(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 859 024 A1**

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

(43) Date of publication:
04.08.2021 Bulletin 2021/31

(21) Application number: **19864451.0**

(22) Date of filing: **24.09.2019**

(51) Int Cl.:
C22C 23/04 $^{(2006.01)}$
C22C 23/06 $^{(2006.01)}$
C22F 1/06 $^{(2006.01)}$
C22C 1/02 $^{(2006.01)}$
B21B 3/00 $^{(2006.01)}$
B21B 37/58 $^{(2006.01)}$

(86) International application number:
PCT/KR2019/012409

(87) International publication number:
WO 2020/067704 (02.04.2020 Gazette 2020/14)

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

(30) Priority: **28.09.2018 KR 20180116033**

(71) Applicant: **POSCO**
Gyeongsangbuk-do 37859 (KR)

(72) Inventors:
- **PARK, Jun Ho**
  Pohang-si Gyeongsangbuk-do 37859 (KR)
- **KIM, Jae Joong**
  Pohang-si Gyeongsangbuk-do 37859 (KR)
- **PARK, Jun Ho**
  Pohang-si Gyeongsangbuk-do 37859 (KR)

(74) Representative: **Potter Clarkson**
The Belgrave Centre
Talbot Street
Nottingham NG1 5GG (GB)

(54) MAGNESIUM ALLOY SHEET AND MANUFACTURING METHOD THEREFOR

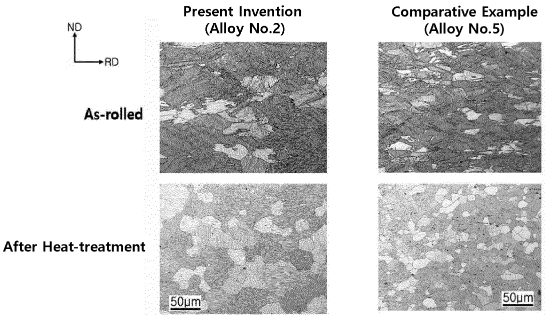
(57) The present invention relates to a magnesium alloy sheet comprising: 0.1 to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities with respect to an entire 100 wt% of the magnesium alloy sheet, and the magnesium alloy sheet may satisfy Relational Expression 1 below.

[Relational Expression 1]

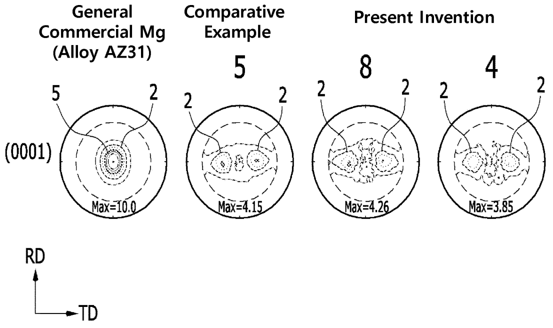
$$[Zn]/[Gd] \geq 3.0$$

The [Zn] and [Gd] may indicate wt % of each component.

【FIG. 3】



【FIG. 4】



Printed by Jouve, 75001 PARIS (FR)

Description

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of Korean Patent Application No. 10-2018-0116033 filed in the Korean Intellectual Property Office on September 28, 2018, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

(a) Field of the Invention

[0002] An embodiment of the present invention relates to a magnesium alloy sheet and a manufacturing method thereof.

(b) Description of the Related Art

[0003] Recently, with strict regulations on carbon dioxide emissions worldwide, weight reduction of a vehicle body has become an essential condition in the automobile industry. Accordingly, several studies are being conducted to reduce weight, and among them, interest in magnesium, the lightest material for structural purposes, is high.

[0004] However, in order to apply magnesium alloy to various industrial fields, it is necessary to improve formability and corrosion resistance. First of all, corrosion resistance is a level that can be overcome to some extent due to the recent development of various surface treatment techniques. However, the low formability of magnesium places restrictions on product development. The reasons for the low formability of magnesium are as follows.

[0005] The crystal structure of magnesium is HCP structure, and the c/a ratio of unit cell is higher than that of materials with other HCP structures, so only the basal slip-based {0001}<11-20> can be activated at room temperature. Particularly, in the case of a rolled or extruded material, the C-axis of the HCP is aligned with the thickness direction of the rolled plate, making it more difficult to accommodate the C-axis deformation. Several techniques have been developed to overcome the low formability of magnesium alloy.

[0006] Particularly, among improvements thorough process there are differentiated speed rolling for providing different speeds to an upper roller and a lower roller, an ECAP process, and a high temperature rolling method for performing rolling at around a eutectic temperature of the magnesium sheet. However, the above-described processes are difficult to be commercially available. Further, warm molding is performed due to insufficient room temperature formability, but there is also a large problem in the additional cost at this time.

[0007] Accordingly, there is also an effort to control the alloy composition to develop a high-forming magnesium alloy material. In the case of a patent (Publication No.: 2012-0055304), a magnesium plate containing Zn: 1 to 10wt% and Ca: 0.1 to 5wt% was disclosed, but this has a problem that cannot be applied to the strip casting method as in an exemplary embodiment of the present invention described below. Therefore, mass production is lacking, and casting for a long time is difficult due to the coalesce phenomenon between the casting material and the roll during casting for a long time.

[0008] Further, another patent (application number: 2015-0185017) was able to obtain a high formability of 7 mm or more in height of the limit dome through process improvement in the existing Al: 3 wt%, Zn: weight 1%, Ca: weight 1% alloy. However, in the case of an alloy to which Ca is added, the Al_2Ca phase, which is a high-temperature crystallized phase, is produced during the process, and is likely to be formed as a segregation zone. The segregation zone has a problem that adversely affects the formability.

[0009] The above information disclosed in this Background section is only for enhancement of understanding of the background of the invention, and therefore it may contain information that does not form the prior art that is already known in this country to a person of ordinary skill in the art.

