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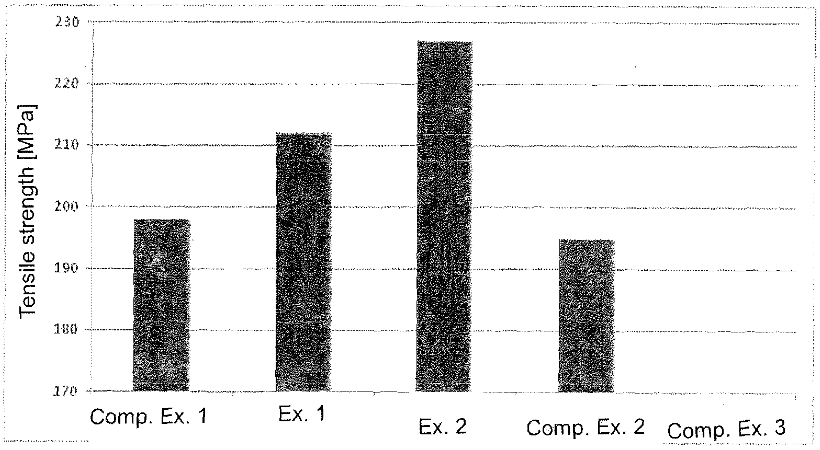
(54) MAGNESIUM ALLOY

(57) The present invention provides magnesium alloy which has sufficiently high strength at room temperature and high temperature.

Disclosed is a magnesium alloy comprising: aluminum (Al): 14.0 to 23.0% by mass, calcium (Ca): 11.0% by mass or less (not including 0% by mass), strontium (Sr): 12.0% by mass or less (not including 0% by mass), and zinc (Zn): 0.2 to 1.0% by mass.

Fig. 4



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Description

Technical Field

[0001] The present invention relates to a magnesium alloy, particularly a magnesium alloy having high strength and high heat resistance, which can be worked into a wrought material such as an extruded or forged material.

Background Art

[0002] It is known that magnesium is the lightest and has the highest specific strength among practical metals. In order to realize reduction in carbon dioxide emission amount due to weight reduction of vehicles, and extension in travelable distance on one charge of electric cars, as measures to cope with global warming, use of a magnesium alloy is expanded in various applications, for example, application of parts which underwent weight reduction using a magnesium alloy.

[0003] Usually, parts of the magnesium alloy are formed by a casting or die-casting method.

[0004] The reason is as follows. That is, conventional various magnesium alloys can achieve comparatively high room-temperature strength by grain size refinement through plastic working including extrusion, rolling and forging. Meanwhile, since grain boundary precipitates formed into a network undergo fracture, tensile characteristics at high temperature deteriorate, thus leading to limitation of use of a wrought material obtained by plastic working as parts to be used at particularly high temperature.

[0005] Patent Document 1 discloses that a magnesium alloy containing 0.1 to 15% by weight of calcium and optionally containing aluminum or zinc in the amount which does not exceed two times the amount of calcium is subjected to plastic working including extrusion and rolling, thereby homogeneously dispersing a crushed intermetallic compound in crystal grains, thus leading to an enhancement in mechanical strength.

[0006] Patent Document 2 discloses that refining of crystal grains is suppressed by performing hot rolling or forging at a predetermined processing temperature and rolling reduction ratio using a Mg-Al-Ca-Sr-Mn based alloy, and heat resistance is improved by controlling an aspect ratio of crystal grains (length of a major axis of crystal grains/length of a minor axis of crystal grains) without causing drastic fracture of a network intermetallic compound precipitated in the grain boundary.

Conventional Art Documents

Patent Documents

[0007]

Patent Document 1: JP 2000-109963 A
Patent Document 2: JP 2007-70688 A

Disclosure of the Invention

Problems to be Solved by the invention

[0008] However, the magnesium alloy according to Patent Document 1 had a problem that it is still insufficient in heat resistance, i.e. strength at high temperature.

[0009] Meanwhile, the magnesium alloy according to Patent Document 2 had a problem that it is necessary to suppress the working degree (rolling reduction ratio) of hot rolling and forging to a low value so as to obtain a defined aspect ratio of crystal grains, so that the strength at room temperature may be sometimes insufficient.

[0010] Thus, the magnesium alloys of Patent Documents 1 and 2 may be sometimes insufficient in high-temperature strength or room-temperature strength.

[0011] Even in the case of a magnesium alloy used at high temperature, the environmental temperature necessarily includes a range from room temperature to high temperature. Therefore, it is necessary that tensile characteristics of the magnesium alloy are excellent in both environments at room temperature and high temperature in practical use. Accordingly, a magnesium alloy having sufficient strength at room temperature and high temperature has been required.

[0012] The present invention has been made so as to meet the requirements, and thus an object thereof is to provide a magnesium alloy which has sufficiently high strength at room temperature and high temperature.

Means for Solving the Problems

[0013] A first aspect of the present invention is directed to a magnesium alloy including: aluminum (Al): 14.0 to 23.0% by mass, calcium (Ca): 11.0% by mass or less (not including 0% by mass), strontium (Sr): 12.0% by mass or less (not including 0% by mass), and zinc (Zn): 0.2 to 1.0% by mass.

