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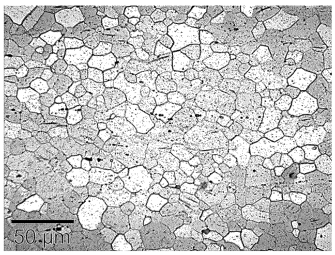
(54) MAGNESIUM ALLOY AND METHOD FOR MANUFACTURING MAGNESIUM ALLOY

(57) Disclosed are a highly versatile magnesium alloy that can achieve both formability and strength in a temperature range including room temperature, and a method for manufacturing the magnesium alloy, wherein the obtained magnesium alloy contains 0.2 to 2 wt% of Al, 0.2 to 1 wt% of Mn, 0.2 to 2 wt% of Zn, and at least 0.2 to 1 wt% of Ca, the remainder comprising Mg and unavoidable impurities, and a precipitate comprising Mg, Ca, and Al is dispersed on the (0001) plane of a magnesium matrix.

FIG.1



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Description

Technical Field

[0001] The present invention relates to a magnesium alloy and a method for manufacturing the same.

Background Art

[0002] Magnesium alloys are known as the lightest commercial metals, and as light materials substituting aluminum alloys, their application to railroad vehicles, airplanes, automobiles, etc. is being considered. However, wrought magnesium alloys are inferior in strength and formability to those in aluminum alloys. To overcome these issues and wider the application, various researches including the development of new wrought materials have been performed.

[0003] Conventional wrought magnesium alloys exhibit strength exceeding 300 MPa by grain size refinement by severe plastic deformation or by the addition of rare-earth element and zinc as alloying elements (Patent Literature 1, for example). However, the alloys fabricated by using above mentioned techniques have many problems from the viewpoint of practical application.

[0004] An alloy containing a rare-earth element has excellent strength as shown in Patent Literature 1. However, since rare-earth metals are expensive, raw material cost becomes high. Also, since primary processing such as hot working and secondary processing to obtain final shape is difficult, processing cost is also high. Consequently, the feasibility of development of versatile materials applicable to automobiles and railroad vehicles is extremely low.

[0005] Wrought materials whose strength has been improved through grain refinement by severe plastic deformation (Non-patent Literature 1, for example) are also known. However, because the material is in a work-hardened state, secondary processing at room temperature is extremely difficult. Furthermore, the manufacturing of large members is also difficult

[0006] Meanwhile, various studies have also been conducted concerning room temperature formability, in addition to the development of high-strength alloys (Patent Literatures 2 and 3). In these reports, the room temperature formability is assessed using the Index Erichsen value (IE value).

[0007] Some reports disclose the development of an alloy having excellent room temperature formability comparable to that of aluminum alloys based on the addition of alloying elements and improvement of rolling process (Patent Literature 3). However, the strength tended to decrease with the improvement of room temperature formability. Cases where the strength was improved by performing aging treatment with specific casted and extruded materials were also reported (Patent Literatures 4 and 5).

Citation List

Patent Literature

[0008]

Patent Literature 1: JP 2013-79436 A
Patent Literature 2: JP 2004-10959 A
Patent Literature 3: JP 2010-13725 A
Patent Literature 4: JP 2002-266044 A
Patent Literature 5: JP 2016-169427 A

Non-Patent Literature

[0009] W.J.Kim, I.B.Park, S.H.Han, Scripta Materialia 66 (2012) 590 - 593

Summary of Invention

Technical Problem

[0010] By the way, in the case of a body panel of automobiles, an alloy having the 0.2% proof strength of 160 MPa and the Index Erichsen value of approximately 8 mm are desired, and in many applications, an alloy that exhibits both strength and excellent secondary workability at room temperature is strongly desired. Meanwhile, with the conventional magnesium alloys and the method for manufacturing those, no materials having both strength and secondary workability at room temperature have been obtained.

[0011] In view of such circumstances, the purpose of the present invention is to provide a highly versatile alloy that achieves a balance between workability and strength in a temperature range including room temperature as well as a method for manufacturing the same.

Solution to Problem

[0012] As a method for solving the problem described above, application of aging treatment is considered. The heat treatment called T6 treatment is a type of heat treatment processes applicable to wrought materials obtained by hot or warm working, comprising solution treatment (T4 treatment) for allowing alloying elements to be dissolved in an alloy to form a supersaturated solid solution and aging treatment for enhancing the strength to the maximum hardness by dispersing precipitates.

[0013] The application of T6 treatment to deformed products such as sheet and rod materials allows them to be softened after T4 treatment due to dissolution of second phase particles into matrix, recovery of the matrix, recrystallization, and decrease in the alignment of crystallographic orientation, thus improving room temperature formability. The subsequent aging treatment allows fine precipitates to form at high density to ensure strength. Since the present commercial magnesium alloy sheet materials, such as Mg-3Al-1Zn alloy, are not age-hardenable, such heat treatment is inapplicable. However, as a result of intensive studies, the inventors found that a specific magnesium alloy could achieve a good balance between formability and strength within a temperature range including room temperature by using T6 treatment, and lead to the present invention.

[0014] Specifically, the magnesium alloy of the present invention achieving the above objective includes 0.2 to 2 wt% of Al, 0.2 to 1 wt% of Mn, 0.2 to 2 wt% of Zn, and at least 0.2 to 1 wt% of Ca, the remainder comprising Mg and unavoidable impurities, and precipitates comprising Mg, Ca, and Al are dispersed on the (0001) plane of magnesium matrix.

[0015] The magnesium alloy of the present invention may further contain precipitates comprising Al and Mn.

[0016] It is preferable that the precipitate comprising Mg, Ca, and Al have a plate-like shape, a longer side of the plate fall within a range from 3 to 6 nm, and the number density of the precipitates fall within a range from 10^{20} to $10^{24}/m^3$. It is also preferable that the average grain size of the magnesium matrix be 20 μm or less.

[0017] With this magnesium alloy, it is preferable that the basal texture intensity of the (0002) pole at the center of sheet thickness on the normalized RD-TD face of the (0002) pole figure measured by the X-ray diffraction be 5.0 mrd or lower.

[0018] It is preferable that the Index Erichsen value of the magnesium alloy of the present invention at room temperature be 6.5 mm or higher. It is also preferable that the 0.2% proof strength of the material having undergone solution treatment be 120 MPa or higher, and that the 0.2% proof strength of the magnesium alloy having undergone aging treatment in the final stage after forming be 160 MPa or higher. It is desirable that the elongation to failure in any stages be 20% or higher.

[0019] A method for manufacturing the magnesium alloy of the present invention to achieve the above objective includes: process 1 where Mg, Al, Mn, Zn, and Ca are melted to obtain a cast ingot; process 2 where the cast ingot is subjected to a homogenization treatment to obtain a homogenized ingot; process 3 where the homogenized ingot is subjected to hot or warm processing to obtain a material; process 4 where the material is subjected to solution treatment to obtain a solution treated sample; and process 5 where the solution treated sample is subjected to an aging treatment to obtain a magnesium alloy, wherein the homogenization treatment is performed at a temperature range from 400°C to 500°C for a specified time period in process 2 to obtain the homogenized ingot, and the aging treatment is performed at a temperature range from 140°C to 250°C for a specified time period in process 5 to obtain the magnesium alloy.

[0020] The method for manufacturing a magnesium alloy of the present invention can include a secondary working process for subjecting the quenched sheet to secondary processing between process 4 and process 5. In that case, it is preferable that the solution treated sample having the 0.2% proof strength of 120 MPa or higher be subjected to the secondary processing, and that the 0.2% proof strength be increased to 160 MPa or higher in process 5. It is also preferable that hot or warm processing be performed in process 3. It is further preferable that the aging treatment be performed in process 5 to increase the hardness of the magnesium alloy.

Advantageous Effects of Invention

[0021] According to the present invention, both good formability and high strength can be achieved at within a temperature range including room temperature, and since expensive rare-earth metal elements are not used as alloying elements, highly versatile magnesium alloy and a method for manufacturing the same can be provided.

Brief Description of Drawings

[0022]

FIG. 1 is an optical micrograph of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 1.

FIG. 2 is the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 1.

FIG. 3 shows the tensile stress-strain curves of the material having undergone solution treatment, which is the solution treated sample in process 4, and the material having undergone aging treatment in process 5, in Example 1.

FIGs. 4 (a), 4 (b) and 4 (c) show the material having undergone aging treatment in Example 1 observed by a transmission-type electron microscope, wherein FIG. 4 (a) is a bright field TEM image, FIG. 4 (b) is a selected area diffraction pattern obtained from [011 (bar) 0] and [112 (bar)0] zone axis, and

FIG. 4 (c) is a three-dimensional atom map observed by a three-dimensional atom probe.

FIGs. 5 (a), 5 (b), 5 (c) and 5 (d) show the material having undergone aging treatment in Example 1 observed under a transmission-type electron microscope, wherein FIG. 5 (a) is a bright field TEM image, FIG. 5 (b) is a high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image, FIG. 5 (c) is a magnified view of the HAADF-STEM image in FIG. 5 (b), and FIG. 5 (d) is a line concentration profile showing the result of elemental analysis along the allow shown in FIG. 5 (c).

FIG. 6 is an optical micrograph of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 5.

FIG. 7 is the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 5.

FIG 8 shows the tensile stress-strain curves of the material having undergone solution treatment, which is the solution treated sample in process 4 and the material having undergone aging treatment in process 5 in Example 5.

FIG. 9 is an optical micrograph of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 7.

FIG. 10 shows the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 7.

FIG. 11 shows the tensile stress-strain curves of the material having undergone solution treatment, which is the solution treated sample in process 4, and the material having undergone aging treatment in process 5 in Example 7.

FIG. 12 is an optical micrograph of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 9.

FIG. 13 shows the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment, which is the solution treated sample in process 4 in Example 9.

FIG. 14 shows the tensile stress-strain curves of the material having undergone solution treatment, which is the solution treated sample in process 4, and the material having undergone aging treatment in process 5 in Example 9.

FIG. 15 is an optical micrograph of the material having undergone solution treatment, which is the solution treated sample in process 4 in Comparative Example 1.

FIG. 16 shows the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment, which is the solution treated sample in process 4 in Comparative Example 1.