SUMMARY OF THE INVENTION

[0010] The present invention has been made in an effort to provide a magnesium alloy sheet having advantages of excellent formability at room temperature and activation of the slip of the non-bottom surface by controlling the relationship between gadolinium (Gd) and zinc (Zn). An exemplary embodiment of the present invention provides a magnesium alloy sheet. Another embodiment of the present invention provides a method for manufacturing a magnesium alloy sheet.

[0011] By controlling the relationship between gadolinium (Gd) and zinc (Zn), it is possible to disperse the texture of the magnesium alloy sheet, and activation of the slip base of the non-bottom surface may be easy. Accordingly, it is intended to possess formability at a level of the aluminum alloy for automobiles.

[0012] A magnesium alloy sheet according to an exemplary embodiment of the present invention may comprises: 0.1

to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities with respect to an entire 100 wt% of the magnesium alloy sheet, and the magnesium alloy sheet may satisfy Relational Expression 1 below.

[Relational Expression 1]

$$[Zn]/[Gd] \geq 3.0$$

[0013] Wherein, the [Zn] and [Gd] may indicate wt % of each component.

[0014] Specifically, the Relational Expression 1 may be 3.0 or more and 15.0 or less.

[0015] More specifically, the Relational Expression 1 may be 3.0 or more and 13.0 or less.

[0016] The magnesium alloy sheet may further comprise 0.3 wt% or less of Mn (excluding 0 wt%) with respect to the total of 100 wt % of the magnesium alloy sheet.

[0017] The magnesium alloy sheet may comprise a secondary phase, and the number of secondary phases per an area of 40000 μm^2 of the magnesium alloy plate may be 1 to 20.

[0018] In this instance, the average particle diameter of the secondary phase may be 0.1 to 3 μm.

[0019] An average crystal grain size of the magnesium alloy sheet may be 5 to 30 μm.

[0020] The limited dome height (LDH) of the magnesium alloy sheet may be 10.5 mm or more.

[0021] An edge crack of the magnesium alloy sheet may be 5mm or less.

[0022] The magnesium alloy plate may have maximum texture intensity of 4.5 or less with respect to the (0001) plane

[0023] A method for manufacturing a magnesium alloy sheet according to another exemplary embodiment of the present invention may comprise: preparing a casting material by casting an alloy melt solution comprising 0.1 to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities for the entire 100 wt%, homogenizing and heat-treating the casting material, preparing a rolled material by rolling the homogenized and heat-treated casting material, finally annealing the rolled material, and the alloy melt solution may satisfy Relational Expression 1 below.

[Relational Expression 1]

$$[Zn]/[Gd] \geq 3.0$$

[0024] Wherein, the [Zn] and [Gd] may indicate wt % of each component.

[0025] Specifically, the Relational Expression 1 may be 3.0 or more and 15.0 or less.

[0026] More specifically, the Relational Expression 1 may be 3.0 or more and 13.0 or less.

[0027] The alloy melt solution may comprise 0.3 wt% or less of Mn (excluding 0 wt%) with respect to the total of 100 wt % of the alloy melt solution.

[0028] The homogenizing and heat-treating of a casting material may perform at a temperature of 300 to 500 °C.

[0029] Specifically, the homogenizing and heat-treating of a casting material may perform for 5 hour or more.

[0030] The preparing of a rolled material may comprise performing rolling at a temperature of 150 to 350 °C.

[0031] Specifically, the preparing of a rolled material comprises performing a rolling with a reduction ratio that is greater than 0 and equal to or less than 30 % for each rolling.

[0032] By controlling the relationship between gadolinium (Gd) and zinc (Zn), it is possible to possess formability at a level of the aluminum alloy for automobiles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

FIG. 1 shows binary phase diagram of Mg-Gd.

FIG. 2 shows the maximum dissolved amount of Gd at 400 °C according to the added element.

FIG. 3 shows an observation of a microstrure step-by-step of Example 1 and Comparative Example 4 with Optical Microscopy.

FIG. 4 shows the results of analysis of the (0001) planes of Example 2, Example 3 and Comparative Example 4 by XRD method of pole figure.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0034] Embodiments of the present invention will be described in detail. However, this is presented as an example, and the present invention should not be constructed as limited thereby but is only defined by the scope of the claims.

[0035] A magnesium alloy sheet according to an exemplary embodiment of the present invention may comprise: 0.1 to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities with respect to an entire 100 wt% of the magnesium alloy sheet.

[0036] A reason for limiting a component and a composition of the magnesium alloy sheet will now be described.

[0037] Zn may be comprised at 0.1 to 1.5 wt%. Specifically, it may be comprised at 1 to 1.5 wt%.

[0038] Specifically, when a Zn element is dissolved in the grain boundary or the twin boundary with a Gd element to be described below, the effect of dispersing the texture may increase.

[0039] Specifically, when a Zn element is less than 0.1 wt%, the effect of improving formability and rollability may be insignificant. On the other hand, when a Zn element is more than 1.5 wt%, mechanical properties and formability may be deteriorated due to an increase in the secondary phase fraction and coarsening.

[0040] 0.08 to 0.7 wt% of Gd may be comprised. Specifically, 0.1 to 0.6 wt% of Gd may be comprised. More specifically, 0.1 to .05 wt% of Gd may be comprised.

[0041] A Gd element may be dissolved and segregated in the grain boundary or the twin boundary. Segregation signifies that solute elements are concentrated in a certain area. In an exemplary embodiment of the present invention, segregation may signify that solute elements are concentrated in a grain boundary or a twin boundary.

[0042] Accordingly, the Gd element may be segregated in the above-described interfaces.

[0043] Specifically, the segregated Gd element may give a solute dragging effect and may accelerate the dispersion of the texture during rolling and heat-treating processes. As described above, when a Gd element is dissolved with a Zn element, the effect of dispersing the texture may be more excellent.

[0044] However, when the Gd element is less than 0.08 wt%, a solute dragging effect may be insignificant.