[0014] A second aspect of the present invention is directed to the magnesium alloy according to the first aspect, further including at least one selected from the group consisting of silicon (Si): 0.1 to 1.5% by mass, rare earth (RE): 0.1 to 1.2% by mass, zirconium (Zr): 0.2 to 0.8% by mass, scandium (Sc): 0.2 to 3.0% by mass, yttrium (Y): 0.2 to 3.0 % by mass, tin (Sn): 0.2 to 3.0% by mass, barium (Ba): 0.2 to 3.0% by mass, and antimony (Sb): 0.1 to 1.5% by mass.

[0015] A third aspect of the present invention is the magnesium alloy according to the first or second aspect, in which a ratio of the content of strontium (Sr) to the content of calcium (Ca) is from 1:0.3 to 1:1.5 in terms of a mass ratio.

[0016] A fourth aspect of the present invention is directed to the magnesium alloy according to any one of the first to third aspects, in which the content of aluminum (Al), the content of calcium (Ca), and the content of strontium (Sr) satisfy a relation shown in the following equation (1):

$$0.8 \times \langle Al \rangle \leq 1.35 \times \langle Ca \rangle + 1.23 \times \langle Sr \rangle + 8.5 \leq 1.2 \times \langle Al \rangle \qquad (1)$$

where <Al> is the content of aluminum (Al) expressed on % by mass basis, <Ca> is the content of calcium (Ca) expressed on % by mass basis, and <Sr> is the content of strontium (Sr) expressed on % by mass basis.

[0017] A fifth aspect of the present invention is directed to the magnesium alloy according to any one of the first to fourth aspects, in which precipitates containing Al_2Ca and Al_4Sr are formed in the grain boundary with an interval from each other.

Effects of the Invention

[0018] According to the present invention, it is made possible to provide a magnesium alloy having sufficient room-temperature strength and sufficient high-temperature strength.

Brief Description of the Drawings

[0019]

Figs. 1A to 1C show metallographic structures observed by a confocal laser scanning microscope, in which Fig. 1A shows a metallographic structure of an as-extruded material, Fig. 1B shows a metallographic structure of a material subjected to a homogenization heat treatment at 400°C for 48 hours, and Fig. 1C shows a metallographic structure of a material subjected to a homogenization heat treatment at 420°C for 48 hours.

Fig. 2 shows the results of a high-temperature tensile test at 150°C (true stress-strain diagram) of an as-extruded material, a material subjected to a homogenization heat treatment at 400°C for 48 hours, and a material subjected to a homogenization heat treatment at 420°C for 48 hours.

Fig. 3 shows the measurement results of a tensile strength at room temperature.

Fig. 4 shows the measurement results of a tensile strength at high temperature.

Embodiments for Carrying Out the Invention

[0020] The present inventors have made a study on simultaneous utilization of both solid solution strengthening and precipitation strengthening known as strengthening mechanisms of a magnesium alloy.

[0021] That is, they have made a study on effective actuation of both solid solution strengthening mechanism and precipitation strengthening mechanism by appropriate control of the contents of aluminum, strontium and calcium.

[0022] Subsequently, the present inventors have determined solid solubility limit of aluminum in a magnesium alloy matrix and found appropriate amounts of aluminum, calcium and strontium on the basis of the solid solubility limit, and thus completing a magnesium alloy according to the present invention, having sufficient strength at both room temperature and high temperature in which a matrix forms a solid solution with a sufficient amount of aluminum, and also an appropriate amount of intermetallic compounds Al_2Ca and Al_4Sr are precipitated.

Detailed description will be made below.

[0023] The magnesium alloy according to the present invention includes aluminum (Al): 14.0 to 23.0% by mass, calcium (Ca): 11% by mass or less (not including 0% by mass), strontium (Sr): 12% by mass or less (not including 0% by mass), and zinc (Zn): 0.2 to 1.0% by mass.

(1) Aluminum

[0024] In the deformation at high temperature of the magnesium alloy, low stacking fault energy suppresses the movement of dislocations, resulting in the difficulty in deformation. Thus, if stacking fault energy can be lowered, heat resistance (high-temperature strength and creep) can be improved.

[0025] Examples of the element capable of being solid-soluted in a magnesium alloy to lower stacking fault energy include In, Tl, Sc, Pb, Al, Y, Sn and Bi. Of these elements, aluminum (Al) is preferable from the viewpoint of safety and economy.

[0026] As a result of the present inventors' study, it has been found the addition of calcium (Ca) and strontium (Sr), together with aluminum, enables refining of the grain size, leading to an enhancement in room-temperature strength, and also intermetallic compounds Al_2Ca and Al_4Sr to be precipitated (crystallized) exist in the grain boundary, together with other second phases (precipitates), thereby improving room temperature and high temperature characteristics.

[0027] If the magnesium alloy is worked into a wrought material by performing plastic working including rolling, extrusion and drawing after casting so as to obtain desired shape, toughness, strength and the like, second phases containing Al_2Ca and Al_4Sr precipitating in the grain boundary are fractured (fragmented) and arranged in the deformation direction.