FIG. 17 shows the tensile stress-strain curve of the material having undergone solution treatment, which is the solution treated sample in process 4, and the material having undergone aging treatment in process 5 in Comparative Example 1.

Description of Embodiments

[0023] Embodiments of the present invention will hereinafter be described in detail.

[0024] The magnesium alloy of the present invention is an alloy containing 0.2 to 2 wt% of Al, 0.2 to 1 wt% of Mn, 0.2 to 2 wt% of Zn, and at least 0.2 to 1 wt% of Ca, and the remainder comprises Mg and unavoidable impurities.

[0025] This magnesium alloy has a magnesium matrix comprising Mg or Mg solid solution including Al, Mn, Zn, and Ca, and a precipitate containing at least one or more of Al, Mn, Zn, and Ca. The form of the magnesium alloy is not particularly limited, and may be in a form of each raw material such as sheet material, for example, or may be in an intermediate form or in a form of final products.

[0026] In the magnesium matrix of the magnesium alloy of the present invention, T4 treatment decreases the alignment of basal planes, and allows Al, Ca, Zn, and Mn, which are alloying elements forming precipitates, to dissolve into the matrix. It is preferable that the average grain size of the magnesium matrix be 20 μm or less. If the grain size is excessively large, the formation of deformation twin, which originates a crack, is facilitated, decreasing formability at room temperature significantly, which is undesirable.

[0027] It is desirable that Al content in the magnesium alloy of the present invention fall within a range from 0.2 wt% or more to 2 wt% or less. If the Al content is low, useful precipitates, which will be described later, cannot be obtained easily. Meanwhile, if it is too high, precipitated phase changes into coarse precipitates such as Al_2Ca phase ineffective

for strengthening, which is undesirable.

[0028] It is preferable that the Mn content in the magnesium alloy of the present invention fall within a range from 0.2 wt% or more to 1 wt% or less. If the Mn content is low, Al-Mn-based compounds suppressing coarsening of grains are not formed easily. Meanwhile if it is too high, Al is used for the formation of Al-Mn-based compounds, not exhibiting large age-hardening effect, which is undesirable.

[0029] It is preferable that the Zn content in the magnesium alloy of the present invention fall within a range from 0.2 wt% or more to 2 wt% or less. If the Zn content is low, the alignment of basal planes increases, inhibiting excellent room temperature formability from being obtained. Meanwhile, if it is excessive, the melting point of the alloy decreases, increasing the possibility of cracking at the time of quenching after the solution treatment, and in addition age-hardening effect decreases significantly, which is undesirable.

[0030] It is preferable that the Ca content in the magnesium alloy of the present invention fall within a range from 0.2 wt% to 1 wt%. If the rate of content of Ca is low, useful precipitates, which will be described later, cannot be obtained easily. Meanwhile, if the content of Ca is too high, precipitates containing Al and Ca, or Mg and Ca, are formed, decreasing formability and ductility, which is undesirable.

[0031] The precipitates on the magnesium alloy of the present invention include the one comprising Mg, Ca, and Al, and the one comprising Al and Mn. The precipitate comprising Mg, Ca, and Al is a nano-size precipitate called Guinier. Preston. Zone (G.P. Zone) dispersed on the (0001) plane of magnesium matrix. By forming the precipitate comprising Mg, Ca, and Al while aging treatment is being performed, the strength of the alloy can be improved. Further, that the precipitates are dispersed may be in the state that a large amount of fine nano-order precipitates are deposited. The precipitates comprising Mg, Ca, and Al (G. P. Zone) observed in the material having undergone aging treatment of magnesium alloy may be those having a plate-like shape. Those nano-size plate-like precipitates have a diameter within a range from 3 to 6 nm, for example, and its chemical formula is $Mg_2(Ca, Al)$. In other words, Mg accounts for 67 at%, and Ca + Al accounts for 33 at%, but the dimensions and element composition are not limited to those only.

[0032] The precipitate comprising Al and Mn is a rod-shaped Al-Mn-based precipitate. The structure of this precipitate can be refined as a result of formation of the precipitate by Al and Mn during the homogenization processing and the solution treatment. The precipitate comprising Al and Mn is observed with the magnesium alloy having undergone solution treatment and aging treatment. The length of the rod-shaped Al-Mn-based precipitate falls within a range approximately from 50 nm to 300 nm, and its diameter falls within a range approximately from 2 to 20 nm, but they are not limited to those only.

[0033] It is preferable that the number density of the precipitate comprising Mg, Ca, and Al (G. P. Zone) fall within a range from 10^{20} to $10^{24}/m^3$. If the number density is extremely low, the effect of improving the strength by nano-sized precipitate becomes difficult to be obtained, which is undesirable. Meanwhile, the number density of the precipitate comprising Al and Mn falls within a range approximately from 10^{20} to $10^{21}/m^3$. Since the number density of the precipitate comprising Al and Mn is lower than that of the G. P. Zone, 10^{20} to $10^{24}/m^3$, by approximately 10^3 to 10^4 m^{-3}, the strength of the magnesium alloy is not affected greatly.

[0034] As the degree of orientation of the grain, the basal texture intensity on the (0002) face of the normalized RD-TD face at the center of sheet thickness in the (0002) pole figure should be less than 5.0 mrd, which allows the degree of orientation of the grain to remain low, ensuring excellent formability.

[0035] It is preferable that the Index Erichsen value of the magnesium alloy of the present invention at room temperature be 6.5 mm or higher, which improves the formability of the magnesium alloy at room temperature such as press forming, and also further improves its formability at elevated temperature. This Index Erichsen value (IE value) is used to assess the room temperature formability by conducting an Erichsen test, in which a ball-head punch is pressed against a thin sheet whose periphery is fastened at a constant speed to deform the thin sheet and the height of the depression is measured until break occurs to the material.

[0036] Meanwhile, it is preferable that the magnesium alloy of the present invention have the 0.2% proof strength of 120 MPa or higher while its room temperature formability be improved, and it is desirable that its elongation to failure be 20% or higher. The 0.2% proof strength is also called the yield stress. Furthermore, it is preferable that its Vickers hardness be 45 HV or higher. The 0.2% proof strength of the magnesium alloy of the present invention is preferably 160 MPa or higher.

[0037] A method for manufacturing the magnesium alloy will then be described.

[0038] This manufacturing method includes: Process 1 for obtaining a cast ingot by melting and casting Mg, Al, Mn, Zn, and Ca; process 2 for obtaining a homogenized ingot by subjecting the cast ingot to a homogenization treatment; process 3 for obtaining a material by subjecting the homogenized ingot to a hot or warm working; process 4 for obtaining a solution treated sample by subjecting the material to a solution treatment; and process 5 for obtaining a magnesium alloy by subjecting the solution treated sample to an aging treatment.

(Process 1: Casting)

[0039] In process 1, by melting and casting alloy content including 0.2 to 2 wt% of Al, 0.2 to 1 wt% of Mn, 0.2 to 2 wt% of Zn, and at least 0.2 to 1 wt% of Ca, the remainder comprising Mg and unavoidable impurities, the cast ingot is produced. A melting furnace used for melting or the size of the cast ingot are not particularly limited, provided that a cast ingot having a desired composition can be produced.

(Process 2: Homogenization treatment)

[0040] In process 2, a homogenized ingot is produced by subjecting the cast ingot to a homogenization treatment at a temperature falling within a range from 400°C or higher to 500°C or lower for a specified time period. By the homogenization treatment, the distribution of alloying elements existing in the cast ingot are homogenized, and precipitates formed while the molten metal is quenched are dissolved in the magnesium matrix to form a solid solution.

[0041] In a region where Zn is macro-segregated at high concentration, it is likely that the alloy is melted if heat treatment is started at a temperature of 340°C or higher. To prevent it from occurring, by performing heat treatment at a temperature lower than 340°C, Zn is made to diffuse by suppressing the initial melting of Mg-Zn phase formed at the time of casting, and then the heat treatment is performed at a temperature ranging from 400°C or higher to 500°C or lower for a specified time period. The distribution of Zn is thus homogenized to obtain the homogenized ingot.

[0042] The conditions for homogenization treatment are not particularly limited and can be set depending on the cast ingot or the elemental component of the alloy, provided that the alloying elements can be dissolved into the magnesium matrix to form the solid solution by the heat treatment.

(Process 3: Hot or warm working)

[0043] In process 3, a sheet-shaped material is produced by working the homogenized ingot into a sheet material by warm rolling. The rolling is performed to roll the homogenized ingot into a sheet material by setting the rolling conditions such as sample temperature, roll temperature, roll speed, circumferential rolling speed, number of passes, existence of intermediate heat treatment of the sample, and temperature and duration of intermediate heat treatment.

[0044] The sample temperature and rolling temperature may be made to be as low as possible, provided that the sample is not cracked during rolling. The rolling rate may also be made to be as large as possible, provided that the sample is not cracked during rolling. The intermediate heat treatment of the sample is a heat treatment performed in the middle of rolling, and can be performed at a high temperature within a range that does not allow cracks and incipient melting to occur.

[0045] The hot or warm working is not particularly limited to rolling only, but any extending processing is allowed, provided that a microstructure can be produced. Any methods including twin roll casting rolling, forging, and extrusion processing are allowed.

(Process 4: Solution treatment)

[0046] In process 4, the sheet-shaped material is subjected to a solution treatment, and by quenching it, the solution treated sample is produced. In the solution treatment, by subjecting the material to heat treatment, fine precipitates formed during the hot or warm processing are made to be dissolved into the matrix and then re-crystalized to form a composition.

[0047] By performing the solution treatment after the hot or warm processing, grains can be made to orient at random, allowing excellent formability to be obtained. The solution treatment is performed at a temperature ranging from 350°C to 500°C depending on the material and by maintaining the solution treatment period of 15 minutes to 24 hours. Note that it is not necessary to perform the treatment for unnecessarily long period because prolonged heat treatment results in increase in the manufacturing cost.

(Secondary processing)

[0048] To produce a magnesium alloy having a shape different from that of the solution treated sample obtained by the solution treatment following process 4, secondary processing can be performed to the solution treated sample. The secondary processing is not particularly limited, but sheet-metal forming such as press forming, spinning and machine processing can be performed as required. Also, to produce a magnesium alloy with the shape of the solution treated sample obtained by the solution treatment as it is, the next process can be performed without performing the secondary processing.