[0045] When the Gd element is more than 0.7 wt%, the size and fraction of MgsGd and MgZn secondary phase may increase. In this case, it may give a negative influence on the formability. Further, as the Gd element is more than 0.7 wt%, the content of Zn must be also more than 2.1 wt% for the value of the Relational expression 1 ([Zn]/[Gd]) to be described below to be 3.0 or more. Therefore, mechanical properties and formability may be deteriorated due to an increase in the secondary phase fraction and coarsening.

[0046] In this instance, the magnesium alloy sheet may satisfy Relational Expression 1 below.

[Relational Expression 1]

$$[Zn]/[Gd] \geq 3.0$$

[0047] Wherein, the [Zn] and [Gd] may indicate wt % of each component.

[0048] Specifically, a ratio of wt% of zinc (Zn) to wt% of gadolinium (Gd) may be 3.0 or more. Specifically, the ratio may be 3.0 or more and 15.0 or less. Specifically, the ration may be 13.0 or less. Specifically, by controlling the weight ratio of Zn to Gd described above, Gd and Zn are simultaneously dissolved in the boundary, so that a solute dragging effect may be excellent.

[0049] More specifically, when the weight ratio of Zinc (Zn) to Gadolinium (Gd) is less than 3, the mount of Gd and Zn elements segregated together at a grain boundary and a twin boundary may be reduced. Therefore, the degree of a solute dragging effect of segregated elements may be lowered. That is, the more the amount of segregation dissolved, the more the slip base of the non-bottom surface is activated, so that the formability may be improved.

[0050] In this instance, the solute segregation is typically distributed along the basal slip of the surface, and thus the basal slip of the surface can be controlled. On the other hand, since there is no effect on the slip of the non-bottom surface, the gap in the degree of activation between the two slip systems is reduced, and the probability of activating the non-bottom slip may increase.

[0051] However, when the weight ratio of Zn to Gd is more than 15.0, it may comprise too little Gd or too much Zn. In this case, the effect of improving formability may be insignificant. Alternatively, workability and formability may be deteriorated due to an increase in the secondary phase fraction and coarsening.

[0052] The magnesium alloy sheet may further comprise 0.3 wt% or less of Mn (excluding 0 wt%) with respect to the total of 100 wt % of the magnesium alloy sheet.

[0053] The manganese forms a Fe-Mn-based compound to thus function to reduce the content of the component of Fe in the sheet. That is, it is easy to control Fe impurities.

[0054] However, the reason why the upper limit of the Mn component is limited to 0.3 wt% is that when manganese is added in an amount more than 0.3 wt%, the Gd solubility becomes low and the formability is deteriorated.

[0055] Specifically, when manganese is comprised in the range above, formability may be excellent. More specifically, an alloy with a small addition amount of an alloying element may have excellent bendability, thermal conductivity, and corrosion resistance.

[0056] The magnesium alloy sheet may comprise a secondary phase, and the number of secondary phases per an area of 40000 μm^2 of the magnesium alloy plate may be 1 to 20.

[0057] In this instance, the secondary phase may be Mg_5Gd, MgZn, or a combination thereof. the average particle diameter of the secondary phase may be 0.1 to 3 μm.

[0058] Specifically, the average particle diameter and the number of secondary phases may be the result of controlling the composition range of the above-described alloy component and Relational Expression 1. By controlling the average particle diameter and the number of secondary phases within the range above, the activation of the slip base of the non-bottom surface may be improved. Therefore, a magnesium alloy sheet excellent in formability may be provided.

[0059] An average crystal grain size of the magnesium alloy sheet may be 5 to 30 μm Specifically, when the average crystal grain size of the magnesium alloy sheet is within the range above, the formability may be more excellent. More specifically, when it is smaller than the range above, the formability at room temperature may be deteriorated. When it is larger than the range above, the formability at high temperature may be deteriorated.

[0060] Therefore, the limited dome height (LDH) of the magnesium alloy sheet may be 10.5 mm or more. Specifically, the limited dome height (LDH) of the magnesium alloy sheet may be 1 mm or more.

[0061] In the present specification, the limited dome height (LDH) means a value derived through the Erichsen test at room temperature. The formability of the material may be compared through the limited dome height (LDH).

[0062] An edge crack of the magnesium alloy sheet may be 5mm or less. Specifically, an edge crack of the magnesium alloy sheet may be 1mm or less.

[0063] The edge crack means a groove formed at the edge of the surface of the magnesium alloy sheet. The edge crack may be caused when the workability is low. That is, the higher the formability of the alloy is, the better the workability is, so the edge cracks may be reduced.

[0064] Accordingly, the edge crack of the magnesium alloy sheet according to an exemplary embodiment of the present invention the present invention may be within the range above. As described above, the smaller the edge crack is, the better the workability is, so the lower limit may be not limited.

[0065] Accordingly, when the edge crack is within the range above, the formability may be excellent. More specifically, the edge crack may be caused more by the Al_2Ca secondary phase, but the alloy according to an exemplary embodiment of the present invention does not contain a Ca component and does not have the secondary phase described above, so that the edge crack may be reduced and thus the magnesium alloy sheet excellent in the formability may be provided.

[0066] The magnesium alloy plate may have maximum texture intensity of 4.5 or less with respect to the (0001) plane. Specifically, the magnesium alloy plate may have a maximum texture intensity of 1.0 to 4.5 or less.

[0067] When the texture intensity with respect to the (0001) plane is within the range above, the fraction of the crystal grain on the bottom surface may be samll, and the activation of the slip base of the non-bottom surface may be easy. Therefore, a magnesium alloy sheet excellent in formability may be provided.

[0068] A method for manufacturing a magnesium alloy sheet according to another exemplary embodiment of the present invention may comprise: preparing a casting material by casting an alloy melt solution comprising 0.1 to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities for the entire 100 wt%, homogenizing and heat-treating the casting material, preparing a rolled material by rolling the homogenized and heat-treated casting material, finally annealing the rolled material.

