



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

(43) Date of publication:
27.08.2014 Bulletin 2014/35

(51) Int Cl.:
C22C 23/00 ^(2006.01) **B22D 21/04** ^(2006.01)
C22C 23/02 ^(2006.01)

(21) Application number: **12841026.3**

(86) International application number:
PCT/KR2012/008357

(22) Date of filing: **15.10.2012**

(87) International publication number:
WO 2013/058504 (25.04.2013 Gazette 2013/17)

(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

(30) Priority: **20.10.2011 KR 20110107405**

(71) Applicant: **Postech Academy-Industry Foundation Pohang-si, Gyeongsangbuk-do 790-784 (KR)**

(72) Inventors:
• **KIM, Nack Joon**
Pohang-si
Gyeongsangbuk-do 790-751 (KR)

- **SHIM, Myoeng Shik**
Gurye-gun
Jeollanam-do 542-806 (KR)
- **SUH, Byeong Chan**
Seoul 134-032 (KR)
- **BAE, Jun Ho**
Pohang-si
Gyeongsangbuk-do 790-390 (KR)
- **KIM, Dong Wook**
Pohang-si
Gyeongsangbuk-do 790-784 (KR)

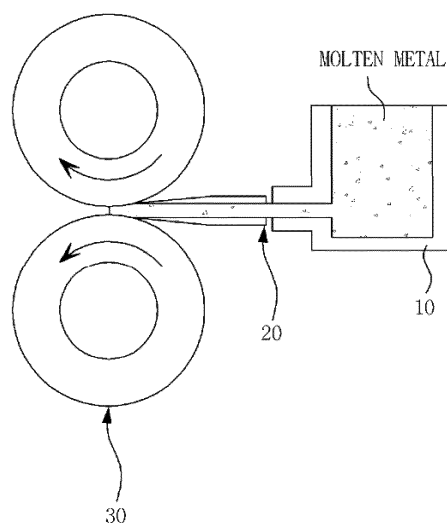
(74) Representative: **Stolmár & Partner**
Blumenstraße 17
80331 München (DE)

(54) **NON-HEAT TREATED MAGNESIUM ALLOY SHEET WITH EXCELLENT FORMABILITY AT ROOM TEMPERATURE IN WHICH SEGREGATION IS MINIMIZED**

(57) Disclosed herein is a non-heat treatable magnesium alloy sheet, including: 1 ~ 3 wt% of aluminum (Al); 0.5 ~ 3 wt% of tin (Sn); and a balance of magnesium, wherein the maximum deviation of average Vickers hardness (Hv) thereof, caused by center segregation and inverse segregation, is 10 Hv or less.

The non-heat treatable magnesium alloy sheet can remarkably reduce a cast defect such as center segregation, inverse segregation or the like by alloy component control, and has excellent formability compared to that of a conventional commercially available magnesium alloy sheet.

[FIG. 1]



Description*BACKGROUND OF THE INVENTION*

1. Technical Field

[0001] The present invention relates to a strip-cast magnesium alloy sheet, and, more particularly, to a non-heat treatable magnesium alloy sheet, which can remarkably reduce a cast defect such as center segregation, inverse segregation or the like by alloy component control, and which can improve room-temperature formability by controlling crystal grain growth in the subsequent heat treatment procedure using a precipitate formed in a rolling procedure.

2. Description of the Related Art

[0002] A magnesium alloy, which is an alloy for structural materials having low specific gravity, high specific strength and high rigidity, has recently been increasingly used as a material for light portable electronic appliances such as mobile phones, notebooks and the like or as a material for automobiles for improving fuel efficiency. However, research into magnesium alloys has been restricted to parts for casting. Particularly, research into the improvement of high-temperature physical properties of magnesium alloys used for automobile engines or gears has attracted considerable attention, whereas research into magnesium alloys for processing, such as magnesium alloy sheets which can be used in more various fields, has not been sufficiently conducted.

[0003] Recently, for the purpose of various applications of magnesium alloys, demand for magnesium alloy products for processing has increased, and thus many research institutes have conducted research into magnesium alloys for processing. Particularly, among the magnesium alloy products, a magnesium alloy sheet, which is manufactured by twin-roll strip casting, can be applied in various fields, so research into the magnesium alloy sheet has been variously conducted, and the magnesium alloy sheet is commercially available.