(Process 5: Aging treatment)

[0049] In process 5, by subjecting the solution treated sample to age-hardening treatment by the heat treatment, precipitates formed on the solution treated sample having undergone solution treatment are made to disperse to enhance its strength, thus producing the magnesium alloy of the present invention. In this case, by performing the aging treatment, which has never been performed with conventional commercial magnesium alloys, significant enhancement in strength of the magnesium alloy can be achieved.

[0050] The aging treatment is performed at a temperature ranging from 140°C to 250°C for a specified time period. The aging treatment is performed for a time period where the hardness of the magnesium alloy is increased, preferably for a time period where the hardness of the magnesium alloy becomes the maximum.

[0051] The magnesium alloy of the present invention thus manufactured comprises 0.2 to 2 wt% of Al, 0.2 to 1 wt% of Mn, 0.2 to 2 wt% of Zn, and at least 0.2 to 1 wt% of Ca, the remnant comprising Mg and unavoidable impurities, with the precipitates comprising Mg, Ca, and Al dispersed on the surface of the (0001) plane of the magnesium matrix, and the alloy preferably further contains precipitates comprising Al and Mn.

[0052] According to the magnesium alloy and the method for manufacturing the same as described above, by performing solution treatment after rolling, grains can be oriented at random, which ensures excellent formability. By randomly orienting the grains, the strength suddenly decreases, but it is possible to ensure formability, strength, and ductility at the same time by forming nano-sized precipitates by the aging treatment.

[0053] Furthermore, according to the magnesium alloy and the method for manufacturing the same, a highly versatile magnesium alloy that satisfies both formability and strength within a temperature range including room temperature can be obtained. For example, as a material for automobiles such as body panels, strength and room temperature formability, which are required as applicable mechanical properties, can be achieved.

[0054] It is possible to achieve formability and room temperature strength much higher than that of conventional commercial magnesium alloy sheet materials by performing heat treatment and working combining heat treatment and simple rolling that use existing facilities and relatively inexpensive alloying elements without using expensive and scarce heavy rare-earth elements. It is thus possible to satisfy characteristics required for automobile applications.

[0055] Note that the embodiment described above can be changed as required within the scope of the present invention. With the above method for manufacturing the magnesium alloy, the example where the magnesium alloy having undergone solution treatment following hot or warm working was subjected to various working such as squeezing and bending to form a deformed product, followed by aging treatment, was described. However, it is also possible to perform solution treatment and aging treatment after the hot or warm working to produce a magnesium alloy, and then various working such as squeezing and bending can be performed to create a formed product. In that case, as the method for manufacturing the magnesium alloy, it is also possible to complete the process by performing solution treatment, following the hot or warm working, without performing the aging treatment. It is thus possible to apply the present invention as a method for manufacturing working materials.

Examples

[0056] Examples of the present invention will hereinafter be described. Note that the alloy compositions are all referred to as wt%.

[Example 1]

(Process 1: Casting)

[0057] By using a high-frequency induction melting furnace (ULVAC, FMI-I-20F), an alloy having the composition of Mg-1.2Al-0.3Ca-0.4Mn-0.3Zn as shown by A-1 in Table 1 was produced as a cast ingot by melting and casting it into a mold. The numeric values in front of each element other than Mg, namely Al, Ca, Mn, and Zn, represent percentage by weight of each element. The thickness of the cast ingot was approximately 10 mm.

(Process 2: Homogenization treatment)

[0058] After the cast ingot was maintained at 300°C for 4 hours, the temperature was increased to 500°C at the heating rate of 10°C/h, the temperature was maintained at that state for 6 hours, and then by decreasing it to a room temperature by water quenching, the homogenization treatment was performed to produce a homogenized ingot. In this homogenization treatment, to suppress the initial melting of the Mg-Zn phase formed at the time of casting, the heat treatment was performed at 300°C first, and then by performing heat treatment at 500°C, the distribution of Zn was homogenized.

(Process 3: Hot or warm working)

[0059] By allowing the homogenized ingot to pass through a rolling passage that can be pressurized by rolling using a rolling equipment (UENOTEX, H9132), the rolling treatment was performed by dividing it into the rough rolling process and the final rolling process, thus producing a material. In the rough rolling process, the rolling equipment whose circumferential rolling speed was 2 m/min. as shown in Table 1 was used. The material was made to pass through the rolling passage 4 times with the sample temperature and rolling temperature maintained at 300°C, and with the rolling rate maintained at 15%, to roll the homogenized ingot having the thickness of 10 mm into the one having the thickness of 5 mm.

[Table 1]

[0060]

[Table 1]

Symbol	Chemical composition (wt. %)	Rolling conditions									
		Rough rolling process (Sheet thickness: 10→5mm, Circumferential rolling speed: 2 m/min.)				Final rolling process (Sheet thickness: 6→1 mm, Circumferential rolling speed: 2 m/min.					
		Sample temperature °C	Rolling temperature °C	Rolling rate %	Number of passes Times	Sample temperature °C	Rolling temperature °C	Sample reheating °C	Rolling rate %	Number of passes Times
A-1	Mg-1.2Al-0.8Ca-0.45Sn-0.5Zn	300	300	15	4	100	100	400	23	6
A-2		300	300	15	4	300	300	400	23	6
A-3		300	300	15	4	300	300	400	23	6
A-4		300	300	15	4	300	300	-	23	6
B-1	Mg-1.2Al-0.8Ca-0.45Sn-0.5Zn	300	300	15	4	100	100	450	23	6
B-2		300	300	15	4	300	300	450	23	6
C-1	Mg-1.2Al-0.8Ca-0.4Mn-0.5Zn	300	300	15	4	100	100	450	23	6
C-2		300	300	15	4	300	300	450	23	6
D-1	Mg-1.2Al-0.8Ca-0.4Mn-1.5Zn	300	300	15	4	100	100	450	23	6
D-2		300	300	15	4	300	300	450	23	6

[0061] Following the primary rolling process, the final rolling process was performed while intermediate heat treatment was conducted by using rolling mill whose circumferential rolling speed was 2 m/min as shown in Table 1. In the final rolling process, the sample temperature and the roll temperature were set to 100°C, and the sample was made to pass through the rolling mill 6 times at the 23% thickness reduction per pass. By performing the final rolling while conducting

intermediate heat treatment, in which the sample was maintained at the sample reheating temperature of 500°C for 5 minutes every time the sample was made to pass through the rolling passage, the sample thickness was rolled down to 1 mm, thus producing the material.

(Process 4: Solution treatment)

[0062] By subjecting the sheet-shaped material to solution treatment, a solution treated sample was prepared. The heating was performed with the solution treatment temperature set at 450°C and the duration of the solution treatment set at one hour.

[0063] The mechanical strength of the obtained solution treated sample was measured to find that, as shown in Table 2, the Index Erichsen value, which indicates the formability (index Erichsen value) assessed by the Erichsen test (testing machine: Erichsen, type 111), was 7 mm, the Vickers hardness was 47 VHN, the 0.2% proof strength was 127 MPa, the tensile strength was 223 MPa, and the elongation to failure was 30%.

[Table 2]

[0064]

[Table 2]

	Symbol	Solution treatment		Mechanical characteristics					Microstructure	
		Temperature	Duration	I.E. (mm)	Hardness	$\sigma_{0.2}$	σ_{UTS}	Er	Grain size	Basal texture intensity of (0002) pole
		°C	h		VHN	MPa	MPa	%	μm	m.r.d.
Example 1	A-1	450	1	7	47	127	201	30	120	3.6
Example 2	A-1	450	2	6.8	-	137	224	28	127	-
Example 3	A-1	450	4	6.8	-	127	223	27	132	-
Example 4	A-2	450	1	6.8	49	150	230	30	135	4.7
Example 5	A-2	450	2	6.6	-	124	222	24	139	-
Example 6	B-1	350	4	6.6	49	162	234	32	93	4.0
Example 7	B-1	450	1	7.5	52	142	231	33	97	3.7
Example 8	B-2	450	1	7.1	50	140	231	30	114	4.3
Example 9	C-1	350	4	7.8	51	166	239	33	93	3.4
Example 10	C-1	450	1	7.7	52	144	242	32	107	3.5
Example 11	C-2	450	1	6.9	53	144	237	29	107	3.5
Example 12	D-1	350	4	8.3	53	160	247	33	85	3.7
Example 13	D-1	450	1	8.1	52	148	249	30	115	3.8
Example 14	D-2	350	1	8	-	157	247	32	108	3.6
Example 15	D-2	450	1	7.2	54	141	247	31	111	3.5
Comparative Example 1	A-1	350	4	6.4	60	149	256	28	99	4.0
Comparative Example 2	A-1	450	0.17	6.2	-	133	228	30	103	-
Comparative Example 3	A-1	600	1	5.6	-	117	226	29	131	-
Comparative Example 4	A-1	600	24	4	-	29	96	17	Huge	-
Comparative Example 5	A-2	450	4	6.3	-	121	230	30	150	-
Comparative Example 6	A-3	450	1	5.4	48	120	221	30	214	4.8
Comparative Example 7	A-3	450	2	5.1	-	118	220	29	287	-
Comparative Example 8	A-3	450	4	5.3	-	118	218	32	229	-
Comparative Example 9	A-4	450	1	6.2	46	123	222	23	128	4.4
Comparative Example 10	A-4	450	2	5.9	-	121	223	29	135	-
Comparative Example 11	A-4	450	4	5.8	-	119	219	26	130	-
Comparative Example 12	B-2	350	1	5.9	-	161	230	27	90	-

[0065] FIG. 1 shows an optical micrograph (Nikon, Eclipse LV-100) of the material having undergone solution treatment, which is the solution treated sample. The grain size was calculated by the linear interception method to be 12.0 μm. The grain size was calculated based on the lineal intercept method (E112-13) by the American Society for Testing and

Materials (ASTM). FIG. 2 shows the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment. The intensity (maximum random distribution, m. r. d., or also called basal texture intensity) of the (0002) pole was 3.6 mrd. The basal texture intensity is an index that indicates the relative strength of the texture on the (0002) surface (random orientation regarded as 1).

