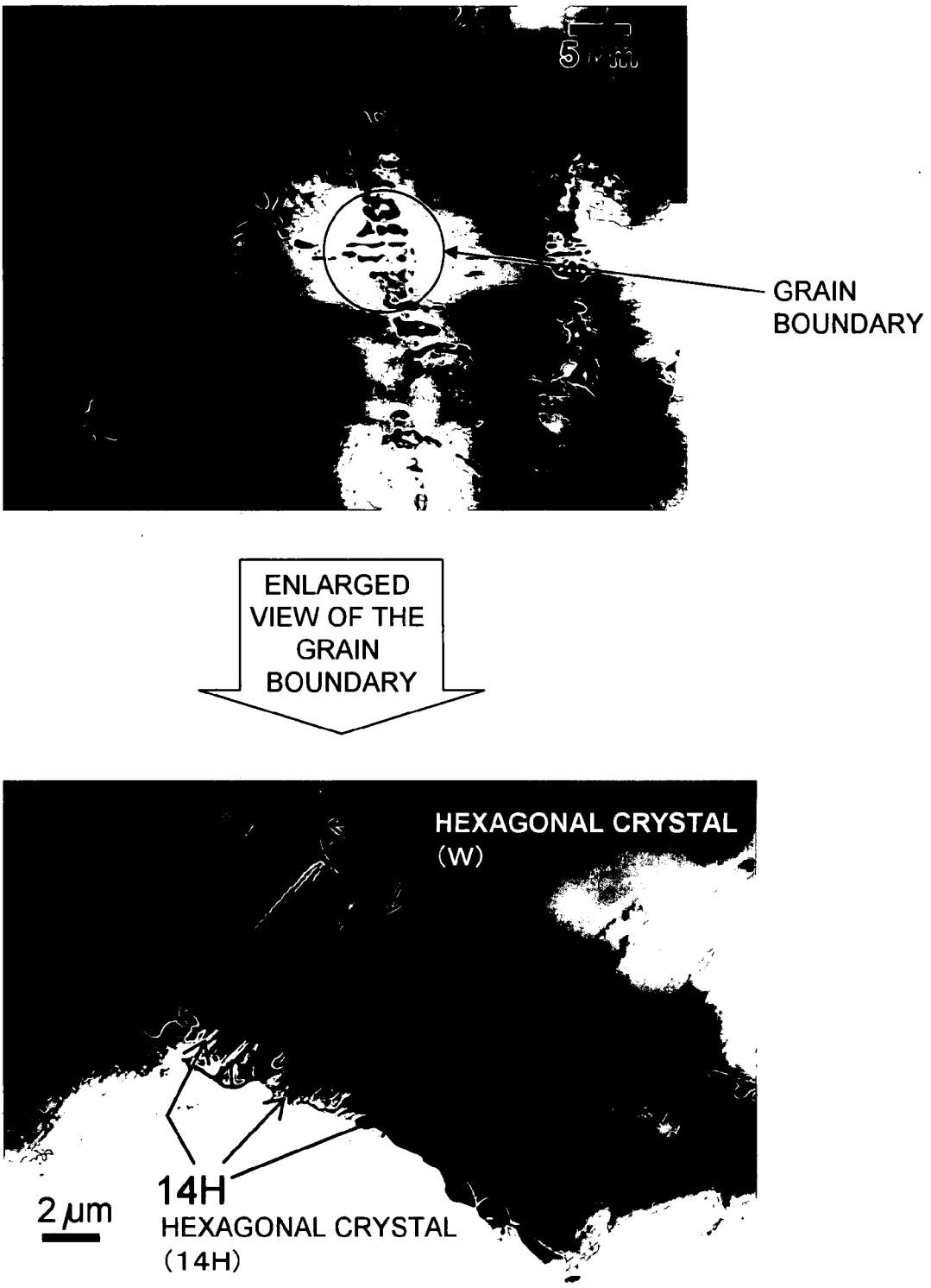


Fig. 3


GRAIN
BOUNDARY
ENLARGED
VIEW OF THE
GRAIN
BOUNDARY
HEXAGONAL CRYSTAL
(W)
2 μm
14H
HEXAGONAL CRYSTAL
(14H)

MAGNESIUM ALLOY

TECHNICAL FIELD

[0001] The present invention relates to a magnesium alloy having superior high-temperature strength. More particularly, the invention relates to a particle-dispersed magnesium alloy having superior high-temperature strength.