[0028] The precipitates containing Al_2Ca and Al_4Sr thus arranged in the deformation direction contribute to an enhancement in high-temperature strength.

[0029] However, the present inventors have intensively studied and found that second phase particles containing Al_2Ca and Al_4Sr can be reprecipitated and dispersed by performing a homogenization heat treatment at 350 to 450°C, leading to more enhancement in strength. It has also been found that, more preferably, second phases containing Al_2Ca and Al_4Sr can be homogeneously dispersed in the grain boundary by performing a homogenization heat treatment at 385°C to 415°C, and thus enabling an increase in strength more certainly.

[0030] As a result of the continued study, the present inventors have found that maximum solubility (solid solubility limit) of aluminum in matrix of the sample subjected to a homogenization heat treatment at 400°C for 48 hours after plastic working such as extrusion is 8.3% by mass (7.5 atomic %). The measurement was performed by point analysis using an electron probe microanalyzer (EPMA).

[0031] Using this solid solubility limit, the present inventors have found that the amount of aluminum of the magnesium alloy according to the present invention is appropriately from 14.0 to 23.0% by mass.

[0032] The reason is that, if the amount of aluminum is 14.0% by mass or more, a sufficient amount of aluminum can form intermetallic compounds Al_2Ca and Al_4Sr with calcium and strontium even if about 8.5% by mass of aluminum is solid-soluted in the matrix. If the amount of aluminum is 23.0% by mass or less, it is possible to ensure ductility such as elongation.

[0033] More preferably, the amount of aluminum is from 15.0% by mass to 20.0% by mass.

[0034] This is because it is possible to form intermetallic compounds Al_2Ca and Al_4Sr more certainly and to ensure ductility if the amount of aluminum is within the above range.

(2) Calcium

[0035] The content of calcium is 11.0% by mass or less (not including 0% by mass).

[0036] The maximum content (11.0% by mass) of calcium is almost equal to the amount of calcium required for almost all aluminum, which was not solid-soluted, to form Al_2Ca ((upper limit of aluminum - maximum solubility)/atomic weight of Al × atomic ratio of Ca to Al of Al_2Ca × atomic weight of Ca = 10.9). Thus, it is made possible to certainly precipitate aluminum, which is not solid-soluted, as a desired intermetallic compound.

[0037] In order to ensure inclusion of calcium, 0% by mass is excluded.

[0038] More preferably, the content of calcium is from 1.0 to 8.0% by mass. This is because it is possible to form Al_2Ca more certainly and to suppress excessiveness.

(3) Strontium

[0039] The content of strontium is 12.0% by mass or less (not including 0% by mass).

[0040] The maximum content (12.0% by mass) of strontium is almost equal to the amount of calcium required for almost all aluminum, which was not solid-soluted, to form Al_4Sr ((upper limit of aluminum - maximum solubility)/atomic weight of Al ×atomic ratio of Sr to Al of Al_4Sr × atomic weight of Sr = 11.9). Thus, it is made possible to certainly precipitate aluminum, which is not solid-soluted, as a desired intermetallic compound.

[0041] In order to ensure inclusion of strontium, 0% by mass is excluded.

[0042] Preferably, the content of strontium is from 0.5 to 8.0% by mass. This is because it is possible to form Al_4Sr more certainly and to suppress excessiveness. More preferably, the content is from 1.0 to 6.0% by mass. This is because it is possible to maximally exert the effect of strontium.

(4) Zinc

[0043] The magnesium alloy according to the present invention contains 0.2 to 1.0% by mass of zinc (Zn).

[0044] This is because zinc has the effect of enhancing the strength and the effect of improving castability.

(5) Relation among Aluminum, Calcium and Strontium

- Ratio of Calcium to Strontium

[0045] In order to form both intermetallic compounds Al_2Ca and Al_4Sr in a more suitable ratio (ratio of formation amount of Al_2Ca and Al_4Sr), a ratio of (content of calcium):(content of strontium) (content of strontium assumed that the content of calcium is 1) is preferably from 1:0.3 to 1:1.5 in terms of a mass ratio, and more preferably 1:0.5 to 1:1.1 in terms of a mass ratio.

- Relation among Aluminum Content, Calcium Content and Strontium Content

[0046] In the magnesium alloy according to the present invention, in order to enable entire strontium and calcium to precipitate as Al_2Ca and Al_4Sr, respectively, the amount of aluminum (% by mass) indicated by the symbol y in the equation (2) is required.

$$y = \langle Ca\rangle/40.08 \text{ (atomic weight of Ca)} \times 2 \text{ (atomic ratio of Al to Ca of } Al_2Ca) \times 26.98 \text{ (atomic weight of Al)} + \langle Sr\rangle/87.62 \text{ (atomic weight of Sr)} \times 4 \text{ (atomic ratio of Al to Sr of } Al_4Sr) \times 26.98 \text{ (atomic weight of Al)} + 8.3 \text{ (maximum solubility of Al)}$$

$$= 1.35 \times \langle Ca\rangle + 1.23 \times \langle Sr\rangle + 8.5 \qquad (2)$$

[0047] In this equation, <Ca> is the content of calcium expressed on % by mass basis and <Sr> is the content of strontium expressed on % by mass basis.