[0004] However, according to the recent trend of magnesium alloy development, since various kinds of alloy elements are added or expensive rare-earth elements are used for the purpose of development of high-strength and high-formability magnesium alloys, price competitiveness has been lowered. Therefore, to date, the only magnesium alloy sheet manufactured by twin-roll strip casting is an AZ31 alloy sheet, and this AZ31 alloy sheet has mechanical properties generally used in industrial markets.

[0005] Meanwhile, considering that an aluminum alloy sheet having a yield strength (mechanical strength) of 200 MPa or less are variously used in an automobile industry and other exterior material industries, it is urgently required to develop a non-heat treatable magnesium alloy for twin-roll strip casting in order to rapidly commercialize a magnesium alloy sheet and increase the price competitiveness thereof.

SUMMARY OF THE INVENTION

[0006] Accordingly, the present invention has been devised to solve the problems of conventional magnesium alloys for twin-roll strip casting, such as cast defects, low mechanical strength and poor room-temperature formability, and an object of the present invention is to provide a non-heat treatable magnesium alloy sheet, which can reduce a cast defect such as segregation or the like by adjusting the composition of a magnesium alloy and which can obtain suitable mechanical strength and good room-temperature formability without including expensive rare-earth elements by controlling the microstructure of a magnesium alloy.

[0007] In order to accomplish the above object, an aspect of the present invention provides a non-heat treatable magnesium alloy sheet, including: 1 ~ 3 wt% of aluminum (Al); 0.5 ~ 3 wt% of tin (Sn); and a balance of magnesium, wherein the maximum deviation of average Vickers hardness (Hv) thereof, caused by center segregation and inverse segregation, is 10 Hv or less.

[0008] The magnesium alloy sheet may be formed by twin-roll strip casting, and may have a microstructure of an Mg₂Sn secondary phase.

[0009] In the magnesium alloy sheet, the Mg₂Sn secondary phase may have a volume fraction of 5% or less.

[0010] The magnesium alloy sheet may have a yield strength of 200 MPa or more and a limit dome height (LDH) of 5 mm or more, and preferably 6 mm or more.

[0011] In the magnesium alloy sheet, the volume fraction of tension twins inclined at an angle of 85 ~ 90° to parent grains may be 5% or more.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The above and other objects, features and advantages of the present invention will be more clearly understood

from the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view showing a twin-roll strip casting apparatus for manufacturing a magnesium alloy sheet according to the present invention;

FIG. 2 is a view showing the thickness-direction hardness distributions of the magnesium alloy sheet of the present invention and a commercially available AZ31 alloy sheet, each of which was divided into five equal parts;

FIG. 3 is a photograph showing the composition distributions of cast structure sections of the magnesium alloy sheet of the present invention and a commercially available AZ31 alloy sheet by EPMA (electron probe X-ray microanalysis);

FIG. 4 is a graph showing the results of X-ray diffraction test of the magnesium alloy sheet of the present invention;

FIG. 5 is a schematic view showing a method of evaluating the limit dome height (LDH) of the magnesium alloy sheet of the present invention;

FIG. 6 shows photographs showing the shapes of the magnesium alloy sheet of the present invention (a) and a commercially available AZ31 alloy sheet (b) after the LDH test thereof;

FIG. 7 is a view showing the section for analyzing a sample after the LDH test; and

FIG. 8 shows graphs showing the crystal grain changes of the magnesium alloy sheet of the present invention (a) and a commercially available AZ31 alloy sheet (b).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] All of the terms used in the specification are taken only to illustrate embodiments, and are not intended to limit the present invention. As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise," "comprising," and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense, that is to say, in the sense of "including, but not limited to."

[0014] The terms and words used in the present specification and claims should not be interpreted as being limited to typical meanings or dictionary definitions, but should be interpreted as having meanings and concepts relevant to the technical scope of the present invention based on the rule according to which an inventor can appropriately define the concept of the term to describe the best method he or she knows for carrying out the invention.

[0015] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the attached drawings. The above detailed descriptions of embodiments of the invention are not intended to be exhaustive or to limit the invention to the precise form disclosed above. While specific embodiments of, and examples for the invention are described above for illustrative purposes, various equivalent modifications are possible within the scope of the invention, as those skilled in the relevant art will recognize.

[0016] The present invention provides a non-heat treatable magnesium alloy sheet, including: 1 ~ 3 wt% of aluminum (Al); 0.5 ~ 3 wt% of tin (Sn); and a balance of magnesium, wherein the maximum deviation of average Vickers hardness (Hv) thereof, caused by center segregation and inverse segregation, is 10 Hv or less.