[0069] The reason for limiting the component and composition of the alloy melt solution corresponds to the above-described reason for limiting the component and the composition of the magnesium alloy sheet, so it will not be described.

[0070] In the step of preparing a casting material by casting an alloy melt solution, the alloy melt solution may satisfy the Relational Expression 1 below.

[Relational expression 1]

$$[Zn]/[Gd] \geq 3$$

[0071] Wherein, the [Zn] and [Gd] may indicate wt % of each component.

[0072] The temperature of the alloy melt solution may be 650 to 750°C.

[0073] Specifically, the magnesium alloy may be cast in the range above.

[0074] More specifically, when the temperature is lower than 650°C, the fusion of the magnesium alloy may not be performed properly. On the other hand, when the temperature is higher than 750°C, it may be difficult to manage the melt solution due to ignition.

[0075] Preparing the casting material may be performed as casting the above-described alloy melt solution.

[0076] Specifically, it may be cast through strip casting, gravity casting, or a combination thereof. However, the method is not limited thereto.

[0077] Thereafter, a step of homogenizing and heat-treating the casting material may be performed.

[0078] A step of homogenizing and heat-treating the casting material may be performed at a temperature of 300 to 500 °C. Specifically, homogenizing and heat-treating the casting material may be performed for 1 hour or more.

[0079] When the temperature is 300 °C or higher, dissolution of a gadolinium (Gd) element may be possible. Further, the higher the temperature is, the higher the dissolved amount of gadolinium. However, when the temperature is higher than 500 °C, the surface of the casting material may be oxidized. Therefore, it may not be suitable for the mass production process.

[0080] The step of preparing the rolled material may be performed at a temperature of 150 to 350 °C.

[0081] Specifically, rolling may be possible without an edge crack when a temperature of 150°C or higher is secured. Rolling at the higher than 350 °C may not be in accord with mass production realistically. Rolling with a reduction ratio that is greater than 0 and equal to or less than 30 % for each rolling may be performed.

[0082] In the present specification, a reduction ratio means that the difference between the thickness of the material before passing through the rolling roll during rolling and the thickness of the material after passing through the rolling roll is divided by the thickness of the material before passing through the rolling roll and multiplied by 100.

[0083] Specifically, rolling may be performed several times at the reduction ratio to roll to the final target thickness.

[0084] Preparing the rolling material may further comprise intermediately annealing the rolled material.

[0085] Intermediately annealing the rolled material may be performed at a temperature of 300 to 500 °C.

[0086] Specifically, it may be performed for 10 minutes to 15 hours.

[0087] Specifically, intermediately annealing the rolled material may be performed after two consecutive rolling. Alternatively, intermediately annealing the rolled material may be performed after three consecutive rolling. Alternatively, it may be rolled without intermediate annealing.

[0088] More specifically, when intermediately annealing the rolled material is performed at a temperature of the range, the stress generated during rolling may be sufficiently relieved.

[0089] The final annealing of the rolled material may be performed in a temperature range of 300 to 500 °C.

[0090] Specifically, it may be performed for 10 minutes to 15 hours.

[0091] Recrystallization may be easily formed by final annealing under the conditions above.

[0092] The Erichsen value of the magnesium alloy sheet manufactured through the above-described process may be 10.5 mm or more. Specifically, it may be 11.0mm or more.

[0093] The above value may mean room temperature formability similar to a level of conventional aluminum metal.

[0094] The following examples illustrate the present invention in more detail. However, the following examples are only preferred examples of the present invention, and the present invention is not limited to the following examples.

Example

[0095] An alloy melt solution of Example and Comparative Example was prepared according to the wt% of the alloy components disclosed in Tabe1 below.

[0096] Thereafter, the melt solution was cast by a strip casting method to prepare the cast material.

[0097] The cast material was then homogenized and heat-treated at 400 °C for 7 hours.

[0098] The homogenized and heat-treated cast material was rolled at 300 °C at a reduction rate of about 20% per rolling. Intermediate annealing was also performed in the middle of the rolling. Specifically, it was performed at 400 °C for an hour.

[0099] Finally, the rolled material was finally annealed at 400 °C for an hour.

[0100] The thickness of the manufactured magnesium alloy sheet was 0.4 to 1.8 mm.

[0101] In addition, the Erichsen values of Examples and Comparative Examples were measured and shown below.

Method of measuring Erichsen value

[0102] A magnesium alloy sheet with a horizontal length and a vertical length of respectively 50 to 60 mm is used, and a lubricant is used on an exterior side of the sheet so as to reduce friction between the sheet and a spherical punch.

[0103] In this instance, when the test is performed, the die and the spherical punch are at room temperature.

[0104] More specifically, the magnesium alloy sheet is inserted between an upper die and a lower die, an exterior circumference portion of the sheet is fixed with a force of 10 kN, and the sheet is deformed at a speed of 5 mm/min by using a spherical punch with a diameter of 20 mm. The punch is inserted until the sheet is broken, and when it is broken, a deformed height of the sheet is measured.

[0105] The above-described deformed height of the sheet is referred to as an Erichsen value or a limited dome height (LDH). From this, it is possible to compare the formability of the sheet. Specifically, the higher the deformed height of the magnesium alloy sheet is, the higher the Erichsen value and the higher the formability may be.

(Table 1)

Division	Al	Gd	Zn	Mn	room temperature Erichsen Value (mm)	Zn/Gd
Comparative Example1	0	0.27	0	0	4.6	0
Comparative Example2	0	0.27	0.49	0	10.2	1.81
Example1	0	0.28	1	0	11.0	3.57
Comparative Example3	0	0.43	0.95	0	10	2.20
Example2	0	0.15	1	0	11.2	6.66
Comparative Example4	0	0.76	0.98	0	9.3	1.28
Comparative Example5	0	0.78	1.41	0	10	1.80
Comparative Example6	1.96	0.11	1.02	0	3.6	9.27
Example3	0	0.25	1.49	0	11.1	5.96
Exam ple4	0	0.25	1.49	0.1	11.1	5.96
Comparative Example7	0	0.28	1.7	0	9.5	6.07
Comparative Example8	0	0.28	2.0	0	9.3	7.14
Example5	0	0.12	1.5	0	11.1	12.5
Comparative Example 9	0	0.07	1.38	0	3.5	19.7

[0106] First, as disclosed in Table 1, an exemplary embodiment of the present invention may not comprise aluminum. When it comprises aluminum, It may not be possible to dissolve Gd.

