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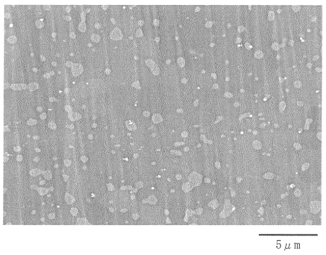
(54) MAGNESIUM ALLOY, MAGNESIUM ALLOY PLATE, MAGNESIUM ALLOY MEMBER, AND METHOD FOR PRODUCING MAGNESIUM ALLOY

(57) A magnesium alloy contains, in mass%, from 1% to 12% inclusive of A1 and from 0.1% to 5% inclusive of Mn and has a structure in which particles of compounds containing Al and Mn are dispersed. The average diameter of the particles of the compounds is from 0.3 μm to 1 μm inclusive, and the area ratio of the particles of the compounds is from 3.5% to 25% inclusive.

FIG. 1

SEM (SECONDARY ELECTRON IMAGE)



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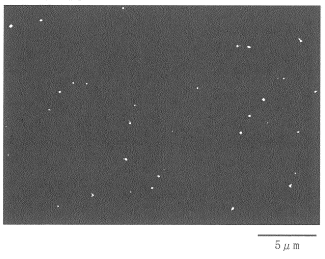

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Description

Technical Field

[0001] The present invention relates to a magnesium alloy suitable for a constituent material of housings, various parts, etc., to a magnesium alloy sheet suitable for raw materials (primary-processed materials) for secondary-processed materials such as housings and various parts, to a magnesium alloy structural member suitable for secondary-processed materials such as housings and various parts, and to a method for producing the magnesium alloy. Particularly, the present invention relates to a magnesium alloy, a magnesium alloy sheet, and a magnesium alloy structural member that are excellent in impact resistance, mechanical properties, and plastic formability and also excellent in productivity.

Background Art

[0002] Magnesium alloys, which are lightweight and excellent in specific strength and specific rigidity, have been increasingly used as constituent materials of various parts such as parts of automobiles and housings of mobile electronic-electric devices such as cellular phones and laptop computers.

[0003] Magnesium alloys are lighter than many other metals, have high specific strength, and also have excellent impact absorption ability. Since various elements are added to active Mg (magnesium), these magnesium alloys also have excellent corrosion resistance and are preferable for the constituent materials of the above-described various parts. Among these magnesium alloys, Mg-Al-based alloys containing A1 (aluminum), in particular, are excellent in strength and corrosion resistance and are preferable for the constituent materials described above.

[0004] PTL 1 discloses a magnesium alloy sheet that is composed of a magnesium alloy containing Al and Mn (manganese) and is excellent in impact resistance and mechanical properties not only at ordinary temperature but also at low temperature.

[0005] This magnesium alloy sheet contains compounds containing Al and Mn (mainly precipitates in crystal. These may be hereinafter referred to as Al-Mn crystallized phases). The Al-Mn crystallized phases are very fine and are very small in amount and preferably are not substantially present. Therefore, in this magnesium alloy sheet, cracking etc. caused by coarse Al-Mn crystallized phases are unlikely to occur. Therefore, the magnesium alloy sheet is excellent in impact resistance and mechanical properties and also excellent in plastic formability such as press formability.

Citation List

Patent Literature

[0006] PTL 1: Japanese Unexamined Patent Application Publication No. 2011-006754

Summary of Invention

Technical Problem

[0007] It is desired to develop a magnesium alloy excellent in impact resistance, mechanical properties such as strength, proof stress, and elongation, and plastic formability such as rolling formability and press formability and also excellent in productivity.