[0017] In a sheet casting process, the solidification range of a cast material influences the segregation of the cast material and degree thereof. When a molten metal is solidified while passing through the set back distance region of rollers during a plating casting process, a liquid region coexisting in a sheet is squeezed from center to surface because the sheet is pressed by two rollers, thus resulting in forming a segregated zone having high composition density on the surface thereof. This phenomenon is referred to as "inverse segregation". Particularly, such inverse segregation severely occurs in the case of an alloy having a long solidification range. In the case of an aluminum alloy having a relatively narrow solidification range, inverse segregation does not easily occur compared to the case of a magnesium alloy having a long solidification range. Further, even in the case of a magnesium alloy, degree of segregation is changed according to the kind of alloy element. Due to such segregation, it is difficult to control the microstructure of a cast material, the cast material must be homogenized at high temperature for a long period of time, the mechanical properties of the cast material become poor, and the surface treatment of the cast material is difficult.

[0018] In order to solve the above problems of segregation, the present inventors have adjusted the solidification range of a magnesium alloy used in twin-roll strip casting to be within the range where it doesn't have mechanical properties leading to deterioration. Like the magnesium alloy according to the present invention, an alloy including 1 ~ 3 wt% of aluminum (Al), 0.5 ~ 3 wt% of tin (Sn) and a balance of magnesium has a solidification range of 30 ~ 50K in

an equilibrium diagram calculated by Factsage V6.2. This solidification range corresponds to half of that (80 ~ 90K) of AZ31, which is a conventional alloy for twin-roll strip casting. Therefore, the magnesium alloy of the present invention has a solidification range of 50K or less, which is similar to that of an aluminum alloy, thus greatly reducing inverse segregation.

[0019] Degree of segregation can be evaluated by the distribution of alloy composition. In the case of an alloy having a long solidification range, center segregation and inverse segregation are highly developed, and thus the distribution of alloy composition in a cast structure appears densely at the center and edge of a sheet. The deviation in the composition of the magnesium alloy of present invention in a thickness direction does not become large. The average deviation in the composition of a commercially available strip-cast AZ31 sheet is 30 ~ 50%, whereas the deviation in the composition of the magnesium alloy of the present invention is 10% or less.

[0020] Meanwhile, generally, when the difference in composition of a cast material is large, hardness thereof becomes partially non-uniform. Thus, when secondary phases composed of high-concentration inverse or center segregation zone and eutectic phase are clustered together, they have higher hardness. Therefore, degree of segregation can be numerically indicated, and the maximum deviation of average Vickers hardness (Hv) of the magnesium alloy sheet of the present invention in the thickness direction thereof may be 10 Hv or less.

[0021] Further, the magnesium alloy sheet of the present invention exhibits excellent mechanical properties compared to a conventional commercially available AZ31 because of the formation of Mg_2Sn secondary phases. In the case of a non-heat treatable alloy, a heat treatment process for controlling the precipitates is not used, and thus a mechanism for enhancing the mechanical strength of the alloy is restricted. The volume fraction of Mg_2Sn secondary phases in the magnesium alloy sheet of the present invention is 5% or less, as optical images were measured using an image pro plus 6.0 program.

[0022] Particularly, in the case of AZ31 having low alloy element content, only thermo-mechanical treatment such as hot rolling may be used as a mechanism for enhancing mechanical strength. In this case, after rolling, due to crystal grain growth together with inner strain, the mechanical strength of AZ31 is rapidly lowered with the passage of annealing time, and this phenomenon becomes remarkable with the increase of annealing temperature.

[0023] The volume fraction of secondary phases in the magnesium alloy of the present invention is greatly decreased in the homogenization process after casting. However, secondary phases are distributed in the microstructure thereof again with dynamic precipitation during rolling, and the secondary phase distribution controls crystal grain growth during annealing, thus preventing the mechanical strength of the magnesium alloy from being rapidly lowered.

[0024] The reasons for limiting the composition ratio of the magnesium alloy to the above range are as follows. When the amount of Al is less than 1 wt%, the effect of improving fluidity and the effect of enhancing strength are insufficient, and, when the amount thereof is more than 3 wt%, the solidification range of the molten magnesium alloy is enlarged, and thus the effect of controlling segregation is not sufficient.

[0025] Further, when the amount of Sn is less than 0.5 wt%, the volume fraction of Mg_2Sn secondary phases in the magnesium alloy is low, the contribution to the improvement of mechanical properties of the magnesium alloy is insufficient, and, when the amount thereof is more than 3 wt%, the homogenization treatment temperature and time increase, and secondary phases formed during a rolling process are locally distributed in the magnesium alloy in large amounts, thus exerting a negative influence on the improvement of formability and elongation.