(Process 5: Aging treatment)

[0066] As shown in Table 3, the aging treatment was performed with the aging temperature set to 200°C and the aging time set at 0.5 hours. The mechanical property of the obtained solution treated sample was measured to be as follows as shown in Table 3: the Vickers hardness; 57 VHN, the 0.2% proof strength; 187 MPa, the tensile strength; 248 MPa, and the elongation to failure; 28%.

[Table 3]

[0067]

[Table 3]

	Symbol	Solution treatment		Aging temperature		Mechanical characteristics			
		Temperature	Duration	Aging temperature	Aging duration	Hardness	σ_{ys}	σ_{UTS}	E_f
		°C	h	°C	h	VHN	MPa	MPa	%
Example 1	A-1	450	1	200	0.5	57	187	248	28
Example 2	A-1	450	2	200	*1	-	*1	*1	*1
Example 3	A-1	450	4	200	*1	-	*1	*1	*1
Example 4	A-2	450	1	200	*1	-	*1	*1	*1
Example 5	A-2	450	2	200	*2	-	*2	*2	*2
Example 6	B-1	850	4	200	2	61	164	234	29
Example 7	B-1	450	1	200	0.25	60	201	257	22
Example 8	B-2	450	1	200	0.25	60	183	252	21
Example 9	C-1	850	4	200	2	52	171	244	31
Example 10	C-1	450	1	200	1	61	204	263	27
Example 11	C-2	450	1	200	0.25	61	189	255	28
Example 12	D-1	850	4	200	1	53	171	251	32
Example 13	D-1	450	1	200	0.5	53	180	254	30
Example 14	D-2	850	1	200		-			
Example 15	D-2	450	1	200	0.25	55	181	259	32

*1: The mechanical characteristics can be estimated as in the case of the mechanical characteristics in Example 1.
*2: The mechanical characteristics can be estimated as in the case of the mechanical characteristics in Example 4.

[0068] FIG. 3 shows the tensile stress-strain curves of the material having undergone solution treatment in process 4 (T4), which is the solution treated sample, and the material having undergone aging treatment in process 5 (T6). By the aging treatment, the yield strength was found to have increased significantly up to 187 MPa.

[0069] FIGs. 4 (a), 4 (b) and 4 (c) show images of the material having undergone aging treatment in Example 1

observed under a transmission electron microscope, wherein FIG. 4 (a) is a Bright field TEM image, FIG. 4 (b) is a selected area diffraction image obtained from [011 (bar)0], [112 (bar)0] zone axis, and FIG. 4 (c) is a chart showing a three-dimensional atom map. The transmission electron microscope by FEI (Titan, G2 80-200) was used.

[0070] Based on the linear distortion contrast in the Bright field TEM image in FIG. 4 (a) and the streak in the selected area diffraction image, the existence of G. P. Zone was confirmed.

[0071] The three dimensional atom probe (3DAP) is a method of measuring elemental distribution in three-dimension by applying a high voltage to a sample, detecting ions undergoing electric field evaporation from the surface of the specimen using a mass spectrometer, continuously detecting the individually detected ions in the depth direction, and arranging the ions in the order of detection. The 3-dimensional atom probe used in this invention was made by the inventor (Kazuhiro Hono) of the National Institute for Materials Science, and a mass spectrometer (ADLD detector) by CAMECA was used for ion analysis.

[0072] Based on the 3-dimensional atom map in FIG. 4 (c), the G. P. Zone observed in FIG. 4 (a) was confirmed to be comprised Mg, Ca, and Al. The typical elemental composition formula of the G. P. Zone is $Mg_2(Ca, Al)$, and Mg accounts for 67 at% and Ca+Al accounts for 33 at%. The observation was found to coincide with this theory.

[0073] FIGs. 5 (a), 5 (b), 5 (c) and 5 (d) show the images of the material having undergone aging treatment in Example 1 observed by the transmission electron microscope, wherein FIG. 5 (a) is a Bright field TEM image, FIG. 5 (b) is a high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image, FIG. 5 (c) is an magnified HAADF-STEM image in FIG. 5 (b), and FIG. 5 (d) shows the result of elemental analysis along the arrow in FIG. 5 (c). The elemental analysis was performed by using an EDS (FEI, EDS elemental analyzer [Super X]) attached to the scanning transmission electron microscope by FEI.

[0074] As shown in FIGs. 5 (a) to 5 (c), a precipitate other than the G. P. Zone comprising Ca and Al shown in FIG. 4 was observed in the magnesium matrix. As shown in FIG. 5 (d), this precipitate was confirmed to be comprised Al and Mn as the result of elemental analysis. The reading in FIG. 5 (d) shows that the Mg accounted for 80 to 90 at%, Al accounted for 5 to 10 at%, Mn accounted for 5 to 10 at%, and Zn and Ca accounted for 0.5 to 1.0 at%. With the TEM-EDS elemental analysis, however, this reading includes the signals emitted from the magnesium matrix surrounding the precipitate because the size of the precipitate is smaller than the film thickness of the sample. In other words, the magnesium matrix affects the elemental analysis signals from the precipitate itself as noise.

[0075] As described above, the magnesium alloy that has both sufficient formability and strength in a temperature range around room temperatures was obtained.

[Example 2]

[0076] A magnesium alloy was manufactured in the same manner as Example 1 except that, as shown in Table 2, the time for the solution treatment was set to 2 hours when producing a solution treated sample by subjecting the material to solution treatment.

[0077] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solids as well as the features of the microstructure. As apparent from Tables 2 and 3, the formability in a temperature range around room temperatures was ensured as in the case of Example 1, and the magnesium alloy that ensures both formability and strength was obtained.

[0078] Regarding the sample having undergone solution treatment in Example 2, the number density of the precipitate comprising Al and Mn observed in Example 1 (see FIG. 5) was measured to be approximately 10^{20} to 10^{21} m^{-3}. The number density of the precipitate comprising Al and Mn was lower than that of G. P. Zone, 10^{20} to $10^{24}/m^3$, by approximately 10^3 to 10^4 m^{-3}. Thus, it was found that the precipitate comprising Al and Mn does not affect the strength of the magnesium alloy very much, compared to G. P. Zone.

[Example 3]

[0079] A magnesium alloy was manufactured in the same manner as Example 1 except that the duration of solution treatment was set to 4 hours, as shown in Table 2, when producing a solution treated sample by subjecting the material to solution treatment in process 4.

[0080] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure.

[0081] As apparent from Tables 2 and 3, formability in a temperature range around room temperatures was ensured, and thus the magnesium alloy that ensures both formability and strength was obtained.

[Example 4]

[0082] In process 1, as shown in A-2 in Table 1, an alloy having a structure of Mg-1.2A1-0.3Ca-0.4Mn-0.3Zn was

melted and casted in a mold to create a cast ingot, with the rolling temperature in the final rolling process set to 200°C. In process 5, as shown in Table 3, the aging temperature was set to 450°C and the aging time was set to 2 hours. A magnesium alloy was manufactured in the same manner as Example 1 except the above.

[0083] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the obtained magnesium alloy was confirmed to ensure both formability and strength even if the rolling conditions and aging conditions were varied.

[Example 5]

[0084] A magnesium alloy was manufactured in the same manner as Example 1 except that when producing a material by subjecting the homogenized ingot to rolling treatment in process 3, the sample temperature and rolling temperature in the final rolling process were set to 200°C as shown in A-2 in Table 1, and that when producing a solution treated sample by subjecting the material to solution treatment in process 4, the duration of solution treatment was set to 2 hours as shown in Table 2.

[0085] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the obtained magnesium alloy was confirmed to ensure both formability and strength even if the rolling conditions and aging conditions were varied.

[Example 6]

[0086] A homogenized ingot was produced by melting and casting in a mold an alloy having the composition of Mg-1.2Al-0.5Ca-0.4Mn-0.3Zn in process 1, as shown in B-1 in Table 1, maintaining the cast ingot at 300°C for 4 hours in process 2, then increasing the temperature to 450°C at the heating rate of 7.5°C/, maintaining it for 6 hours, and then water-quenching it down to a room temperature, thus performing the homogenization treatment.

[0087] The sample reheating temperature in the final rolling process in process 3 was set to 450°C, and the aging temperature set to 350°C and the aging time set to 4 hours in process 5 as shown in Table 3. The magnesium alloy was manufactured in the same manner as Example 1 except the above.

[0088] Table 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the obtained magnesium alloy was confirmed to ensure both formability and strength even if the compositions, homogenization conditions, rolling treatment conditions, and aging treatment conditions were varied.

[Example 7]

[0089] A homogenized ingot was produced by melting and casting in a mold an alloy having the composition of Mg-1.2Al-0.5Ca-0.4Mn-0.3Zn in process 1, as shown in B-1 in Table 1, maintaining the cast ingot at 300°C for 4 hours in process 2, then increasing the temperature to 450°C at the heating rate of 7.5°C/h, maintaining it for 6 hours, and then water-quenching it down to a room temperature, thus performing the homogenization treatment.

[0090] The magnesium alloy was manufactured in the same manner as Example 1 except that the sample reheating temperature in the final rolling process in process 3 was set to 450°C, and the aging time in process 5 set to 0.25 as shown in Table 3.

[0091] Tables 2 and 3 and FIGs. 6 to 8 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure.

[0092] FIG. 6 shows an optical microscope image of the material having undergone the solution treatment. The grain size was calculated by the linear interception method to be 9.7 μm. FIG. 7 shows the (0002) pole figure obtained by subjecting the material having undergone solution treatment to the X-ray diffraction. The basal texture intensity of the (0002) pole was 3.7 mrd, inclining in the rolling direction.

[0093] FIG. 8 shows the tensile stress-strain curves of the material having undergone solution treatment (T4), which is the solution treated sample in process 4, and that of the material having undergone aging treatment (T6) in process 5. Table 3 shows the 0.2% proof strength, the tensile strength, and the elongation (E_f) read from the tensile stress-strain curves.

[0094] The yield strength of the material having undergone solution treatment exhibited the excellent formability at room temperature, the yield strength being 142 MPa and the Index Erichsen value being 7.5 mm. The aging treatment then performed significantly increased the yield strength up to 201 MPa.

[0095] As described above, the magnesium alloy that ensures both formability and strength in a temperature range around room temperatures was obtained.

[Example 8]

[0096] A magnesium alloy was manufactured in the same manner as in Example 7 except that the sample temperature and the rolling temperature were set to 200°C in the final rolling process in process 1 as shown in B-2 in Table 1.