BACKGROUND ART

[0002] Magnesium has the specific gravity of 1.74 and is the lightest among the metal materials for industrial purposes. Its mechanical property is comparable to that of aluminum alloy, and for that reason it has drawn attention as a material suitable for aircraft and automobiles, particularly as a material contributing to light weight and improved mileage.

[0003] For example, magnesium alloy has already been used as the material for automotive wheels or engine head covers. There is currently a growing demand for making components of all kinds more lightweight, and the range of application of magnesium alloy is becoming wider. Applications of magnesium alloy under consideration include structural components, such as engine blocks, and even functional components such as pistons, that experience high temperature. If the piston is made of magnesium alloy instead of aluminum alloy, not only the piston becomes lighter in weight but also other components can be made lighter because of the decrease in inertia weight or the like.

[0004] Magnesium alloy products are usually made of cast products including die-cast products.

[0005] Among the conventional magnesium alloys, Mg—Al alloys (ASTM standards—AM60B, AM50A, AM20A, for example) contain 2 to 12% Al, to which small amounts of Mn are added. The Mg component consists of eutectic crystal of α-Mg solid solution and β-$Mg_{17}Al_{12}$ compound, in which age hardening is caused by the precipitation of a $Mg_{17}Al_{12}$ mesophase upon heat treatment. Strength and toughness also improve by solution heat treatment.

[0006] In the Mg—Al—Zn alloys (ASTM standards-AZ91D, for example) in which 5 to 10% Al and 1 to 3% Zn are contained, there is a wide α-solid solution region on the Mg side, where a Mg—Al—Zn compound crystallizes. While they are strong and highly anticorrosive in the as-cast condition, their mechanical property can be improved by aging heat treatment, and a pearlite-like compound phase is precipitated at the grain boundary by hardening and tempering.

[0007] In Mg—Zn alloys, the maximum strength and elongation can be obtained in the as-cast condition when 2% Zn is added to Mg. In order to improve castability and obtain a robust cast product, greater amounts of Zn are added. The as-cast Mg-6% Zn alloy has a tensile strength on the order of 17 kg/mm^2, which, although it can be improved by the T6 treatment, is much inferior to that of Mg—Al alloys. One example of such Mg—Zn alloys is ZCM630A (Mg-6% Zn-3% Cu-0.2Mn).

[0008] Meanwhile, efforts have been made to search for a magnesium alloy that has superior heat resistance and is suitable for use at high temperatures. As a result, it has been found that an alloy to which a rare earth element (R.E.) is added provides a mechanical property that, although somewhat inferior to that of aluminum alloys in room temperature, is comparable to that of aluminum alloys at high temperatures from 250 to 300° C. Examples of alloys that contain R.E. that have been put to practical use include EK30A alloy (2.5 to 4% R.E.-0.2% Zr) which contains no Zn, and ZE41A alloy (1% R.E.-2.0% Zn-0.6% Zr) that contains Zn.

[0009] In such Mg alloys, strength is improved by the following way.

[0010] (1) In JP Patent Publication (Kokai) No. 2002-309332 A, after casting an Mg—Zn—Y alloy, a quasicrystal phase that forms eutetic crystal with α-Mg is uniformly and finely dispersed in the microstructure by hot forming. The quasicrystal is a quasicrystal-phase-reinforced magnesium alloy that is much harder than a crystalline compound with an approximate composition and that has superior strength and elongation property. The composition is limited to Mg, 1-10 at. % Zn, 0.1-3 at. % Y. In the as-cast microstructure of Mg—Zn—Y alloy, an eutetic crystal microstructure of quasicrystal is formed at the α-Mg crystal grain boundary. By hot forming the eutetic crystal microstructure, the quasicrystal can be finely and uniformly dispersed so as to achieve enhanced strength.

[0011] (2) In sand casting Mg alloys such as AZ91C and ZE41, after the casting of an alloy, a predetermined strength is obtained by heat treatment such as T6 or T5. Such alloys are precipitation hardening alloys and that is why they require heat treatment such as T6 or T5 in order to adjust them to a predetermined strength and obtain long-term-stability in their characteristics. If exposed to temperatures above room temperature (generally 50° C. or higher) for a long time, aging precipitation of dissolved elements might occur, resulting in a gradual change in alloy microstructure and characteristics.