[0026] Generally, the formability of magnesium at room temperature is poor due to the absence of a slip system, and thus it is important that twins be used as a deformation factor replacing the slip system.

[0027] The magnesium alloy sheet according to the present invention exhibits excellent room-temperature formability compared to that of a conventional AZ31 alloy because of tension twins inclined at an angle of 85 ~ 90° to parent grains.

[0028] Hereinafter, the present invention will be described in more detail with reference to the following Examples.

Manufacture of magnesium alloy sheet

[0029] First, pure Mg (99.9%), pure Al (99.9%) and pure Sn (99.9%) were melted by a furnace 10 of a twin-roll strip casting apparatus shown in FIG. 1 under a mixed gas atmosphere of CO_2 and SF_6 to prepare a molten metal, and then the molten metal was injected between two cooling rolls 30 using a nozzle 20 to manufacture a magnesium alloy sheet. In this case, the distance between the two cooling rolls was maintained about 2 mm, the rotation speed of the two cooling rolls was maintained about 4 m/min at the time of injecting the molten metal, and the cooling rate of the molten metal was maintained 200 ~ 300 K/s, thus obtaining a magnesium alloy sheet having a length of about 5 m, a width of about 70 mm and a thickness of about 2 mm.

[0030] Then, in order to evaluate the degree of segregation of the obtained magnesium alloy sheet in the solidification range thereof, EPMA (electron probe X-ray microanalysis) and hardness measurement were carried out.

[0031] FIG. 2 shows the thickness-direction hardness distributions of a strip-cast AZ31 sheet (Comparative Example) manufacture by POSCO Corporation and an AT33 magnesium alloy sheet (Example 2), wherein samples having a length of 50 cm were respectively divided into five equal parts to obtain samples having a length of 10 cm, and then the

hardness of each of the samples was measured in the thickness direction thereof, and wherein the Vickers hardness thereof was measured under conditions of a load of 100 g_f and a holding time of 5 seconds.

[0032] As shown in FIG. 2, it can be ascertained that AZ31 sheet locally exhibits high hardness at the center and surfaces thereof, and thus the hardness thereof are entirely non-uniform. In contrast, it can be seen that AT33 sheet (Example 2) partially shows the hardness deviation to some degree due to segregation, but, entirely, the average deviation of hardness (Hv) thereof is 10 Hv or less, whereas AZ31 shows an average hardness deviation of 10 ~ 20 Hv. Consequently, it can be ascertained that the entire hardness distribution of AT33 sheet is uniform compared to that of AZ31 sheet.

[0033] Further, from the result of EPMA analysis shown in FIG. 3, it can be ascertained that degree of center segregation and inverse segregation of AT31 sheet (Example 1) was remarkably reduced compared to that of AZ31 sheet. Further, from the mapping result of composition distributions of AT31 sheet and AZ31 sheet, it can be ascertained that the concentration of composition of AZ31 sheet increases near the center and surfaces thereof, whereas that of AT31 sheet hardly changes according to the thickness thereof. Consequently, it can be ascertained that, when an alloy having a relatively narrow solidification range was strip-cast, degree of center segregation and inverse segregation thereof is greatly reduced.

Thermo-Mechanical treatment

[0034] The sheet manufactured as above was heat-treated as follows. First, the sheet was solution-treated at 400°C for 3 hours. Subsequently, the solution-treated sheet was preheated to 200°C, and was then hot-rolled by rollers heated to 200°C.

[0035] During the hot rolling, the preheated sheet was hot-rolled five times at a reduction ratio of 10% per pass to a final reduction ratio of 50%, thereby finally obtaining a sheet having a thickness of 1 ~ 0.7 mm.

Evaluation of mechanical properties

[0036] The above strip-cast and heat-treated magnesium alloy sheet was annealed as shown in Table 1 below, and then the mechanical properties and formability thereof were evaluated.

[0037] In order to evaluate the tensile characteristics of the magnesium alloy sheet, a sample having a length of 12.6 mm, a width of 5 mm and a thickness of 1 mm was fabricated, and then the tensile characteristics of the sample were tested at a deformation ratio of $6.4 \times 10^{-4} \text{s}^{-1}$.