[0097] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the magnesium alloy, that achieves formability in a temperature range around room temperatures, thus ensuring both formability and strength, was obtained.

[Example 9]

[0098] The homogenized ingot was produced by melting and casting in a mold an alloy having the composition of Mg-1.2Al-0.5Ca-0.4Mn-0.8Zn in process 1 as shown in C-1 in Table 1, and by maintaining the cast ingot at 300°C for 4 hours in process 2, then increasing the temperature to 450°C at the heating rate of 7.5°C/h, maintaining it for 6 hours, and then water-quenching it down to a room temperature.

[0099] The sample reheating temperature in process 3 was set to 450°C, the solution treatment temperature was set to 350°C, and the duration of solution treatment was set to 4 hours, as shown in Table 2, when a solution treated sample was produced by subjecting the material to solution treatment in process 4, and the aging temperature was set to 200°C and aging time was set to 2 hours in process 5 as shown in Table 3.

[0100] The magnesium alloy was manufactured in the same manner as Example 1 except the above.

[0101] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the solid obtained as well as the features of the microstructure. As apparent from Tables 2 and 3, the magnesium alloy that achieves both formability and strength was obtained even if the composition, homogenization conditions, rolling treatment conditions, and aging treatment conditions were varied.

[Example 10]

[0102] The homogenized ingot was produced by melting and casting in a mold an alloy having the composition of Mg-1.2Al-0.5Ca-0.4Mn-0.8Zn in process 1 as shown in C-1 in Table 1, and by maintaining the cast ingot at 300°C for 4 hours in process 2, then increasing the temperature to 450°C at the heating rate of 7.5°C/h, maintaining it for 6 hours, and then water-quenching it down to a room temperature. The magnesium alloy was manufactured in the same manner as Example 1 except that the sample reheating temperature in the final rolling process was set to 450°C in process 3, and that the aging time was set to 1 hour in process 5 as shown in Table 3.

[0103] Tables 2 and 3 and FIGs. 9 to 11 show the manufacturing conditions and the mechanical properties of the solid obtained as well as the features of the microstructure.

[0104] FIG. 9 shows an optical microscope image of the material having undergone solution treatment, which is the solution treated sample. The grain size was calculated by the linear interception method to be 10.7 μm. FIG. 10 shows the

[0105] (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment. The basal texture intensity of the (0002) pole figure was 3.5 mrd.

[0106] FIG. 11 shows tensile stress-strain curves of the material having undergone solution treatment (T4), which is the solution treated sample in process 4, and the material having undergone aging treatment (T6) in process 5. Table 3 shows the 0.2% proof strength, the tensile strength, and the elongation, all of which were read from the tensile stress-strain curves, and the Index Erichsen value. The material having undergone solution treatment exhibited the excellent room temperature formability, its yield strength being 144 MPa and the Index Erichsen value being 7.7 mm. By the subsequent aging treatment, the yield strength increased significantly up to 204 MPa.

[0107] As described above, the magnesium alloy that achieves both formability and strength within a temperature range around room temperatures was obtained.

[Example 11]

[0108] A magnesium alloy was manufactured in the same manner as Example 10 except that the sample temperature and the rolling temperature in the final rolling process in process 1 were set to 200°C as shown in C-2 in Table 1.

[0109] Tables 2 and 3 show the manufacturing conditions and mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the formability within a temperature range around room temperatures was ensured as in the case of Example 10, meaning that the magnesium alloy that achieves both formability and strength was obtained.

[Example 12]

[0110] The homogenized ingot was produced by melting and casting in a mold an alloy having the composition of Mg-1.2Al-0.5Ca-0.4Mn-1.6Zn in process 1 as shown in D-1 in Table 1, and by maintaining the cast ingot at 300°C for 4 hours in process 2, then increasing the temperature to 450°C at the heating rate of 7.5°C/h, maintaining it for 6 hours, and then water-quenching it down to a room temperature. The magnesium alloy was manufactured in the same manner as Example 1 except that the sample reheating temperature in the final rolling process was set to 450°C in process 3, the solution treatment temperature was set to 350°C, and the duration of solution treatment was set to 4 hours, as shown in Table 2, when a solution treated sample was produced by subjecting the material to solution treatment in process 4, and that the aging time in process 5 was set to 1 hour as shown in Table 3.

[0111] Tables 2 and 3 and FIGs 12 to 14 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. FIG. 12 shows an optical microscope image of the material having undergone solution treatment, which is the solution treated sample. The grain size was calculated by the linear interception method to be 8.5 μm. FIG. 13 shows the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment. The basal texture intensity of the (0002) pole was 3.7 mrd.

[0112] FIG. 14 shows tensile stress-strain curves of the material having undergone solution treatment (T4), which is the solution treated sample in process 4, and the material having undergone aging treatment (T6) in process 5. Table 3 shows the 0.2% proof strength, the tensile strength and the elongation, all of which were read from the tensile stress-strain curves, and the Index Erichsen value.

[0113] The material having undergone solution treatment exhibited the excellent room temperature formability, its yield strength being 160 MPa and the Index Erichsen value being 8.3 mm. The yield strength did not increase much even if the aging treatment was performed.

[0114] As described above, the magnesium alloy that can achieve both formability and strength in a temperature range around room temperatures was obtained.

[Example 13]

[0115] A magnesium alloy was manufactured in the same manner as in Example 12 except that the solution treatment temperature was set to 450°C when the solution treated sample was produced by subjecting a material to solution treatment in process 4 as shown Table 2 and the aging time set to 0.5 h (30 minutes) in process 5 as shown in Table 3.

[0116] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the magnesium alloy having the formability in a temperature range around room temperatures, ensuring both formability and strength, was obtained as in the case of Example 12.

[Example 14]

[0117] A magnesium alloy was manufactured in the same manner as Example 12 except that the sample temperature and the rolling temperature in the final rolling process were set to 200°C as shown in D-2 in Table 1 and that the duration of solution treatment set to 1 hour as shown in Table 2.

[0118] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the magnesium alloy having the formability in a temperature range around room temperatures, ensuring both formability and strength, was obtained as in the case of Example 12.

[Example 15]

[0119] A magnesium alloy was manufactured in the same manner as Example 12 except that the solution treatment temperature was set to 450°C when the solution treated sample was produced by subjecting a material to solution treatment in process 4 as shown in Table 2 and that the aging time was set to 0.25 h (15 minutes) in process 5 as shown in Table 3.

[0120] Tables 2 and 3 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Tables 2 and 3, the magnesium alloy having the formability in a temperature range around room temperatures, ensuring both formability and strength, was obtained as in the case of Example 12.

[Comparative Example 1]

[0121] A magnesium alloy was manufactured in the same manner as Example 1 except that the solution treatment temperature was set to 350°C and the duration of solution treatment was set to 4 hours, as shown in Table 2, when a solution treated sample was produced by subjecting a material to solution treatment in process 4 and that aging treatment was not performed in process 5.

[0122] Tables 1 to 3 and FIGs. 15 to 17 show the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. FIG. 15 shows an optical microscope image of the material having undergone solution treatment, which is the solution treated sample. The grain size was calculated by the linear interception method to be 9.9 μm. FIG. 16 shows the (0002) pole figure obtained by the X-ray diffraction of the material having undergone solution treatment. The basal texture intensity of the (0002) pole was 4.0 mrd.

[0123] FIG. 17 shows tensile stress-strain curves of the material having undergone solution treatment (T4), which is the solution treated sample in process 4 and the material having undergone aging treatment in process 5 (T6). Table 3 shows the 0.2% proof strength, the tensile strength, and the elongation, all of which were read from the tensile stress-strain curves, and the Index Erichsen value. The yield strength of the material having undergone solution treatment was 149 MPa and its Index Erichsen value was 6.4 mm. Therefore, the formability was insufficient as apparent from Table 2.

[Comparative Example 2]

[0124] A magnesium alloy was manufactured in the same manner as Comparative Example 1 except that the solution treatment temperature was set to 450°C when the solution treated sample was produced by subjecting a material to solution treatment in process 4 as shown in Table 2 and that the duration of solution treatment was set to 0.17 hours.

[0125] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As shown in Table 2, the Index Erichsen value of the material having undergone solution treatment in Comparative Example 2 was 6.2 mm, and it exhibits that the formability was obviously insufficient.

[Comparative Example 3]

[0126] A magnesium alloy was manufactured in the same manner as Comparative Example 1 except that the solution treatment temperature was set to 500°C when the solution treated sample was produced by subjecting a material to solution treatment in process 4 as shown in Table 2 and that the duration of solution treatment was set to 1 hour.

[0127] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As shown in Table 2, the Index Erichsen value of the material having undergone solution treatment in Comparative Example 3 was 5.6 mm, exhibiting that the formability was obviously insufficient.

[Comparative Example 4]

[0128] A magnesium alloy was manufactured in the same manner as Comparative Example 1 except that the solution treatment temperature was set to 500°C when a solution treated sample was produced by subjecting the material to solution treatment in process 4 as shown in Table 2 and that the duration of solution treatment was set to 24 hours.

[0129] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Table 2, the grain size was excessively large and the 0.2% proof strength was insufficient.

[Comparative Example 5]

[0130] A magnesium alloy was manufactured in the same manner as Comparative Example 1 except that the sample temperature and the rolling temperature in the final rolling process were set to 200°C when a material was produced by subjecting a homogenized ingot to rolling treatment in process 3 as shown in A-2 in Table 1 and that the solution treatment temperature was set to 450°C and the duration of solution treatment was set to 4 hours in process 4 as shown in Table 2.

[0131] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As shown in Table 2, the Index Erichsen value of the material having undergone solution treatment in Comparative Example 4 was 4 mm, exhibiting that the formability was obviously insufficient.

[Comparative Examples 6, 7, and 8]

[0132] A magnesium alloy was manufactured in the same manner as Comparative Example 1 except that the sample

temperature and the rolling temperature in the final rolling process were set to 300°C when a material is produced by subjecting a homogenized ingot to rolling treatment in process 3 as shown in A-3 in Table 1 and that the solution treatment temperature was set to 450°C and the duration of solution treatment was set to 1 hour (Comparative Example 6), 2 hours (Comparative Example 7), and 4 hours (Comparative Example 8) in process 4 as shown in Table 2.