[0107] This may also be confirmed in FIG. 1 and FIG. 2 of the present specification.

[0108] FIG. 1 shows binary phase diagram of Mg-Gd.

[0109] Specifically, FIG. 1 shows the phase diagram of Mg-ZnO.5wt%-xGd, and it may be seen that the dissolved amount of Gd at 400 °C. In addition, it is possible to derive FIG. 2 by drawing a phase diagram according to the content of each element as shown in FIG. 1.

[0110] FIG. 2 shows the maximum dissolved amount of Gd at 400 °C according to the added element.

[0111] Specifically, FIG. 2 shows the measurement of the amount of Gd that may be dissolved when the phase diagram of the three elements Al, Zn, and Mg is prepared as in the Mg-Gd binary phase diagram of FIG. 1.

[0112] As shown in Fig. 2, it may be seen that when aluminum is included, Gd dissolution is not possible. As described above, an exemplary embodiment of the present invention may not comprise aluminum. However, aluminum may exist as a level of an impurity.

[0113] More specifically, it may comprise 0.005wt% or less of aluminum.

[0114] In addition, as disclosed in Table 1, in the case of the present example in which gadolinium (Gd) and zinc (Zn) are comprised together, and the weight ratio of zinc to gadolinium is 3 or more, it may be seen that the Erichsen value is excellent.

[0115] On the other hand, in the case of Comparative Example 1 comprising Gd alone, it may be confirmed that the result of low formability compared to the Examples of the present specification is an Erichsen value at room temperature of 4.6 mm.

[0116] On the other hand, it may be seen that, as in Comparative Example 2, when both Gd and Zn are comprised, the Erichsen value is significantly increased compared to Comparative Example 1. This is because Gd and Zn are dissolved together and segregated at the grain boundary, resulting in a solute dragging effect.

[0117] However, in the case of Comparative Example 2, it may be seen that the value of Zn/Gd (Relational Expression 1) is less than 3. As a result, it may be seen that the Erichsen value is excellent compared to Comparative Example 1, but the Erichsen value is inferior to the Example.

[0118] More specifically, Examples of the present specification may be formability at room temperature similar to a level of conventional aluminum metal. Al5083, among commercially available aluminum alloys, has an Erichsen value of about 12mm at room temperature.

[0119] The characteristics of this example may also be confirmed through FIGS. 3 and 4 of the present specification.

[0120] FIG. 3 shows the microstructures of Example 1 and Comparative Example 4 by observing with an optical microscopy.

[0121] Specifically, as shown in the photo after the heat treatment of FIG. 3, it may be confirmed visually that the number of secondary phases in Example 1 is significantly smaller than that of Comparative Example 4. More specifically, in the case of Example 1, it may be seen that the number of secondary phases per area of 40000 μm^2 is less than about 20. On the other hand, Comparative Example 4 may be seen that more than the Example at the level of 50 to 100 per the same area.

[0122] In this instance, the secondary phase is Mg_5Gd and MgZn.

[0123] In addition, it may be seen that more secondary phases having a coarse particle diameter are comprised in the Comparative Examples compared to the Examples.

[0124] In Comparative Example 4, as a result of adding more than the range of gadolinium (Gd) according to an exemplary embodiment of the present invention, it may be seen that the particle diameter of the secondary phase is coarse and the fraction of the secondary phase is larger than that of the Example.

[0125] Accordingly, as previously disclosed in Table 1, the Erichsen value at room temperature of Comparative Example 4 is 9.3 mm, whereas the Erichsen value at room temperature of Example 1 is 11.0 mm, indicating that the formability at room temperature is more excellent.

[0126] That is, the fraction and size of the secondary phase may be controlled through the composition range of gadolinium (Gd) and the relationship between gadolinium and zinc (Zn/Gd) as in the Examples of the present specification, thereby reducing factors that hinder deformation behavior.

[0127] Such characteristics may also be confirmed through FIG. 4.

[0128] FIG. 4 shows the results of analyzing the (0001) plane of Example 2 and 3 and Comparative Example 4 by the XRD method of pole figure.

[0129] Through the XRD method of pole figure, it is possible to represent the texture according to the crystal orientation of the crystal grain.

[0130] Specifically, the pole figure is shown by a stereoscopic projection of the direction of an arbitrarily fixed crystal coordinate system onto the specimen coordinate system. That is, poles with respect to the (0001) plane of crystal grains of various orientations may be displayed in the reference coordinate system, and the pole figure may be represented by drawing a density contour line according to the pole density distribution. In this instance, the pole is fixed in a specific lattice direction by the Bragg angle, and multiple poles may be displayed for a monocrystalline.

[0131] Therefore, a numerical expression of the density distribution value of the contour line represented by the method of pole figure may be referred to as the maximum texture intensity for the (0001) plane.

[0132] The smaller the maximum texture intensity, the more the crystal grains of various orientations are distributed, and the fraction of the crystal grain on the bottom surface is low, which means that the formability is excellent.

[0133] However, as shown in FIG. 4, it may be seen that Example 3 has a slightly higher maximum aggregation strength value than Comparative Example 4. In addition, it may be seen that the shape of the pole figure in Example 3 is similar to that of Comparative Example 4.

[0134] Methods of improving the workability of the magnesium alloy sheet comprise a method of dispersing the texture and a method of the slip base of the non-bottom surface. Specifically, considering that the shape of the pole figure is similar in Example 3 and Comparative Example 4, it is possible to derive a relatively random orientation of the crystal grains.