[0038] Further, in order to evaluate the formability of the magnesium alloy sheet, a limit dome height (LDH) test was carried out. FIG. 5 is a schematic view showing a method of evaluating the limit dome height (LDH) of the magnesium alloy sheet according to an embodiment of the present invention. In the limit dome height (LDH) test, a disk-shaped sample having a diameter of 50 mm and a thickness of 0.7 mm was fabricated, inserted between upper and lower dies and then fixed therebetween by a force of 5 kN, and a commonly-known press oil was used as a lubricating oil. Subsequently, the fixed disk-shaped sample was deformed at a deformation rate of 0.1 mm/sec using a spherical punch having a diameter of 27.5 mm until the disk-shaped sample was torn by the movement of the punch, and then the deformation height of the disk-shape sample at this time was measured.

[Table 1]

Alloy	Process condition	YS (MPa)	UTS (MPa)	El. (%)	LDH (mm)
AZ31 (Comparative Example)	As received (POSCO)	200	281	25	2.9
AT31 (Example 1)	50% rolled	249	280	13.5	
	50% rolled + 150/1h	216	270	12	5.2
	50% rolled + 150/5h	213	268	12.5	
	50% rolled + 200/1h	165	248	20	
	50% rolled + 200/3h	168	245	19	6.6
	50% rolled + 200/5h	170	248	20.2	7.3
	50% rolled + 250/1h	146	233	15	6.8
	50% rolled	275	316	3.5	

(continued)

Alloy	Process condition	YS (MPa)	UTS (MPa)	El. (%)	LDH (mm)
AT33 (Example 2)	50% rolled + 150/1h	255	299	6.5	4.3
	50% rolled + 150/3h	233	278	15.3	4.7
	50% rolled + 200/1h	219	283	21	5.2
	50% rolled + 200/3h	210	273	19	6.2

[0039] The magnesium alloy sheet, which is a non-heat treatable magnesium alloy sheet, similarly to AZ31 (typical non-heat treated alloy), is characterized in that its mechanical strength is decreased with the increase of annealing time and annealing temperature, and its elongation and formability (that is, LDH) is increased with the increase of annealing time and annealing temperature.

[0040] Generally, tensile elongation is used as an alternative item to formability, but, as given in Table 1 above, elongation is not absolutely proportional to LDH representing formability. Therefore, it is preferred that a test accompanying an actual forming procedure is conducted compared to when a uniaxial tensile elongation is used as an index representing formability.

[0041] Comparing AT alloys with a conventional AZ31 alloy, it can be ascertained that the formability of an AT alloy is more excellent than that of the conventional AZ31 alloy under the condition that they have similar yield strengths to each other, and that the yield strength of an AT33 alloy further including Sn is higher than those of other AT alloys under the condition that they have similar LDH values to each other. Entirely, yield strength is inversely proportional to LDH, but an AT alloy has more excellent mechanical properties than those of the conventional AZ31 alloy and have higher LDH values than that of the conventional AZ31 alloy.

[0042] FIG. 6 shows photographs showing the shapes of an AT alloy sheet sample and a commercially available AZ31 alloy sheet sample after the LDH tests thereof.

[0043] Fig. 8 shows graphs showing the changes of the most severely deformed top portion of each sample and the non-deformed edge portion of each sample at a crystal direction difference between in a normal direction of a sheet and in a direction of a (0002) basal plane of magnesium hexagonal crystal.

[0044] From FIG. 8, it can be ascertained that the texture of (0002) plane is developed because the fraction of crystal grains having a low crystal direction difference is high. It means that the magnesium sheet has a random structure as the crystal direction difference of crystal grains is diverged.

[0045] As shown in Fig.8, The fraction of grains having a high crystal direction difference of the magnesium alloy sheet of the present invention is considerably increased. On the other hand, the fraction of grains having a high crystal direction difference of the AZ31 alloy sheet is slightly increased.

[0046] This difference is caused by the amount of tension twins formed in the deformation process thereof. These tension twins contribute greatly to the improvement of formability of the magnesium alloy sheet lacking a slip system.

[0047] The present invention provides a magnesium alloy sheet, which can make a uniform cast structure by controlling alloy elements having a narrow solidification range, which can make up for defects caused by segregation, and which has excellent mechanical strength and formability without using expensive rare-earth elements. Further, the magnesium alloy sheet according to the present invention can be used in various application fields because it is a non-heat treatable magnesium alloy sheet and its yield strength and LDH value are linearly changed depending on annealing time.