[0048] Physical meaning of a numerical value in the equation is shown in parentheses behind the numerical value.

[0049] In the magnesium alloy according to the present invention, it is preferred to satisfy the following equation (1).

[0050] That is, aluminum is preferably contained such that the amount of aluminum (y) represented by the equation (2), which is required for entire strontium and calcium to precipitate as Al_2Ca and Al_4Sr, respectively, is within a range of the amount which is 0.8 to 1.2 times the content of aluminum.

[0051] This is because, when the content of aluminum is within a range represented by the equation (1), Al_2Ca and Al_4Sr, which are almost equal to the stoichiometric composition, are precipitated and also aluminum is sufficiently solid-soluted in the matrix in just proportion of all elements of aluminum, calcium and strontium.

[0052]

$$0.8 \times \langle Al\rangle \leq 1.35 \times \langle Ca\rangle + 1.23 \times \langle Sr\rangle + 8.5 \leq 1.2 \times \langle Al\rangle \qquad (1)$$

where <Al> is the content of aluminum expressed on % by mass basis.

(6) Other Components

[0053] The alloy of the present invention may contain the above-mentioned aluminum, calcium, strontium and zinc, with the balance being magnesium (Mg) and inevitable impurities.

[0054] However, the magnesium alloy may contain any element capable of improving characteristics of the alloy. In this case, the alloy preferably contains 40% by mass or more of magnesium, and more preferably 50% by mass or more of magnesium, so as not to lose characteristics such as high specific strength possessed by the magnesium alloy.

[0055] Even when containing any other elements, the magnesium alloy containing 40% or more of magnesium and also containing aluminum, calcium, strontium and zinc in each amount defined above can exert the above-mentioned effect of the present invention in most cases without depending on the type of elements.

[0056] Examples of any element, which can be added as mentioned above, include the followings. It is possible to contain at least one selected from the group consisting of:

silicon (Si): 0.1 to 1.5% by mass,
rare earth (RE): 0.1 to 1.2% by mass,
zirconium (Zr): 0.2 to 0.8% by mass,
scandium (Sc): 0.2 to 3.0% by mass,
yttrium (Y): 0.2 to 3.0 % by mass,
tin (Sn): 0.2 to 3.0% by mass,
barium (Ba): 0.2 to 3.0% by mass, and
antimony (Sb): 0.1 to 1.5% by mass.

[0057] The effects of the respective elements exemplified above will be mentioned below.

[0058] Since silicon forms an intermetallic compound with magnesium and the obtained intermetallic compound is stable at high temperature, heat resistance can be improved by effectively suppressing grain boundary sliding in deformation at high temperature. If the content of silicon is from 0.1 to 1.5% by mass, it is possible to sufficiently exert the effect.

[0059] Since rare earth forms an intermetallic compound with magnesium and the obtained intermetallic compound is stable at high temperature, heat resistance can be improved by effectively suppressing grain boundary sliding in the deformation at high temperature. If the content of rare earth is from 0.1 to 1.2% by mass, it is possible to sufficiently exert the effect.

[0060] Since zirconium forms an intermetallic compound with magnesium and the obtained intermetallic compound is stable at high temperature, heat resistance can be improved by effectively suppressing grain boundary sliding in the deformation at high temperature. If the content of zirconium is from 0.2 to 0.8% by mass, it is possible to sufficiently exert the effect.

[0061] Scandium exerts the effect of lowering stacking fault energy to decrease a deformation rate at high temperature when added to magnesium. If the content of scandium is from 0.2 to 3.0% by mass, it is possible to sufficiently exert the effect.

[0062] Yttrium has the effect of lowering stacking fault energy to decrease a deformation rate at high temperature when added to magnesium. If the content of yttrium is from 0.2 to 3.0% by mass, it is possible to sufficiently exert the effect.

[0063] Tin exerts the effect of lowering stacking fault energy to decrease a deformation rate at high temperature when added to magnesium. If the content of tin is from 0.2 to 3.0% by mass, it is possible to sufficiently exert the effect.

[0064] Barium exerts the effect of lowering stacking fault energy to decrease a deformation rate at high temperature when added to magnesium. If the content of barium is from 0.2 to 3.0% by mass, it is possible to sufficiently exert the effect.

[0065] Antimony exerts the effect of lowering stacking fault energy to decrease a deformation rate at high temperature when added to magnesium. If the content of scandium is from 0.1 to 1.5% by mass, it is possible to sufficiently exert the effect.

(7) Heat Treatment

[0066] Al_2Ca and Al_4Sr are often precipitated in the grain boundary, as second phases containing Al_2Ca and Al_4Sr, in the form of a network. As mentioned above, when subjected to plastic working, the second phases containing network Al_2Ca and Al_4Sr (precipitates) tend to be fractured (fragmented) and arranged in the deformation direction.

[0067] Since the thus fragmented precipitates containing Al_2Ca and Al_4Sr contribute to an improvement in high-temperature strength, a magnesium alloy article (magnesium alloy wrought material) obtained by plastic working (plastic deformation) also has high-temperature strength.