[0135] However, as described above Table 1, Comparative Example 4 is a case in which more than the range of gadolinium (Gd) is added according to an exemplary embodiment of the present invention. As a result, the Zn/Gd value of Comparative Example 4 was 1.28, and a value less than 3 was derived. That is, it may be seen that Comparative Example 4 does not satisfy the composition of gadolinium and the Zn/Gd value of the Relational expression 1 according to an exemplary embodiment of the present invention.

[0136] When the amount of gadolinium is large, the size of the secondary phase becomes coarse, and the fraction of the secondary phase increases, thus formability may deteriorate. This is as confirmed in FIG. 3 above.

[0137] In addition, when the value according to the Relational expression 1 is less than 3, the amount of gadolinium and zinc segregated at the grain boundary or the twin boundary may be reduced, and thus the slip base of the non-bottom surface may be deteriorated.

[0138] As previously disclosed in Table 1, FIG. 3 and FIG. 4, in case of Comparative Example 4, the activation of the slip base of the non-bottom surface was lowered, and thus the result in which the Erichsen value is inferior to that of the Example may be derived. As previously disclosed in Tabe 1, The Erichsen value at room temperature Comparative Example 4 is 9.3 mm, whereas the Erichsen value at room temperature of Example 3 is 11.1mm. That is, when the orientation of the crystal grain is random and the maximum texture intensity with respect to the (0001) plane is 4.5 or less, the formability of the alloy sheet having better activation of the slip base of the non-base surface may be more excellent. In addition, the formability of the alloy sheet having a smaller size of the secondary phase and a lower fraction of the secondary phase may be excellent.

[0139] Specifically, as the value of Zn/Gd(Relational expression 1) increases, the slip base of the non-bottom surface may be activated. In addition, as the content of the gadolinium (Gd) component decreases, the fraction of the secondary phase also decreases, so deformation behavior may be easy.

[0140] In addition, as in Comparative Example 9, when the composition of gadolinium did not satisfy the range according to an exemplary embodiment of the present invention, the Erichsen value at room temperature was at the level of 3.5 mm.

[0141] In this case, it may be seen that a solute dragging effect may be insignificant because the content of gadolinium is too small.

[0142] The present invention is not limited to the above-mentioned exemplary embodiments and may be manufactured in various forms, those who have ordinary knowledge of the technical field to which the present invention belongs may understand that it may be carried out in different and concrete forms without changing the technical idea or fundamental feature of the present invention. Therefore, it should be understood that the exemplary embodiments described above are illustrative and non-limiting in all respects.

[0143] While this invention has been described in connection with what is presently considered to be practical exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. On the contrary, it is intended to cover various modifications and equivalent arrangements comprised within the spirit and scope of the appended claims.

Claims

1. A magnesium alloy sheet comprising:
   0.1 to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities with respect to an entire 100 wt% of the magnesium alloy sheet,
   wherein the magnesium alloy sheet satisfies Relational Expression 1:

   [Relational Expression 1]

   $$[Zn]/[Gd] \geq 3.0$$

   wherein the [Zn] and [Gd] indicate wt % of each component.

2. The magnesium alloy sheet of claim 1, wherein
   the magnesium alloy sheet satisfies Relational Expression 2:

   [Relational Expression 2]

   $$15.0 \geq [Zn]/[Gd] \geq 3.0$$

   wherein the [Zn] and [Gd] indicate wt % of each component.

3. The magnesium alloy sheet of claim 2, wherein
   the magnesium alloy sheet satisfies Relational Expression 3:

   [Relational Expression 3]

   $$13.0 \geq [Zn]/[Gd] \geq 3.0$$

   wherein the [Zn] and [Gd] indicate wt % of each component.

4. The magnesium alloy sheet of claim 3, further comprising
   0.3 wt% or less of Mn (excluding 0 wt%) with respect to the total of 100 wt % of the magnesium alloy sheet.

5. The magnesium alloy sheet of claim 4, wherein
   the magnesium alloy sheet comprises a secondary phase, and
   the number of secondary phases per an area of 40000μm^2 of the magnesium alloy plate is 1 to 20.

6. The magnesium alloy sheet of claim 5, wherein

the magnesium alloy sheet comprises a secondary phase, and
the average particle diameter of the secondary phase is 0.1 to 3 μm.

7. The magnesium alloy sheet of claim 6, wherein
an average crystal grain size of the magnesium alloy sheet is 5 to 30μm.

8. The magnesium alloy sheet of claim 7, wherein
the limited dome height (LDH) of the magnesium alloy sheet is 10.5 mm or more.

9. The magnesium alloy sheet of claim 8, wherein
an edge carck of the magnesium alloy sheet is 5mm or less.

10. The magnesium alloy sheet of claim 9, wherein
the magnesium alloy plate has a maximum texture intensity of 4.5 or less with respect to the (0001) plane.

11. A method for manufacturing a magnesium alloy sheet, comprising:

preparing a casting material by casting an alloy melt solution comprising 0.1 to 1.5 wt% of Zn, 0.08 to 0.7 wt% of Gd, a remainder of Mg, and other inevitable impurities for the entire 100 wt%;
homogenizing and heat-treating the casting material;
preparing a rolled material by rolling the homogenized and heat-treated casting material; and
finally annealing the rolled material,
wherein the alloy melt solution satisfies Relational Expression 4:

[Relational Expression 4]

$$[Zn]/[Gd] \geq 3.0$$

wherein the [Zn] and [Gd] indicate wt % of each component.

12. The method of claim 11, wherein
the alloy melt solution satisfies Relational Expression 5:

[Relational Expression 5]

$$15.0 \geq [Zn]/[Gd] \geq 3.0$$

wherein the [Zn] and [Gd] indicate wt % of each component.

13. The method of claim 12, wherein
the alloy melt solution satisfies Relational Expression 6:

[Relational Expression 6]

$$13.0 \geq [Zn]/[Gd] \geq 3.0$$

wherein the [Zn] and [Gd] indicate wt % of each component.