[0008] The magnesium alloy sheet disclosed in PTL 1 is excellent in impact resistance etc. as described above. However, to reduce the amount of the Al-Mn crystallized phases, the temperature of a melt of the alloy is set to be relatively high, i.e., 700°C. Theoretically, the Al-Mn crystallized phases are formed and grow most easily when the temperature of the melt of the magnesium alloy containing Al and Mn is around 630°C, particularly lower than 630°C. Therefore, when the temperature of the melt of the alloy is sufficiently higher than 630°C, preferably higher than 690°C, the formation and growth of the Al-Mn crystallized phases can be effectively prevented. However, when the temperature of the melt of the alloy is increased, the following occurs. (α) The melt of the alloy is easily oxidized, and this causes a reduction in yield due to formation and mixing of the oxide. (β) When, for example, a high-vacuum atmosphere is used in order to prevent oxidation, the melt of the alloy becomes difficult to handle because of high vapor pressure of Mg, so that workability deteriorates. (γ) A large amount of energy is needed to maintain the melt of the alloy at high temperature. (δ) Since the melt of the alloy is at high temperature, thermal degradation of the facility is accelerated. From the above points of view, it is difficult to improve the productivity. The above (α) to (δ) can also cause an increase in cost.

[0009] One object of the present invention is to provide a magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability and also excellent in productivity.

[0010] Another object of the present invention is to provide a magnesium alloy sheet excellent in impact resistance, mechanical properties, and plastic formability and also excellent in productivity.

[0011] Still another object of the present invention is to provide a magnesium alloy structural member excellent in impact resistance and mechanical properties and also excellent in productivity.

[0012] Yet another object of the present invention is to provide a magnesium alloy production method that can produce a magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability with high productivity. Solution to Problem

[0013] A magnesium alloy according to one aspect of the present invention contains, in mass%, from 1% to 12% inclusive of Al and from 0.1% to 5% inclusive of Mn and has a structure in which particles of a compound containing Al and Mn are dispersed. The average diameter of the particles of the compound is from 0.3 μm to 1 μm inclusive, and the area ratio of the particles of the compound is from 3.5% to 25% inclusive.

[0014] A magnesium alloy production method according to one aspect of the present invention includes the step of subjecting a melt of a magnesium alloy containing, in mass%, from 1% to 12% inclusive of A1 and from 0.1% to 5% inclusive of Mn to continuous casting. In this production method, the temperature of the melt immediately before it comes into contact with a mold is from 630°C to 690°C inclusive, and the cooling rate of the melt is 560°C/second or higher.

Advantageous Effects of Invention

[0015] The above magnesium alloy is excellent in impact resistance, mechanical properties, and plastic formability and also excellent in productivity. The above magnesium alloy production method can produce a magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability with high productivity. Brief Description of Drawings

[0016]

[Fig. 1] Figure 1 shows, in its upper part, a microphotograph (secondary electron image) of a cross section of a magnesium alloy sheet in an embodiment (sample No. 1-1) observed under a scanning electron microscope (SEM) and also shows, in the lower part, a binary image obtained by changing the contrast of the secondary electron image.

[Fig. 2] Figure 2 is a microphotograph (backscattered electron image) of the cross section of the magnesium alloy sheet in the embodiment (sample No. 1-1) observed under the SEM.

[Fig. 3] Figure 3 shows a compositional mapping of the cross section of the magnesium alloy sheet in the embodiment (sample No. 1-1), the compositional mapping showing the concentration distribution of Mn and being obtained by a field-emission electron probe microanalyzer (FE-EPMA) at an electron gun acceleration voltage of 15 kV.

[Fig. 4] Figure 4 is a histogram showing the concentration of Mn (the number of Mn counts) versus the frequency of the concentration and the cumulative frequency, the histogram being produced using the compositional mapping shown in Figure 3 and obtained by the FE-EPMA (15 kV).

[Fig. 5] Figure 5 shows, in its left part, a compositional mapping of the cross section of the magnesium alloy sheet in the embodiment (sample No. 1-1), the compositional mapping showing the concentration distribution of Mn and being obtained by the field-emission electron probe microanalyzer (FE-EPMA) at an electron gun acceleration voltage of 5 kV. Figure 5 also shows, in the right part, a microphotograph (backscattered electron image) of the same region as the region of the compositional mapping, the microphotograph being observed under the SEM.