[0048] As described above, the magnesium alloy sheet according to the present invention is advantageous in that it can remarkably improve defects, such as inverse segregation, center segregation and the like, occurring in a conventional magnesium alloy sheet prepared by a twin-roll strip casting process due to the change of a solidification range by the addition of alloy elements, and in that its mechanical strength is excellent compared to that of a conventional non-heat treatable strip-cast magnesium alloy sheet even after it is heat-treated to have high formability.

[0049] Further, the magnesium alloy sheet according to the present invention can exhibit excellent formability without using expensive rare-earth elements added to impart high formability and high strength, thus increasing competitiveness thereof in the light structural materials market.

[0050] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

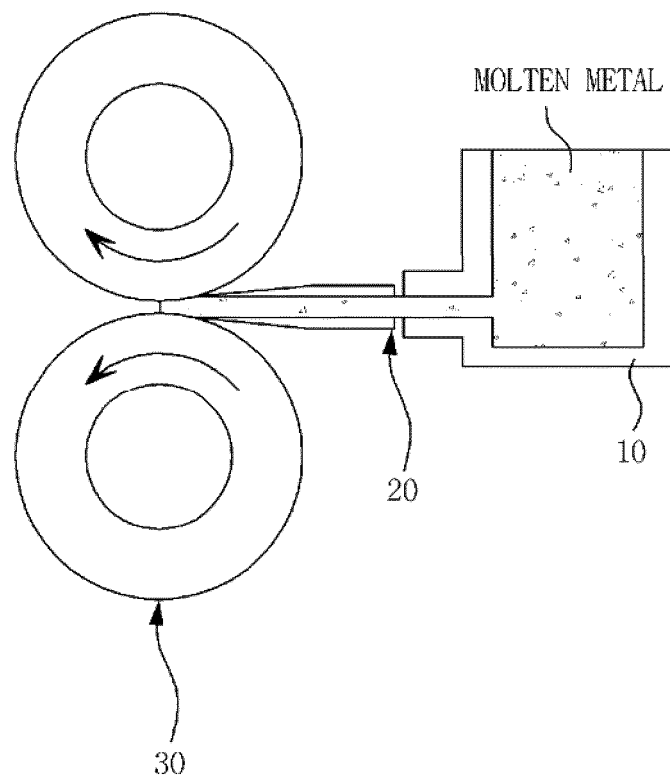
1. A non-heat treatable magnesium alloy sheet, comprising:

EP 2 770 072 A2

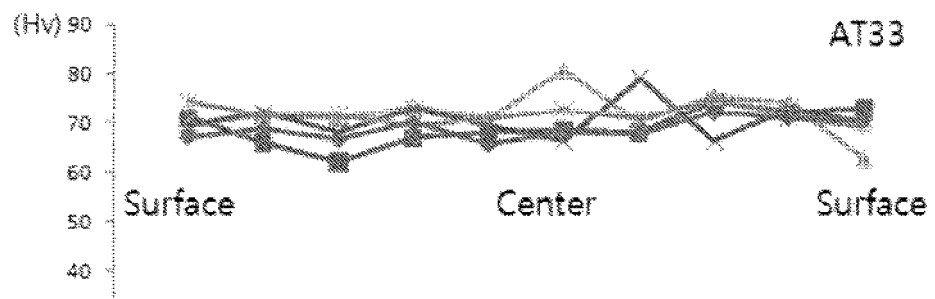
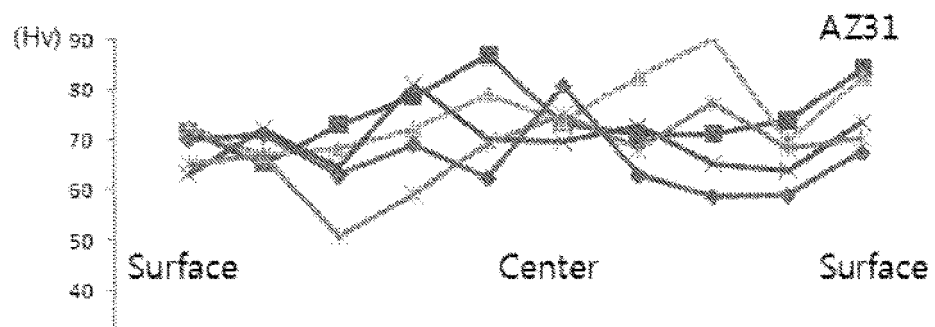
1 ~ 3 wt% of aluminum (Al) ; 0.5 ~ 3 wt% of tin (Sn); and a balance of magnesium, wherein a maximum deviation of average Vickers hardness (Hv) thereof, caused by center segregation and inverse segregation, is 10 Hv or less.