[0012] (3) In Mg alloys for forging, such as AZ61A and AZ31B, the crystal grain is made finer by recrystallization caused by intense processing such as rolling and extrusion, thereby enhancing strength. The major reinforcing mechanism for such alloys is the refinement of crystal grains. Refinement of crystal grains, however, triggers a decrease in strength at high temperatures of 1000° C. and above where a strong grain boundary sliding unique to Mg occurs. Furthermore, grain growth occurs at high temperatures, so that such alloys, once exposed to high temperature, would potentially not be able to regain their original strength even after the temperature is lowered.

SUMMARY OF THE INVENTION

[0013] The Mg—Zn—Y alloy cast material disclosed in JP Patent Publication (Kokai) No. 2002-309332 is a general eutetic crystal alloy, and it has a strength comparable to that of commercially available alloys with a similar composition, such as ZE41. In sand casting Mg alloys such as AZ91C and ZE41, the thermal stability of precipitates is so low that aging proceeds continuously at room temperature or above. Furthermore, Mg alloys for forging, such as AZ61A and AZ31B, have no mechanism for pinning the grain boundary or controlling grain growth at high temperatures.

[0014] The high-strength magnesium alloy of the invention has been made in view of the aforementioned problems,

and it is an object of the invention to improve the strength, particularly high-temperature strength, of a Mg—Zn-RE alloy.

[0015] The invention is based on the inventors' realization that by substituting a part of RE in an Mg—Zn-RE alloy with a particular element, a high-strength magnesium alloy can be obtained that has such a microstructure that nanoparticles having a complex structure deriving from a quasicrystal are dispersed in the crystalline magnesium parent phase.

[0016] The invention provides a high-strength magnesium alloy which comprises 2.0 to 10 at. % zinc, 0.05 to 0.2 at. % zirconium, 0.2 to 1.50 at. % rare earth element, and the balance being magnesium and unavoidable impurities.

[0017] Preferably, the rare earth element (RE) is yttrium (Y).

[0018] Preferably, the magnesium alloy of the invention is expressed by the following general formula:

$$Mg_{100-(a+b+c)}Zn_aZr_bRE_c$$

where RE is a rare earth element, and a, b, and c are atomic percentages of zinc (Zn), zirconium (Zr), and rare earth element (RE), respectively, where the following relationship is satisfied:

$$\frac{a}{12} \le b + c \le \frac{a}{3}$$

$$1.5 < a < 10$$

$$0.05 < b < 0.25c.$$

[0019] The magnesium alloy of the invention having the above composition has the following characteristics:

[0020] (1) The α-Mg crystal grains occupy 50% or more in volume, and the alloy contains nanoparticles having a complicated structure, such as quasicrystal or approximate crystal, at the α-Mg crystal grain boundary. The quasicrystal herein refers to a new ordered structure having no translational symmetry but having fivefold or tenfold symmetry and quasiperiodicity, which are not crystallographically allowed. Alloys known to produce quasicrystal include Al—Pd—Mn, Al—Cu—Fe, Cd—Yb, and Mg—Zn—Y, for example. Because of its specific structure, the quasicrystal has specific characteristics, such as high degree of hardness, high melting point, and low μ, as compared with ordinary crystals.

(2) Fine precipitates (1 μm or smaller) are uniformly dispersed within the α-Mg crystal grains. Such fine precipitates enhance the strength of the magnesium alloy of the invention.

[0021] (3) The major fine precipitates are approximate crystals and MgY intermetallic compounds. The approximate crystal, which is related to quasicrystal, herein refers to an intermetallic compound having a structure and composition similar to those of the quasicrystal ($Mg_3Zn_6Y_1$).

[0022] (4) Upon solution beat treatment, the quasicrystal or approximate crystal phase of the α-Mg crystal grain boundary pins the shifting of the crystal grain boundary. Therefore, growth of crystal grain is controlled, and the decrease in strength due to the coarsening of the crystal grain does not occur even at high temperature of 300° C. or above.