[0068] However, second phase particles containing Al_2Ca and Al_4Sr can be reprecipitated and dispersed by performing a homogenization heat treatment at 350 to 450°C after plastic working, thereby finding that high-temperature strength can be more enhanced. Therefore, the magnesium alloy according to the present invention (magnesium alloy article (wrought material)) is preferably subjected to a homogenization heat treatment at 350 to 450°C after plastic working. In the homogenization heat treatment at 350 to 450°C, it is preferred to maintain within such temperature range for 24 to 72 hours. This is because this treatment enables redissolution (reprecipitation) of precipitates, leading to an improvement in heat stability.

[0069] The present inventors have also found that a homogenization heat treatment at 385°C to 415°C enables reprecipitation of second phase particles containing Al_2Ca and Al_4Sr and homogeneous dispersion of the second phase particles along the grain boundary, leading to further improvement in high-temperature strength. In case a homogenization treatment is performed at 385°C to 415°C after plastic working, second phase particles containing Al_2Ca and Al_4Sr (precipitates) are precipitated in the form of particles, instead of a network, with an interval from each other (i.e. discontinuously) along the grain boundary. The thus obtained precipitates in this form remarkably contribute to an improvement in high-temperature strength. Therefore, the magnesium alloy according to the present invention (magnesium alloy article (wrought material)) is preferably subjected to a homogenization heat treatment at 385 to 415°C after plastic working. In the homogenization heat treatment at 385 to 415°C, it is preferred to maintain within such temperature range for 24 to 72 hours. This is because this treatment enables redissolution of precipitates and homogenization of the structure, leading to homogenization and stabilization of an intermetallic compound structure with high heat stability of the grain boundary.

[0070] As used herein, plastic working includes various hot and cold plastic workings. Examples of the plastic working include extrusion, rolling, forging, drawing, swaging, and combinations thereof.

Examples

[0071] Alloy samples, each containing components shown in Table 1, were prepared.

[0072] The value y in the equation (2) of samples of Examples (Example 1 and Example 2) shown in Table 1 is 15.5 in Example 1 and is 20.9 in Example, and therefore alloy samples satisfy the equation (1). In both Example 1 and Example 2, a ratio of (content of calcium):(content of strontium) is 1:1 in terms of a mass ratio.

Table 1

	Comparative Example 1		Example 1		Example 2		Comparative Example 2		Comparative Example 3	
	Mass %	Atomic %	Mass %	Atomic %	Mass %	Atomic %	Mass %	Atomic %	Mass %	Atomic %
Mg	88.1	90.0	79.1	80.8	69.9	71.4	60.9	62.2	51.9	53.0
Al	10.0	9.2	15.0	13.8	20.0	18.4	25.0	23.0	30.0	27.6
Ca	0.7	0.4	2.7	1.7	4.8	3.0	6.8	4.2	8.8	5.5
Sr	0.7	0.2	2.7	0.8	4.8	1.4	6.8	1.9	8.8	2.5
Zn	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2

[0073] Each alloy sample was melted at 700°C and then cast into a billet using a cylindrical die. The casted billet was heated to 400°C at a heating rate of 0.5°C/minute, maintained for 48 hours and then water-cooled. After removing a surface oxide layer by machining, the billet was extruded at an extrusion temperature of 350°C, an extrusion rate of 0.2 mm/second and an extrusion ratio of 16 to obtain a round bar (10 mm in diameter).

1) Homogenization Heat Treatment

[0074] In order to examine an influence of a homogenization heat treatment, regarding the above-mentioned sample of Example 1 (extruded round bar), an as-extruded material, a material subjected to a homogenization heat treatment at 400°C for 48 hours, and a material subjected to a homogenization heat treatment at 420°C for 48 hours were produced.

[0075] Figs. 1A to 1C show metallographic structures observed by a confocal laser scanning microscope, in which Fig. 1A shows a metallographic structure of an as-extruded material, Fig. 1B shows a metallographic structure of a material subjected to a homogenization heat treatment at 400°C for 48 hours, and Fig. 1C shows a metallographic structure of a material subjected to a homogenization heat treatment at 420°C for 48 hours.

[0076] In the as-extruded material, precipitates containing Al_2Ca and Al_4Sr (second phases) are fragmented and arranged in the extrusion direction (up/down direction in the drawing). In contrast, in the material subjected to a homogenization heat treatment at 400°C for 48 hours and the material subjected to a homogenization heat treatment at 420°C for 48 hours, precipitates containing Al_2Ca and Al_4Sr (second phases) are dispersed. Particularly in the material subjected to a homogenization heat treatment at 400°C for 48 hours, granular precipitates containing comparatively fine Al_2Ca and Al_4Sr are homogeneously distributed with an interval from each other along the grain boundary.

[0077] Fig. 2 shows the results of a high-temperature tensile test at 150°C (true stress-strain diagram) of an as-extruded material, a material subjected to a homogenization heat treatment at 400°C for 48 hours, and a material subjected to a homogenization heat treatment at 420°C for 48 hours. The tensile test was carried out at a temperature of 150°C and a tension speed of 1×10^{-3}/second.