[0133] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Table 2, the Index Erichsen value in each of Comparative Examples, 6, 7, and 8 was as small as 6.3 mm, 5.4 mm, and 5.3 mm respectively, exhibiting that the grain size was large and thus the formability was insufficient.

[Comparative Examples 9, 10, and 11]

[0134] A magnesium alloy was produced in the same manner as Comparative Example 1 except that the sample temperature and the rolling temperature in the final rolling process were set to 300°C when a material was produced by subjecting a homogenized ingot to rolling treatment in process 3 as shown in A-4 in Table 1, hot or warm treatment was performed without reheating the sample, and that the solution treatment temperature was set to 450°C and the duration of solution treatment to 1 hour (Comparative Example 9), 2 hours (Comparative Example 10), and 4 hours (Comparative Example 11) in process 4 as shown in Table 2.

[0135] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As apparent from Table 2, the Index Erichsen value in Comparative Examples 9, 10, and 11 was as small as 5.3 mm, 6.2 mm, and 5.9 mm respectively, exhibiting that the grain size was large and thus the formability was insufficient.

[Comparative Example 12]

[0136] A homogenized ingot was produced by melting and casting in a mold an alloy having the composition of Mg-1.2Al-0.5Ca-0.4Mg-0.3Zn to produce a cast ingot in process 1 as shown in B-2 in Table 1, maintaining the cast ingot at 300°C for 4 hours, then increasing the temperature to 450°C at the heating rate of 7.5°C/h, maintaining it for 6 hours, and then water-quenching it down to a room temperature as the homogenized treatment in process 2. A magnesium alloy was manufactured in the same manner as Comparative Example 1 except that the sample temperature and the rolling temperature in the final rolling process were set to 200°C in process 3 and that the solution treatment temperature was set to 350°C and the duration of solution treatment to 1 hour when a solution treated sample was produced by subjecting a material to solution treatment in process 4 as shown in Table 2.

[0137] Table 2 shows the manufacturing conditions and the mechanical properties of the obtained solid as well as the features of the microstructure. As shown in Table 2, the Index Erichsen value of the material having undergone solution treatment in Comparative Example 12 was 5.8 mm, exhibiting that the formability was obviously insufficient.

[0138] Examples 1 to 15, of the above Examples 1 to 15 and Comparative Examples 1 to 12 as shown above, were found to exhibit large Index Erichsen values as well as the high strength.

[0139] The present invention is not limited to the above embodiments only, but can be varied within the scope of the claims of the present invention, and it goes without saying that they are included in the scope of the present invention.

Claims

1. A magnesium alloy, comprising:

   0.2 to 2 wt% or less of Al,
   0.2 to 1 wt% or less of Mn,
   0.2 to 2 wt% of Zn, and
   at least 0.2 to 1 wt% of Ca,

   the remainder comprising Mg and unavoidable impurities, wherein
   a precipitate comprising Mg, Ca, and Al is dispersed on the (0001) plane of a magnesium matrix.

2. The magnesium alloy as set forth in claim 1, further containing a precipitate comprising Al and Mn.

3. The magnesium alloy as set forth in claim 1, wherein the precipitate comprising Mg, Ca, and Al has a plate-like shape, a longer side of the plate falls within a range from 3 to 6 nm, and the number density of the precipitate falls within a range from 10^{20} to $10^{24}/m^3$.

4. The magnesium alloy as set forth in claim 1, wherein the average grain size of the magnesium matrix is 20 μm or less.

5. The magnesium alloy as set forth in claim 1, wherein the basal texture intensity of the (0002) pole on a normalized RD-TD face of the (0002) pole figure measured by the X-ray diffraction is 5.0 mrd or less.

6. The magnesium alloy as set forth in claim 1, wherein the Index Erichsen value at room temperature is 6.5 mm or higher.

7. The magnesium alloy as set forth in claim 1, wherein the 0.2% proof strength of a material having undergone solution treatment is 120 MPa or higher.

8. The magnesium alloy as set forth in claim 1, wherein the 0.2% proof strength of a material having undergone aging treatment is 160 MPa or higher.

9. The magnesium alloy as set forth in claim 1, wherein the elongation to failure is 20% or higher.

10. A method for manufacturing a magnesium alloy, comprising:

process 1 for melting Mg, Al, Mn, Zn, and Ca to obtain a cast ingot;
process 2 for subjecting the cast ingot to a homogenization treatment to obtain a homogenized ingot;
process 3 for subjecting the homogenized ingot to hot or warm working to obtain a material;
process 4 for subjecting the material to a solution treatment to obtain a solution treated sample; and
process 5 for subjecting the solution treated sample to an aging treatment to obtain a magnesium alloy, wherein

the homogenization treatment is performed at a temperature ranging from 400°C to 500°C for a specified time period in the process 2 to obtain the homogenized ingot, and
the aging treatment is performed at a temperature ranging from 140 to 250°C for a specified time period in the process 5 to obtain the magnesium alloy.

11. The method for manufacturing a magnesium alloy as set forth in claim 10, wherein a secondary working process for subjecting the solution treated sample to secondary processing is included between the process 4 and the process 5.

12. The method of manufacturing a magnesium alloy as set forth in claim 10, wherein the solution treated sample having the 0.2% proof strength of 120 MPa or higher is subjected to a secondary processing, and the 0.2% proof strength is increased to 160 MPa or higher by the process 5.

13. The method for manufacturing a magnesium alloy as set forth in claim 10, wherein the aging treatment is performed in the process 5 to increase the hardness of the magnesium alloy.

FIG.1

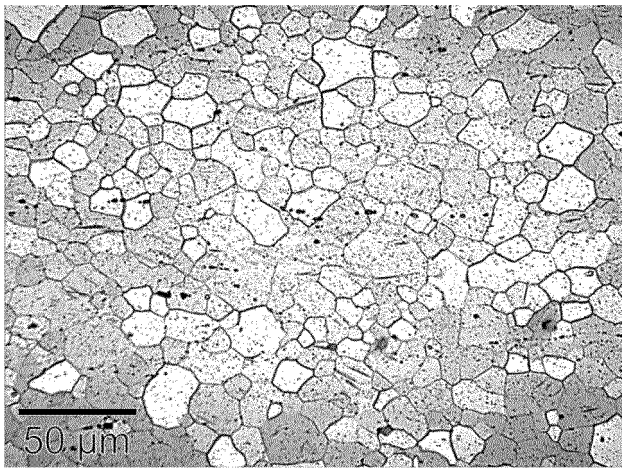


FIG.2

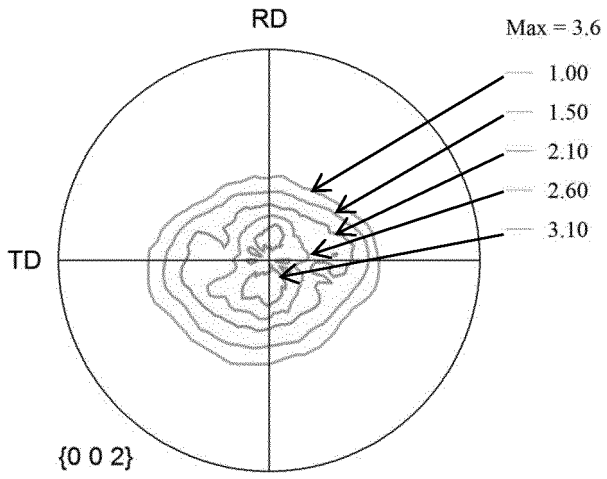


FIG.3

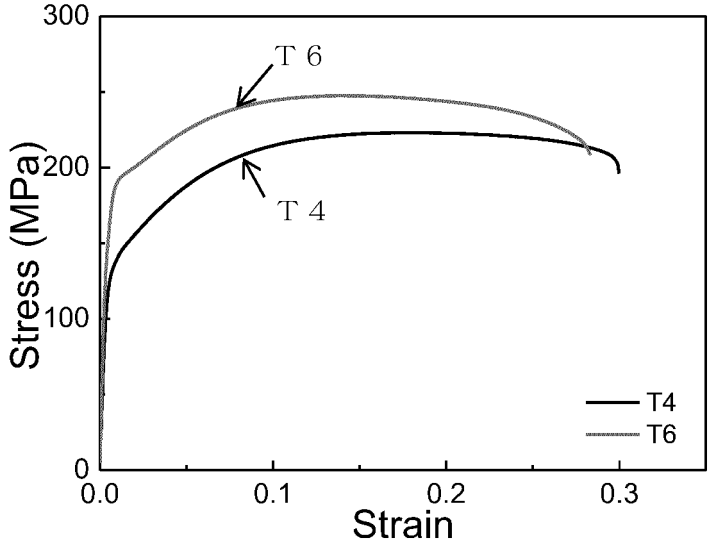


FIG.4 (a)

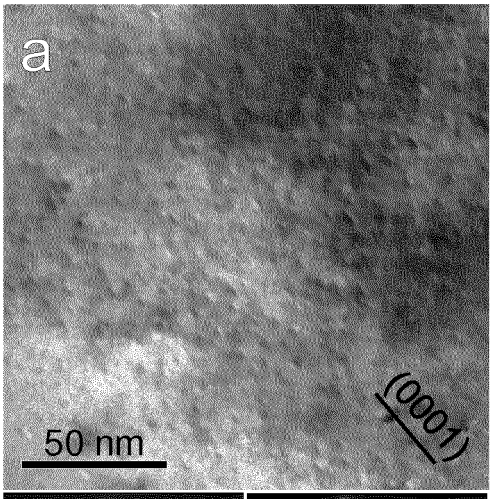


FIG.4 (b)

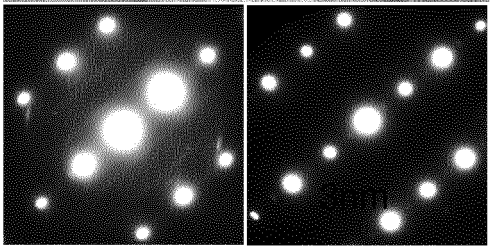


FIG.4 (c)