[0023] (5) Due to aging after solution heat treatment, approximate crystals or the like having grain diameter of 100 nm or smaller are precipitated at high number density. As a result, precipitates having grain diameter of several tens to hundreds of nm are dispersed at high concentration within the α-Mg grains, together with products crystallized upon casting. Such precipitates highly interact with dislocation and do not become dissolved until nearly 230° C. The quasicrystal and approximate crystal that exist in the α-Mg crystal grain boundary control the grain boundary sliding at high temperature. Their synergistic effect provides very high-temperature strength.

[0024] In the magnesium alloy of the invention having the above composition, the α-Mg phase occupies 50% or more of the volume, and quasicrystal or approximate crystal particles exist in the α-Mg crystal grain boundary. These particles pins the shifting of the crystal grain boundary, so that the growth of crystal grain can be controlled. Thus, no decrease in strength due to the coarsening of the crystal occurs even at high temperature. Further, fine crystals are also precipitated within the grains. The major fine precipitates are approximate crystals and Mg—Y intermetallic compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. **1**A shows an SEM microstructure image of Example 1. FIG. **1**B shows an SEM microstructure image of Comparative Example.

[0026] FIG. **2** shows enlarged images of the inside of a grain of a Mg-6Zn-0.1Zr-0.9Y (at. %) cast material according to Example 1.

[0027] FIG. **3** shows enlarged images of the grain boundary (more strictly, an eutetic crystal-like portion) of a Mg-6Zn-0.1Zr-0.9Y (at. %) cast material according to Example 1.

BEST MODES FOR CARRYING OUT THE INVENTION

[0028] The magnesium alloy of the invention is manufactured by adding all predetermined additive elements in molten Mg, mixing them uniformly, and casting the mixture in a casting mold. The casting method is not particularly limited and a variety of methods, such as gravity casting, die-casting, or rheocast, may be employed.

[0029] Preferably, the magnesium alloy of the invention is not just cast but subjected to heating process after casting, or to hot working and heating process after casting, so as to improve strength.

[0030] Examples of the rare earth element of which the magnesium alloy of the invention is composed include scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu), of which yttrium (Y) is preferable.

[0031] In the following, examples and a comparative example of the invention will be described.

Example 1

[0032] An alloy of Mg-6Zn-0.1Zr-0.9Y (at. %) cast material was manufactured by the following steps.

(1) Materials

Pure Mg (99.9%): 1649 g

Pure Zn (99.99%): 286 g

Pure Zr (99.9%): 6.7 g

Pure Y (99.9%): 58 g

(2) Dissolution

[0033] Pure Mg was dissolved in an iron crucible, and molten metal was maintained at 700° C. Other constituent materials were added in the molten metal, which was stirred while its temperature was maintained at approximately 700° C. until all the materials were uniformly dissolved. The order of addition of the constituent materials in the molten metal does not affect characteristics and is therefore not specified.

(3) Casting

[0034] The alloy molten metal whose temperature was maintained at approximately 700° C. was cast in a JIS **4** boat-shaped mold which had been preheated to about 100° C.

COMPARATIVE EXAMPLE

[0035] Mg-3Zn-0.5Y, which is a conventional material, was cast in the same way as in Example 1 except that the following materials were used.

Pure Mg (99.9%): 1814 g

Pure Zn (99.99%): 151.4 g

Pure Y (99.9%): 34.6 g

[Microstructural Comparison Between Example 1 and Comparative Example]

[0036] FIG. **1**A shows an SEM microstructure image of Example 1, and FIG. **1**B shows an SEM microstructure image of Comparative Example. Example 1 and Comparative Example have similar exterior, having an eutetic crystal structure of approximate crystal (Example 1) or Mg_3Zn_6Y, quasicrystal (Comparative Example) at the α-Mg crystal grain boundary. However, the shape of the eutetic crystal structure is different between Example 1 and Comparative Example; in Example 1, the eutetic crystal structure is generally finer and more uniformly dispersed.

[0037] FIG. **2** shows an enlarged image of the inside of a grain of the Mg-6Zn-0.1Zr-0.9Y (at. %) cast material of Example 1. The image shows the α-Mg phase, a MgY intermetallic compound that could be either $Mg_{24}Y_5$ or $Mg_{12}Y$, and an unidentifiable phase.