[0078] All samples exhibit excellent high-temperature strength (heat resistance), that is, tensile strength at 150°C of 250 MPa. Of these, the material subjected to a homogenization heat treatment at 400°C for 48 hours and the material subjected to a homogenization heat treatment at 420°C for 48 hours exhibit high-temperature strength which is higher than that of the as-extruded material. Particularly, the material subjected to a homogenization heat treatment at 400°C for 48 hours has high-temperature strength which is remarkably high strength of more than 300 MPa.

[0079] Considering the above results, subsequent evaluation was carried out after homogenizing the extruded round bars of Examples 1 and 2 as well as Comparative Examples 1 to 3 at 400°C for 48 hours and processing them into tensile test specimens.

2) Measurement Results of Grain Size

[0080] The grain size of each alloy sample is shown in Table 2.

[0081] The grain size was measured by the electron back scattered diffraction patterns (EBSD) method. Crystal grains were defined by regarding deviation of orientation of 15° or more as the grain boundary.

[0082] The average grain size was determined by simply dividing the total area by the number of crystal grains.

Table 2

Alloy	Grain size (μm)
Comparative Example 1	20.1
Example 1	9.2
Example 2	4.9
Comparative Example 2	4.2
Comparative Example 3	-

[0083] In Comparative Example 3, the grain size could not be measured since precipitates underwent coarsening. Except for Comparative Example 3, the grain size (both peak-top grain size and area average particle size) decreases as addition amounts of aluminum, calcium and strontium increases.

3) Room-Temperature Tensile Characteristics

[0084] Fig. 3 shows the measurement results of the tensile strength at room temperature. The drawing shows the measurement results of the tensile strength, 0.2% proof stress, and elongation of each alloy sample. In Comparative Examples 2 and 3, 0.2% proof stress could not be measured since the material is brittle.

[0085] In Comparative Example 1, Example 1 and Example 2, the tensile strength exhibited excellent value such as 300 MPa or more. However, it is apparent that, in Comparative Example 1, the 0.2% proof stress is less than 250 MPa, and the samples of Example 1 and Example 2 having the 0.2% proof stress of 250 MPa or more are excellent in room-temperature strength as compared with the samples of Comparative Examples. It is also apparent that the samples of Example 1 and Example 2 exhibit the elongation of 2% or more and have sufficient ductility.

[0086] It is also known that the sample, which is produced by extruding an AZ91 alloy known as a high strength magnesium alloy at an extrusion temperature of 360°C and an extrusion ratio of 22, each being the same level as that of the samples of Examples 1 and 2, exhibits the tensile strength of 295 MPa (Hanlin Ding et al., Journal of alloys and compounds, 456(2008) 400-406). As is apparent from these results, the samples of Examples 1 and 2 have high room-temperature strength.

4) High-Temperature Strength

[0087] Fig. 4 shows the measurement results of high-temperature tensile strength. The high-temperature tensile test was carried out at a measuring temperature of 175°C and a strain rate of 1 × 10^{-4}/second.

[0088] Since the sample of Comparative Example 3 was fractured soon after applying tensile stress, high-temperature strength could not be measured.

[0089] The samples of Example 1 and Example 2 exhibited high-temperature strength which is higher than that in Comparative Examples, that is, high-temperature strength at 175°C is 210 MPa or more.

[0090] As is apparent from the above results, the samples of Examples exhibit high strength at both room temperature and high temperature.

[0091] This application claims priority on Japanese Patent Application No. 2011-72505, the disclosure of which is incorporated by reference herein.

Claims

1. A magnesium alloy comprising:

aluminum (Al): 14.0 to 23.0% by mass,
calcium (Ca): 11.0% by mass or less (not including 0% by mass),
strontium (Sr): 12.0% by mass or less (not including 0% by mass), and
zinc (Zn): 0.2 to 1.0% by mass.

2. The magnesium alloy according to claim 1, further comprising at least one selected from the group consisting of:

silicon (Si): 0.1 to 1.5% by mass,
rare earth (RE): 0.1 to 1.2% by mass,
zirconium (Zr): 0.2 to 0.8% by mass,
scandium (Sc): 0.2 to 3.0% by mass,
yttrium (Y): 0.2 to 3.0 % by mass,
tin (Sn): 0.2 to 3.0% by mass,
barium (Ba): 0.2 to 3.0% by mass, and
antimony (Sb): 0.1 to 1.5% by mass.

3. The magnesium alloy a ccording to claim 1 or 2, wherein a ratio of the content of strontium (Sr) to the content of calcium (Ca) is from 1:0.3 to 1:1.5 in terms of a mass ratio.

4. The magnesium alloy according to any one of claims 1 to 3, wherein the content of aluminum (Al), the content of calcium (Ca), and the content of strontium (Sr) satisfy a relation shown in the following equation (1):

$$0.8 \times \langle Al \rangle \leq 1.35 \times \langle Ca \rangle + 1.23 \times \langle Sr \rangle + 8.5 \leq 1.2 \times \langle Al \rangle \qquad (1)$$

where <Al> is the content of aluminum (Al) expressed on % by mass basis, <Ca> is the content of calcium (Ca) expressed on % by mass basis, and <Sr> is the content of strontium (Sr) expressed on % by mass basis.