2. The non-heat treatable magnesium alloy sheet of claim 1, wherein the magnesium alloy sheet is formed by twin-roll strip casting, and has a microstructure of a Mg_2Sn secondary phase.
3. The non-heat treatable magnesium alloy sheet of claim 2, wherein the Mg_2Sn secondary phase has a volume fraction of 5% or less.
4. The non-heat treatable magnesium alloy sheet of any one of claims 1 to 3, wherein the magnesium alloy sheet has a yield strength of 200 MPa or more and a limit dome height (LDH) of 5 mm or more.
5. The non-heat treatable magnesium alloy sheet of any one of claims 1 to 3, wherein the magnesium alloy sheet has a yield strength of 200 MPa or more and a limit dome height (LDH) of 6 mm or more.
6. The non-heat treatable magnesium alloy sheet of any one of claims 1 to 3, wherein a volume fraction of tension twins inclined at an angle of $85^\circ \sim 90^\circ$ to parent grains is 5% or more.

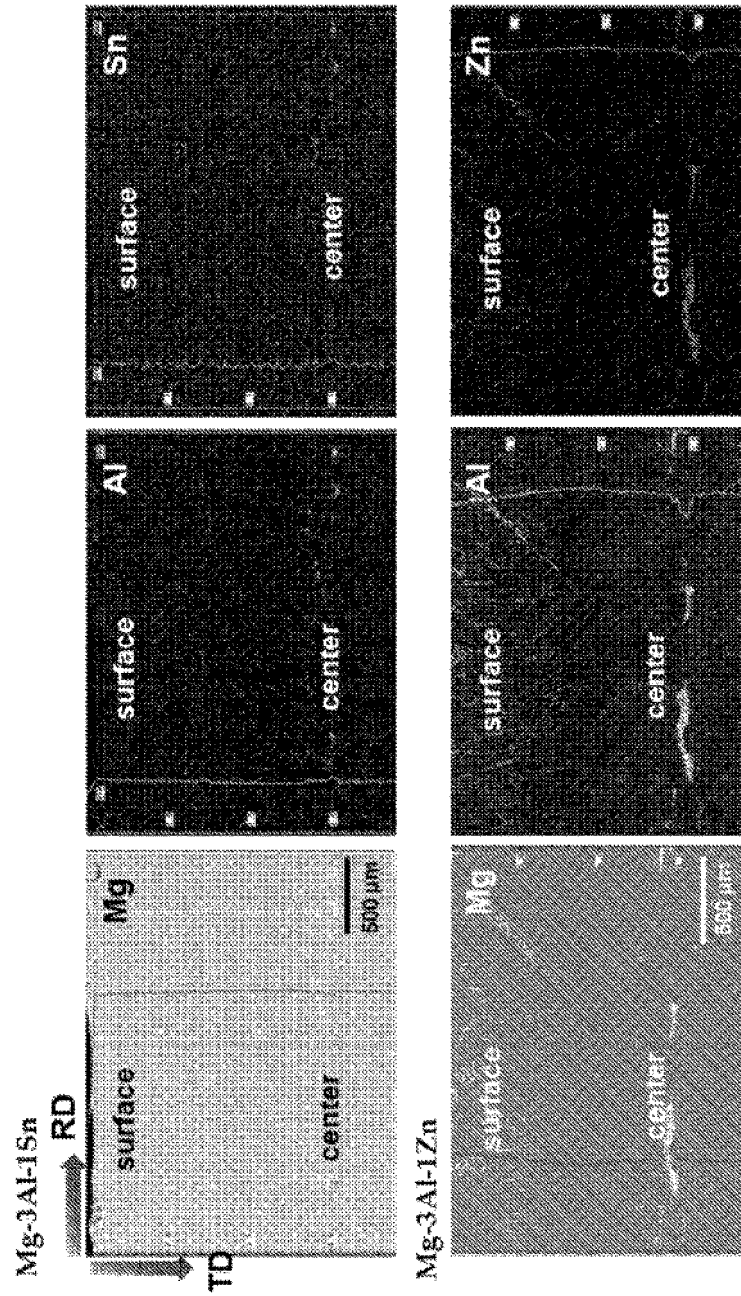
[FIG. 1]