[Fig. 6] Figure 6 is a histogram showing the concentration of Mn (the number of Mn counts) versus the frequency of the concentration and the cumulative frequency, the histogram being produced using the compositional mapping shown in Figure 5 and obtained by the FE-EPMA (5 kV).

[Fig. 7] Figure 7 is an illustration illustrating a test method of a shock resistance test. Description of Embodiments

[0017] The present inventors have produced magnesium alloys having compositions containing Al and Mn and capable of providing, in particular, excellent strength and corrosion resistance under various production conditions to examine the structure of a magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability. Then the inventors have found that a magnesium alloy having a structure in which compounds containing Al and Mn (Al-Mn crystallized phases) and having a size within a specific range are contained in an amount within a specific range can have impact resistance, mechanical properties, and plastic formability substantially comparable to those of a magnesium alloy containing only a very small amount of the above-described compounds or substantially no such compounds. Specifically, when the magnesium alloy has a structure containing a certain amount of the above-described compounds and these compounds are relatively fine and distributed uniformly, the magnesium alloy can have impact resistance, mechanical properties, and plastic formability substantially comparable to those of a magnesium alloy containing only a very small amount of the above-described compounds or substantially no such compounds. The inventors have also found that the magnesium alloy having the above-described specific structure can be produced by a specific casting process including performing continuous casting such that the temperature of the melt of the alloy before it comes into contact with the mold is set to be as low as possible and that the rate of cooling is very high. In this production method, the melt of the alloy is maintained at a relatively low temperature. This can mitigate the above-described problems (α) to (δ) and other problems that can occur when the melt of the alloy is at high temperature, so that the productivity of the magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability can be improved. The present invention is based on the above findings. First, the details of the embodiments of the present invention will be enumerated and described.

[0018]

(1) A magnesium alloy according to one aspect of the present invention comprises, in mass%, from 1% to 12% inclusive of Al and from 0.1% to 5% inclusive of Mn and has a structure in which particles of a compound containing Al and Mn are dispersed. In this magnesium alloy, the average diameter of the particles of the compound is from 0.3 μm to 1 μm inclusive, and the area ratio of the particles of the compound is from 3.5% to 25% inclusive.

[0019] The average diameter of the particles of the compound is measured using an image observed under an optical microscope.

[0020] The area ratio of the particles of the compound is measured by a compositional mapping of a cross section of the magnesium alloy by an FE-EPMA at an electron gun acceleration voltage of 5 kV or 15 kV. The details of the measurement method will be described later.

[0021] The above magnesium alloy contains Al and Mn in amounts within the specific ranges and is therefore excellent in strength and also excellent in corrosion resistance. Particularly, in the magnesium alloy, although the particles of the compound containing Al and Mn are present in a certain amount within the specific range, the particles are fine. Therefore, even when the magnesium alloy receives an impact of, for example, dropping or is subjected to plastic forming such as rolling or press forming, the particles are unlikely to serve as starting points of cracking etc., so that the magnesium alloy is excellent in impact resistance, plastic formability, and mechanical properties such as strength proof stress, and elongation. The magnesium alloy has a dispersion strengthened structure in which the above-described fine particles of the compound are dispersed. This dispersion strengthened structure increases the proof stress, and therefore the magnesium alloy is resistant to denting and is excellent in impact resistance. The magnesium alloy having the above-described specific composition and structure can be produced by, for example, a specific casting step described later and is therefore also excellent in productivity.

[0022]

(2) In one exemplary form of the magnesium alloy, the maximum diameter of the particles of the compound is less than 2.5 μm.

In the above-described form, although a certain amount of the particles of the compound containing Al and Mn is present, these particles are sufficiently small. Therefore, in the above-described form, cracking originating from coarse compound particles is unlikely to occur, and the magnesium alloy is more excellent in impact resistance, mechanical properties such as strength, proof stress, and elongation, and plastic formability.