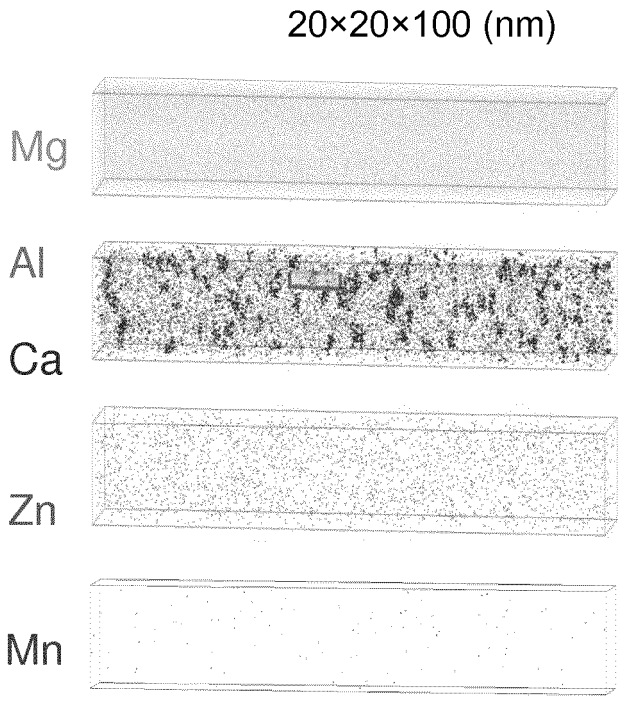


FIG.5 (a)

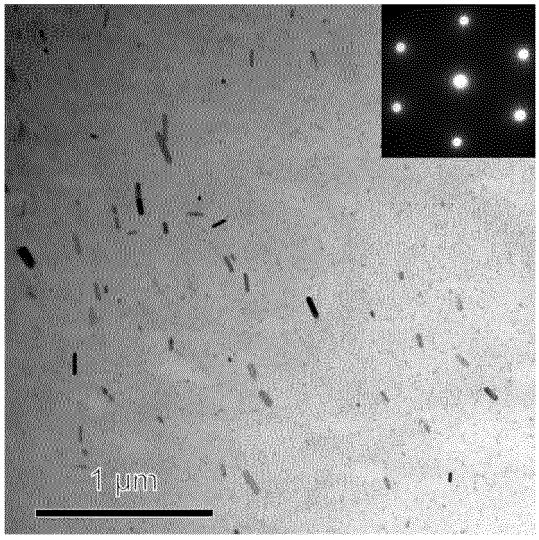
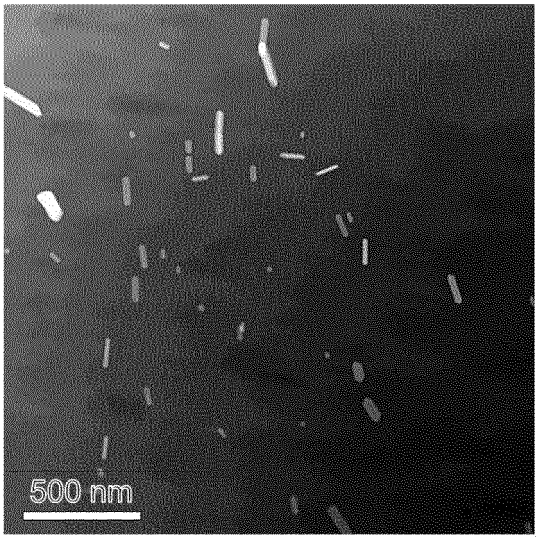


FIG.5 (b)



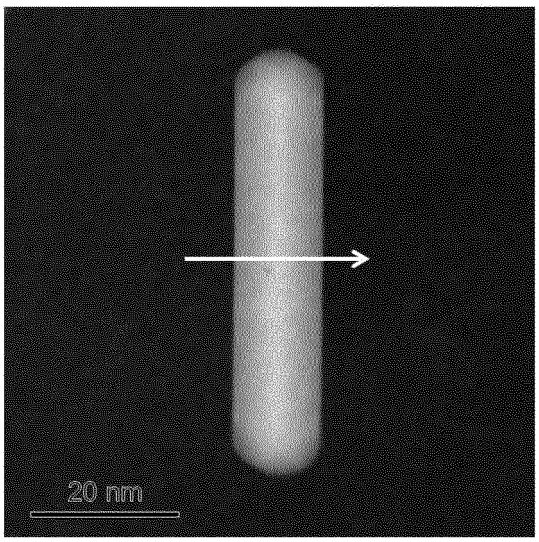


FIG.5 (c)

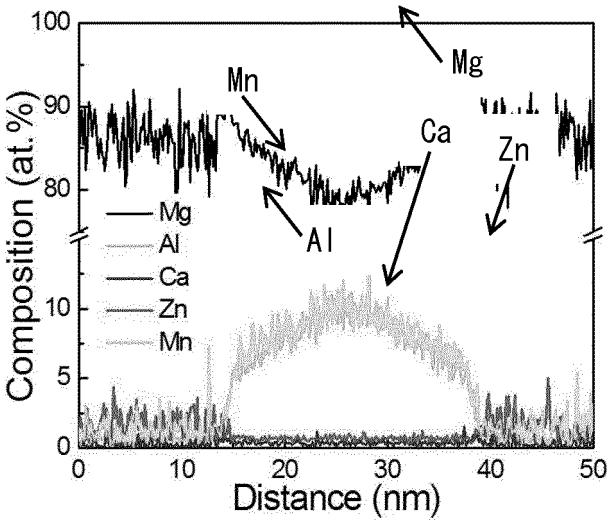


FIG.5 (d)