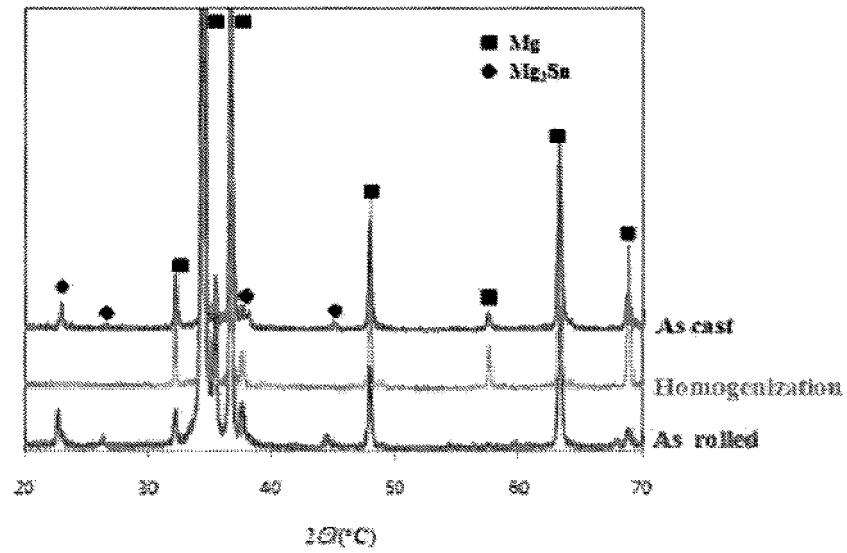
[FIG. 2]



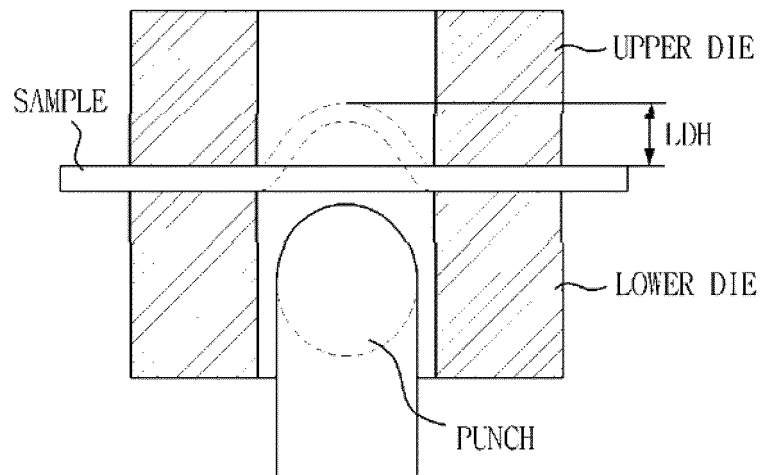
[FIG. 3]



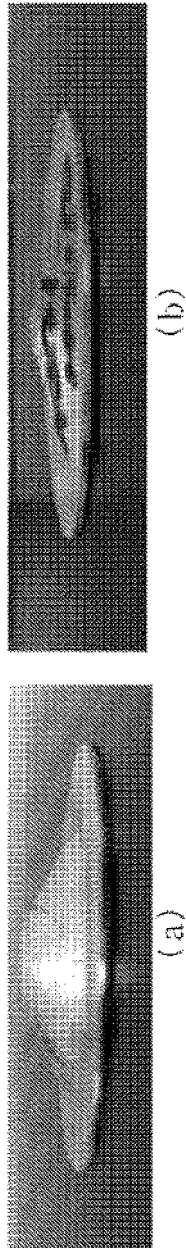
[FIG. 4]



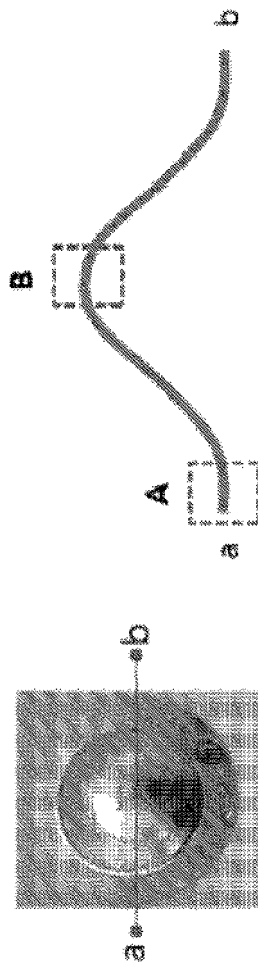
[FIG. 5]



[FIG. 6]



[FIG. 7]



[FIG. 8]