14. The method of claim 11, wherein
the alloy melt solution further comprises 0.3 wt% or less of Mn (excluding 0 wt%) with respect to the total of 100 wt % of the magnesium alloy sheet.

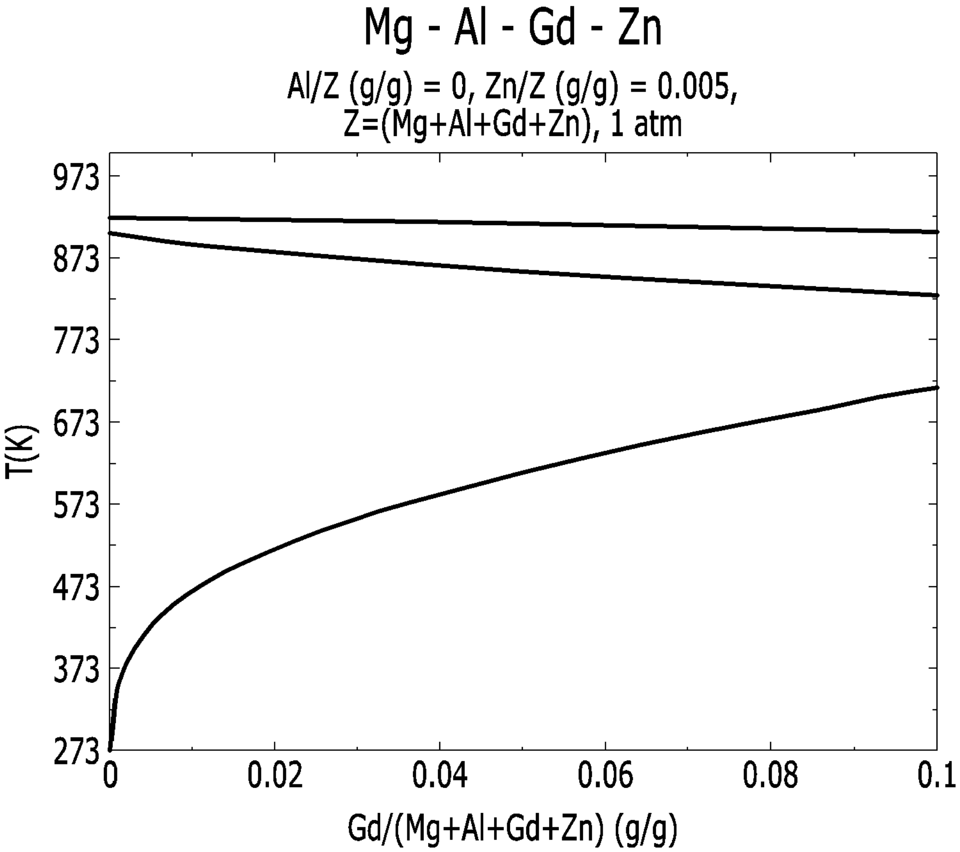
15. The method of claim 11, wherein
the homogenizing and heat-treating of a casting material is performed at a temperature of 300 to 500 °C.

16. The method of claim 15, wherein
the homogenizing and heat-treating of a casting material is performed for 5 hour or more.

17. The method of claim 11, wherein
the preparing of a rolled material comprises performing rolling at a temperature of 150 to 350 °C.

18. The method of claim 17, wherein
the preparing of a rolled material comprises performing a rolling with a reduction ratio that is greater than 0 and equal to or less than 30 % for each rolling.

【FIG. 1】

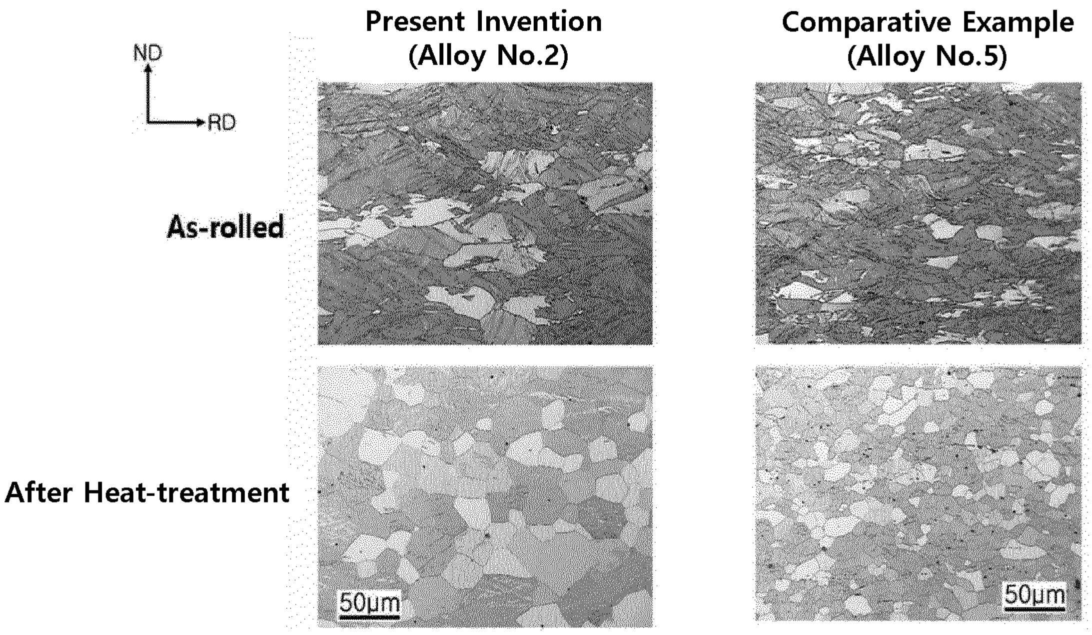

Mg - Al - Gd - Zn
Al/Z (g/g) = 0, Zn/Z (g/g) = 0.005,
Z=(Mg+Al+Gd+Zn), 1 atm
T(K)
973
873
773
673
573
473
373
273
0
0.02
0.04
0.06
0.08
0.1
Gd/(Mg+Al+Gd+Zn) (g/g)