FIG.6

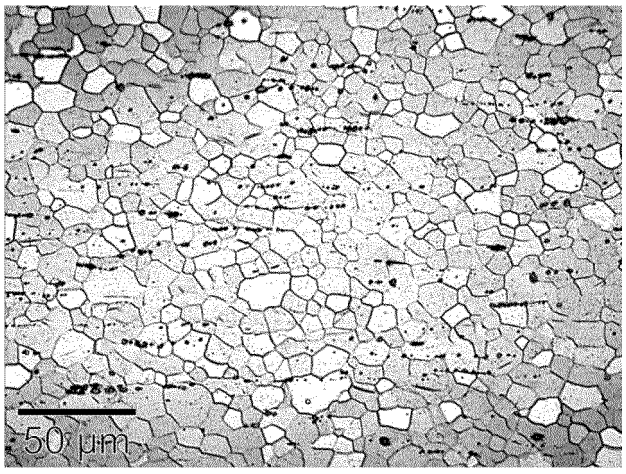


FIG.7

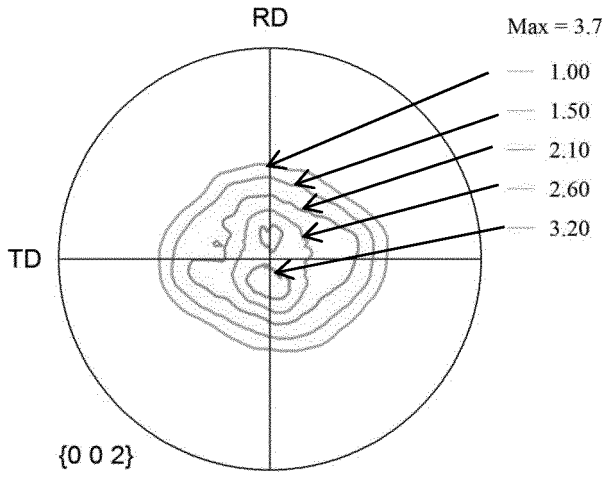


FIG.8

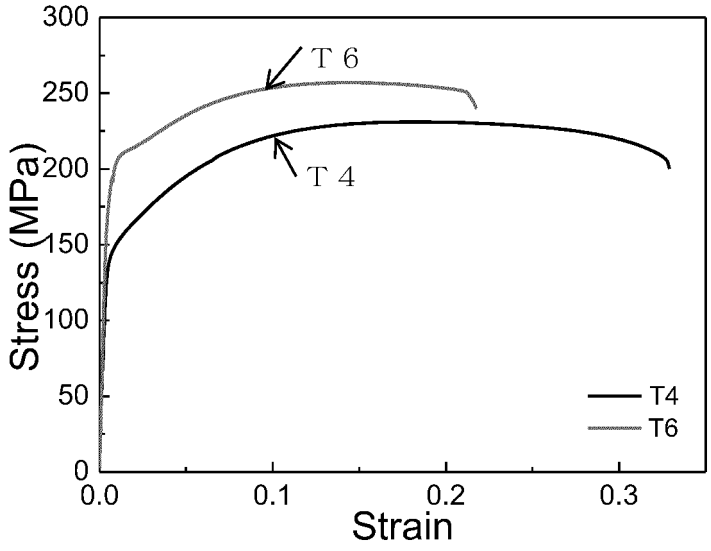


FIG.9

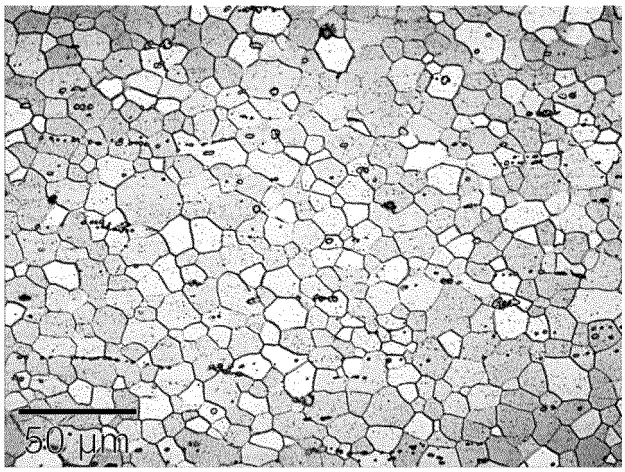


FIG.10

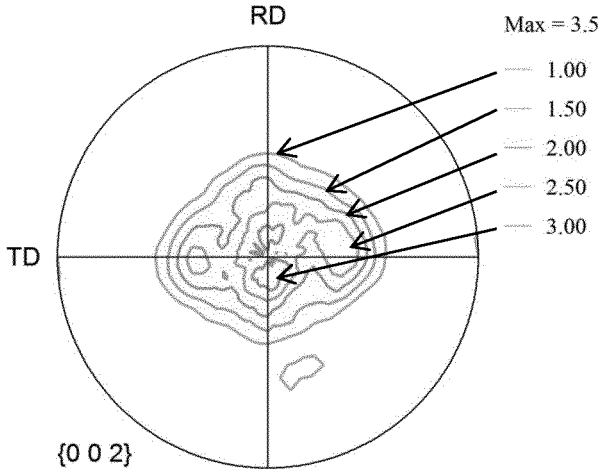


FIG.11

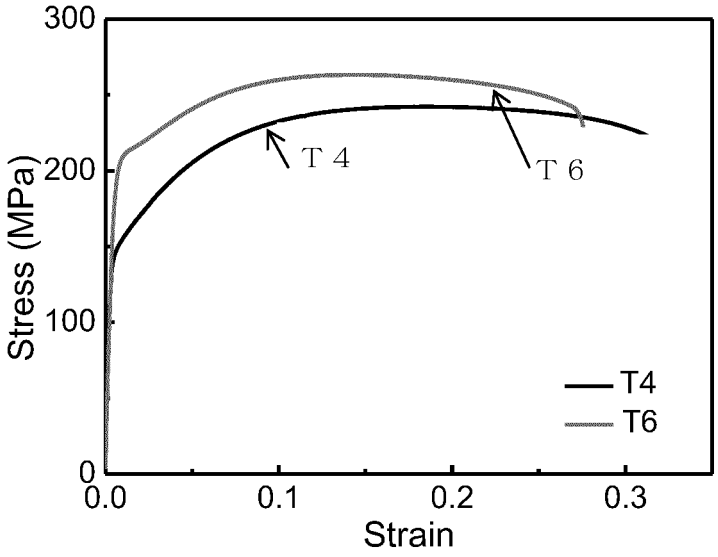


FIG.12

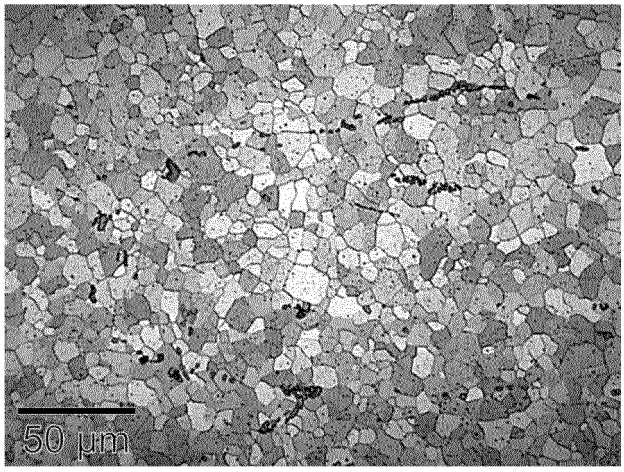


FIG.13

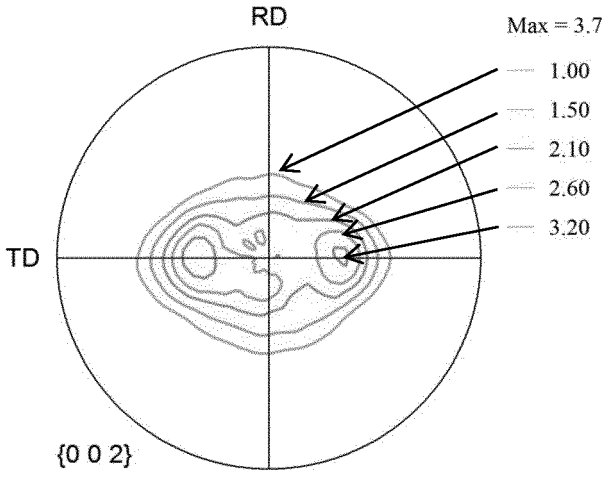


FIG.14

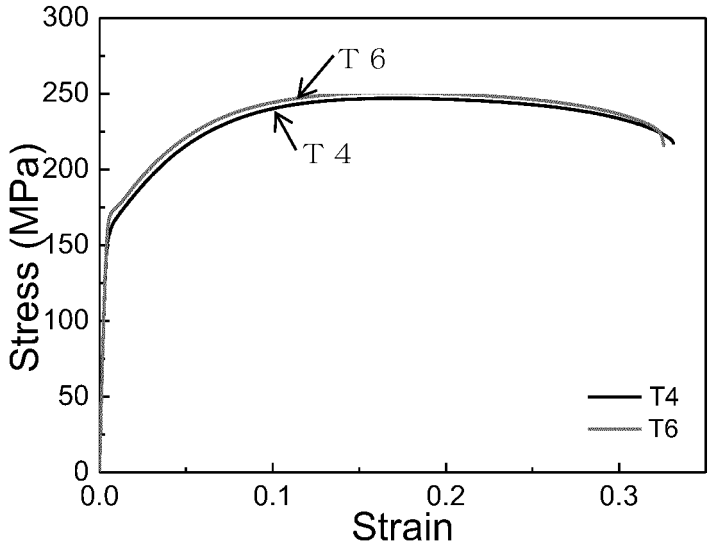


FIG.15

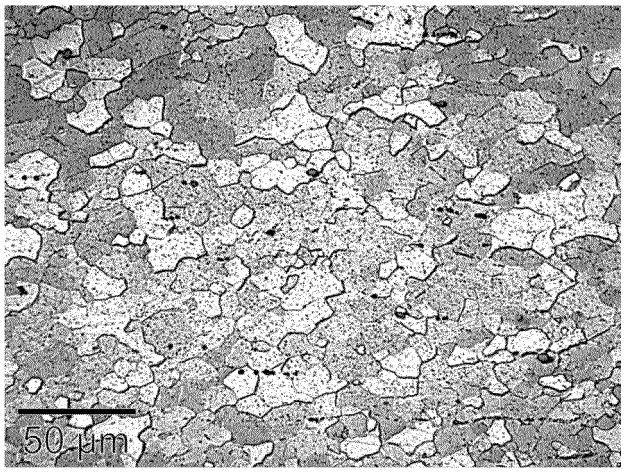


FIG.16

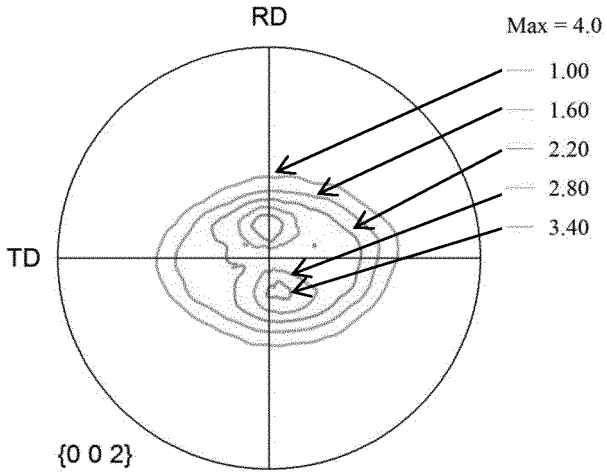
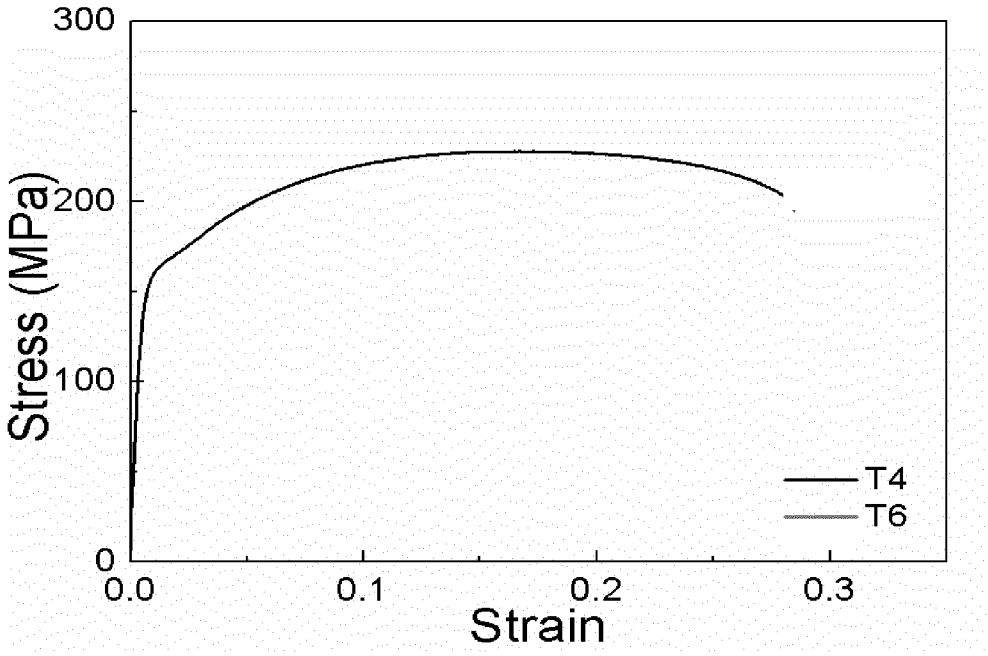


FIG.17



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/006088

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C22C23/02(2006.01)i, C22C23/00(2006.01)i, C22C23/04(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)
Int. Cl. C22C1/00-49/14, C22F1/00-3/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2018
Registered utility model specifications of Japan 1996-2018
Published registered utility model applications of Japan 1994-2018

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.
X A	US 3146096 A (THE DOW CHEMICAL COMPANY) 25 August 1964, claims, column 2, lines 49-70, tables 1-4 & GB 989324 A & DE 1291905 B1	1-2, 9 3-8, 10-13
A	JP 2009-120883 A (MITSUBISHI ALUMINUM CO., LTD.) 04 June 2009 (Family: none)	1-13
A	WO 2012/049990 A1 (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 19 April 2012 & US 2013/0209195 A1 & CN 103180473 A	1-13
A	CN 101629260 A (INSTITUTE OF METAL RESEARCH CHINESE ACADEMY OF SCIENCES) 20 January 2010 (Family: none)	1-13

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

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Date of the actual completion of the international search	Date of mailing of the international search report
16.05.2018	29.05.2018
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

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- JP 2013079436 A **[0008]**
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- JP 2002266044 A **[0008]**
- JP 2016169427 A **[0008]**

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- **W.J.KIM ; I.B.PARK ; S.H.HAN.** *Scripta Materialia,* 2012, vol. 66, 590-593 **[0009]**