[0038] FIG. **3** shows an enlarged image of the grain boundary (or, to be more precise, the eutetic crystal-like portion) of the Mg-6Zn-0.1Zr-0.9Y (at. %) cast material of Example 1. The image shows the W phase (cubic crystal z $Zn_3Mg_3Y_2$), a Zn_6Y_4 binary compound, a hexagonal compound, and an unidentifiable phase.

[Strength Comparison Between Example and Comparative Example]

[0039] From ingots of the above JIS **4** boat-shaped mold according to Example 1 (Mg-6Zn-0.1Zr-0.9Y) and Comparative Example (Mg-3Zn-0.5Y), cylindrical tensile specimens measuring φ5×25 mm at the parallel portion were acquired and subjected to tensile test at room temperature and 150° C. Similar tensile tests were conducted on Examples 2 to 4 with various composition ratios and on AZ91C-T6 and ZE41A-T5, which are conventional materials. The tests were conducted using AG-250kND manufactured by Shimadzu Corporation as a tensile tester, at the pulling rate of 0.8 mm/min. The results are shown in Table I below.

TABLE 1

	Composition					Tensile strength		
	Mg	Zn(a)	Zr(b)	Y(c)	b + c	Room temperature	150° C.	200° C.
Example 1	93.0	6.00	0.10	0.90	1.0	4	23	25
Example 2	95.0	4.29	0.07	0.64	0.71	4	24	26
Example 3	97.4	2.24	0.06	0.30	0.36	6	25	27
Example 4	90.6	8.06	0.14	1.20	1.34	1	10	14
Comparative Example	96.5	3.00	0	0.5	0.5	5	25	28
AZ91C-T6						5	31	33
ZE41A-T5						5	15	29

[0040] The results in Table I show that the cast materials of Examples 1 to 4 are superior to the conventional cast materials such as Comparative Example in terms of tensile strength at 150° C. Further, Examples 1 to 4 show much lower decrease in strength associated with the temperature increase from room temperature to 150° C. One cause for these results is believed to be an increase in the fine precipitates in the α-Mg crystal grains. Since fine precipitates, such as approximate crystals and MgY intermetallic compounds, have high thermal stability, they are supposedly functioning as an effective dislocation barrier even at 150° C.

INDUSTRIAL APPLICABILITY

[0041] In the magnesium alloy of the invention, nanoparticles deriving from quasicrystal are present at the Mg crystal grain boundary, and fine crystals are precipitated even within the grains. As a result, there is no decrease in

strength due to the coarsening of crystals at high temperature. Thus, high strength can be maintained at high temperature.

[0042] Normally, high-temperature strength can be increased by increasing the content of rare earth element. This, nevertheless, results in an increased cost. For example, WE54 can exhibit high strength by increasing the rare earth content to nearly 10% and carrying out T6 heat treatment, although at very high cost. In accordance with the invention, high-temperature strength comparable to the strength of conventional heat-treated material can be achieved in the as-cast condition; namely, without heat treatment.

1. A magnesium alloy comprising:

2.0 to 10 at. % zinc;

0.05 to 0.2 at. % zirconium;

0.2 to 1.50 at. % rare earth element; and

the balance being magnesium and unavoidable impurities, the alloy comprising nanoparticles having a complex structure such as quasicrystal or approximate crystal at the magnesium crystal boundary, wherein a fine precipitate is uniformly dispersed inside the magnesium crystal grains

2. The magnesium alloy according to claim 1, wherein the rare earth element is yttrium.

3. The magnesium alloy according to claim 1 or 2, having the general formula:

$$Mg_{100-(a+b+c)}Zn_aZr_bRE_c$$

where RE is a rare earth element, and a, b, and c indicate atomic percentages of Zn, Zr, and RE, respectively, where the following relationships are satisfied:

$$\frac{a}{12} \leq b + c \leq \frac{a}{3}$$

$$1.5 < a < 10$$

$$0.05 < b < 0.25c.$$

4. The magnesium alloy according to claims 1 to 3, wherein the quasicrystal comprises one or more alloys selected from the group consisting of Al—Pd—Mn, Al—Cu—Fe, Cd—Yb, and Mg—Zn—Y.

5. The magnesium alloy according to claims 1 to 4, wherein the fine precipitate comprises an approximate crystal or an MgY intermetallic compound.

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