5. The magnesium alloy according to any one of claims 1 to 4, wherein precipitates containing Al_2Ca and Al_4Sr are formed in the grain boundary with an interval from each other.

Fig. 1A

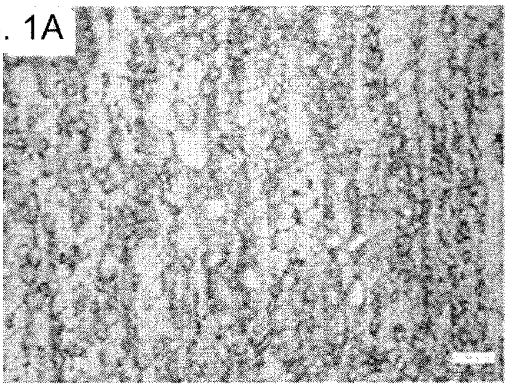


Fig. 1B

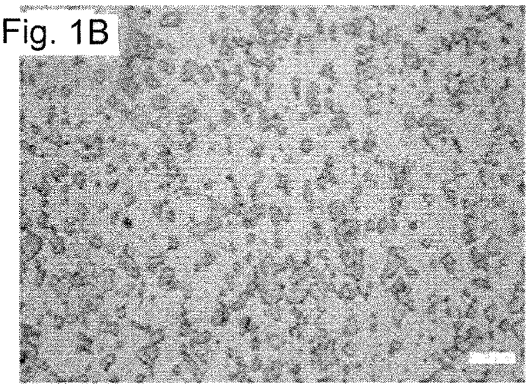


Fig. 1C

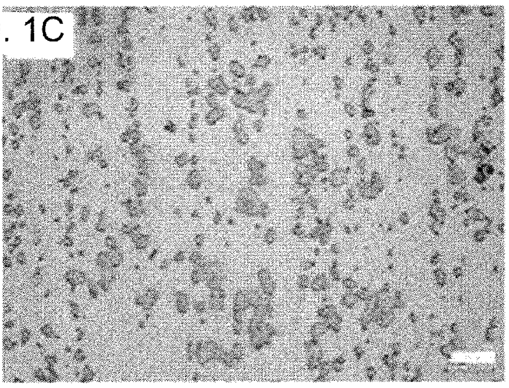


Fig. 2

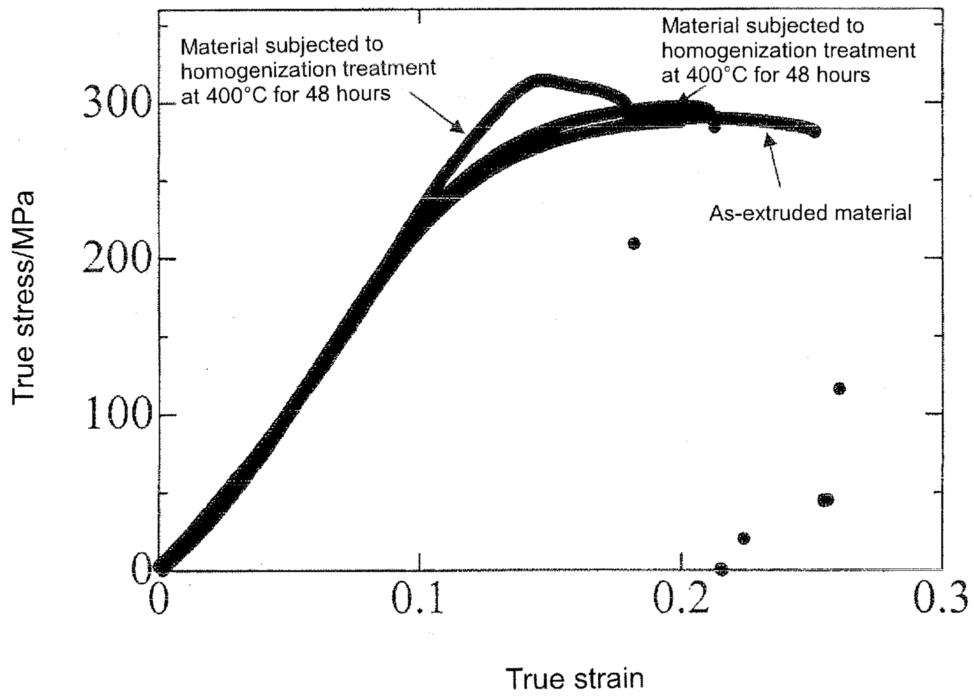


Fig. 3

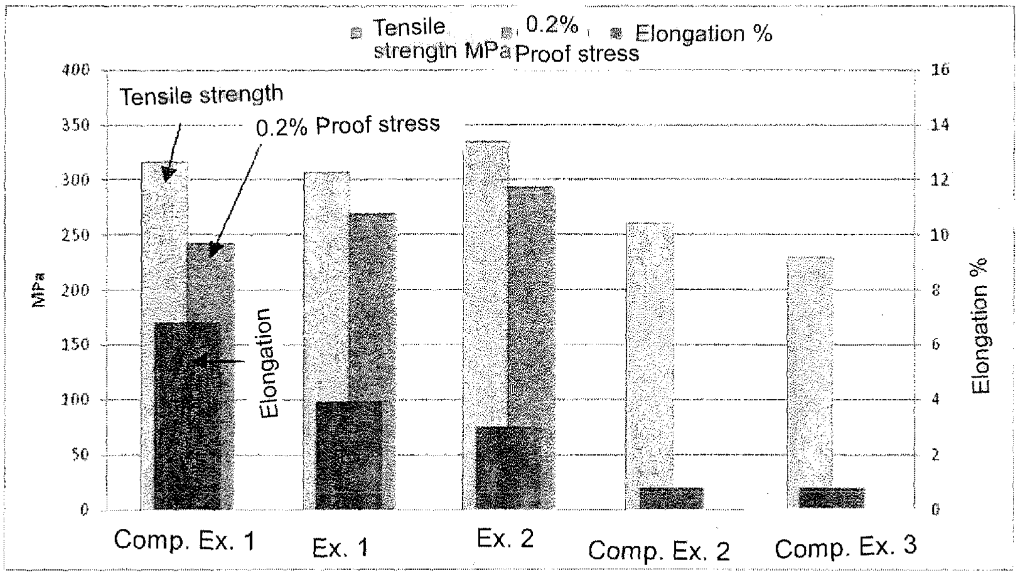
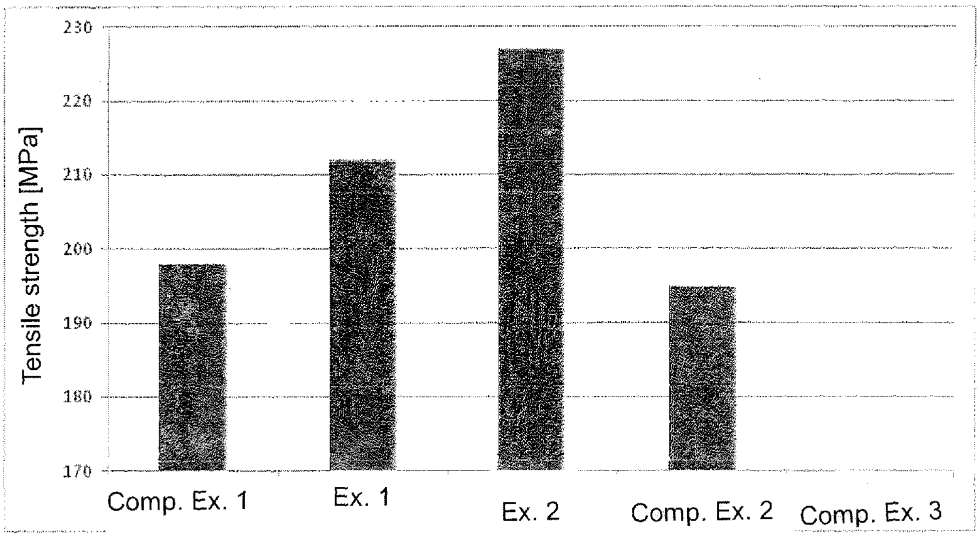

Tensile strength MPa
0.2% Proof stress
Elongation %
Tensile strength
0.2% Proof stress
Elongation
MPa
400
350
300
250
200
150
100
50
0
16
14
12
10
8
6
4
2
0
Elongation %
Comp. Ex. 1
Ex. 1
Ex. 2
Comp. Ex. 2
Comp. Ex. 3

Fig. 4


Tensile strength [MPa]
230
220
210
200
190
180
170
Comp. Ex. 1
Ex. 1
Ex. 2
Comp. Ex. 2
Comp. Ex. 3

INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2012/058113

A. CLASSIFICATION OF SUBJECT MATTER
C22C23/02(2006.01)i, *C22F1/06*(2006.01)i, *C22F1/00*(2006.01)n

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)
C22C23/02, C22F1/00-1/18

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	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	V.Raghavan,Al-Ca-Mg-Sr(Aluminum-Calcium-Magnesium-Strontium), Journal of Phase Equilibria and Diffusion, Vol.30 No.6, 2009.12, Page.636-637	1,2 3-5
Y A	JP 2010-242146 A (Toyota Central Research and Development Laboratories, Inc.), 28 October 2010 (28.10.2010), claims 1, 3 (Family: none)	1,2 3-5
Y A	JP 2004-360042 A (Takata Corp.), 24 December 2004 (24.12.2004), claim 1 (Family: none)	1,2 3-5

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search 26 April, 2012 (26.04.12)	Date of mailing of the international search report 15 May, 2012 (15.05.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000109963 A **[0007]**
- JP 2007070688 A **[0007]**
- JP 2011072505 A **[0091]**

Non-patent literature cited in the description

- **HANLIN DING et al.** *Journal of alloys and compounds,* 2008, vol. 456, 400-406 **[0086]**