【FIG. 2】

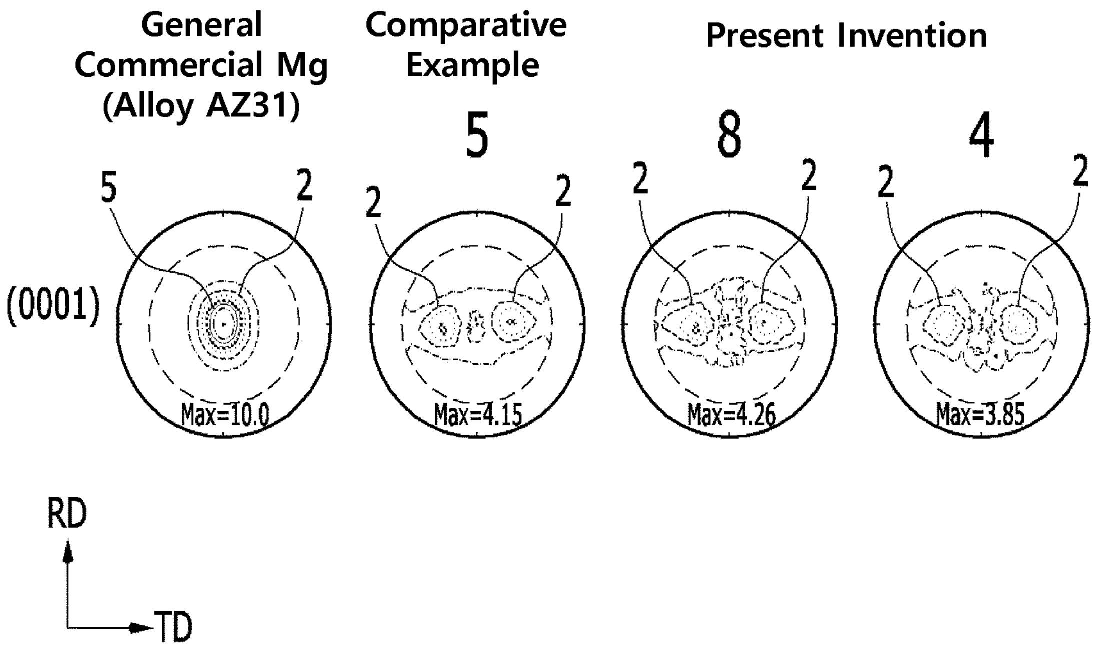
(400℃/wt%)

	Amount of Input			Max. Dissolved Amount
	Al	Zn	Mn	Gd
Gd	-	0.5	-	7.8
	-	1.0	-	7.8
	0.5	1.0	-	0
	0.5	0.5	-	0
	0.5	0.5	0.1	0

【FIG. 3】


Present Invention
(Alloy No.2)
Comparative Example
(Alloy No.5)
ND
RD
As-rolled
After Heat-treatment
50μm
50μm

【FIG. 4】


General
Commercial Mg
(Alloy AZ31)
Comparative
Example
Present Invention
5
8
4
5
2
2
2
2
2
2
2
(0001)
Max=10.0
Max=4.15
Max=4.26
Max=3.85
RD
TD

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2019/012409

A. CLASSIFICATION OF SUBJECT MATTER

C22C 23/04(2006.01)i, C22C 23/06(2006.01)i, C22F 1/06(2006.01)i, C22C 1/02(2006.01)i, B21B 3/00(2006.01)i, B21B 37/58(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 23/04; C22C 23/00; C22C 23/06; C22F 1/06; C22C 1/02; B21B 3/00; B21B 37/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: gadolinium(Gd), magnesium(Mg), zinc(Zn), rolling, casting, homogenization

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2013-0075749 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 05 July 2013 See paragraphs [0014]-[0015], [0038] and claims 1, 8, 11, 14, 19-20.	1-18
X	CN 106995908 A (INSTITUTE OF METAL RESEARCH, CHINESE ACADEMY OF SCIENCES) 01 August 2017 See paragraphs [0002], [0009]-[0016] and claims 1-10.	1-18
A	LIU et al. Effects of Zn/Gd ratio and content of Zn, Gd on phase constitutions of Mg alloys. Materials Transactions. 2008, Vol. 49, No. 5, pp. 941-944. See pages 941-944.	1-18
A	HUANG et al. Precipitation of secondary phase in Mg-Zn-Gd alloy after room-temperature deformation and annealing. Journal of materials research and technology. 2017, pp. 1-7. See pages 1-7.	1-18
A	JP 2015-224388 A (FUJI LIGHT METAL CO., LTD.) 14 December 2015 See paragraph [0030] and claim 1.	1-18

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

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

Date of the actual completion of the international search
07 JANUARY 2020 (07.01.2020)

Date of mailing of the international search report
09 JANUARY 2020 (09.01.2020)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
Government Complex Daejeon Building 4, 189, Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer

Telephone No.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2019/012409

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-2013-0075749 A	05/07/2013	AU 2011-257953 A1	06/12/2012
		AU 2011-257953 B2	08/05/2014
		CN 103038379 A	10/04/2013
		CN 106399783 A	15/02/2017
		EP 2576851 A1	10/04/2013
		EP 2576851 B1	26/06/2019
		JP 2013-533375 A	22/08/2013
		JP 2016-138336 A	04/08/2016
		JP 6339616 B2	06/06/2018
		KR 10-1828629 B1	12/02/2018
		US 2013-0199677 A1	08/08/2013
		US 9945011 B2	17/04/2018
		WO 2011-146970 A1	01/12/2011
CN 106995908 A	01/08/2017	CN 106995908 B	20/07/2018
JP 2015-224388 A	14/12/2015	JP 6389378 B2	12/09/2018

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- KR 1020180116033 **[0001]**
- WO 20120055304 A **[0007]**
- WO 20150185017 A **[0008]**