(3) In one exemplary form of the magnesium alloy, the average crystal grain size of the magnesium alloy is 10 μm or less.

In the above form, the crystals themselves are fine, and therefore cracking originating from coarse crystal grains is unlikely to occur, so that the magnesium alloy is more excellent in impact resistance, mechanical properties such as strength, proof stress, and elongation, and plastic formability.

(4) A magnesium alloy sheet according to one aspect of the present invention is formed from the magnesium alloy according to any one of (1) to (3) above.

This magnesium alloy sheet, which is an example of the magnesium alloy, is composed of the magnesium alloy having the above-described specific structure and is therefore excellent in impact resistance, mechanical properties such as strength, proof stress, and elongation, and plastic formability such as press formability and also excellent in productivity. The above magnesium alloy sheet can be preferably used for raw materials for secondary-processed materials (e.g., a magnesium alloy structural member described later) subjected to plastic forming such as press forming.

(5) A magnesium alloy structural member according to one aspect of the present invention is formed from the magnesium alloy according to any one of (1) to (3) above. The magnesium alloy structural member has, in at least a part thereof, a plastically formed portion subjected to plastic forming.

This magnesium alloy structural member, which is an example of the magnesium alloy, is composed of the magnesium alloy having the above-described specific structure and is therefore excellent in impact resistance and mechanical properties such as strength, proof stress, and elongation and also excellent in productivity. In the magnesium alloy structural member, cracking is unlikely to occur during plastic forming such as press forming. Therefore, the magnesium alloy structural member is excellent in productivity.

(6) A magnesium alloy production method according to one aspect of the present invention comprises the step of

subjecting a melt of a magnesium alloy to continuous casting, the magnesium alloy containing, in mass%, from 1% to 12% inclusive of A1 and from 0.1% to 5% inclusive of Mn. In this production method, the temperature of the melt immediately before the melt comes into contact with a mold is from 630°C to 690°C inclusive, and the cooling rate of the melt is 560°C/second or higher.

[0023] In the above magnesium alloy production method, the melt of the magnesium alloy containing Al and Mn in amounts within the specific ranges is used, and this allows the magnesium alloy produced to have excellent strength and corrosion resistance. Particularly, in the above magnesium alloy production method, the temperature of the melt is set to be lower than the temperature conventionally used. At the set temperature, compounds containing Al and Mn (Al-Mn crystallized phases) are easily formed. However, the cooling rate is set to be very high, so that the time during which the material is held at around 630°C in the course of solidification can be shortened. Therefore, with the above magnesium alloy production method, only an appropriate amount of the Al-Mn crystallized phases can be formed in the alloy. In addition, the growth of the particles of the Al-Mn crystallized phases is suppressed, so that relatively fine particles of the Al-Mn crystallized phases, typically particles of the Al-Mn crystallized phases having an average diameter of 1 μm or less, are present. With the above magnesium alloy production method, such fine particles of the Al-Mn crystallized phases can be uniformly dispersed.

[0024] If, although the temperature of the melt is high, the cooling rate is low, the particles of the Al-Mn crystallized phases grow. In this case, for example, a structure in which coarse particles having a maximum diameter of 2.5 μm or more are unevenly distributed may be obtained. These coarse particles can serve as starting points of cracking etc. Since Al and Mn are contained in the coarse particles, the amounts of Al and Mn necessary for fine particles may not remain, so that the amount of the fine particles present may not be sufficient. In this case, the dispersion strengthening effect of the fine Al-Mn crystallized phases may not be obtained sufficiently. Therefore, in a magnesium alloy in which coarse Al-Mn crystallized phases are present locally, impact resistance, mechanical properties, and plastic formability may deteriorate. However, with the above magnesium alloy production method, the magnesium alloy produced can be excellent in impact resistance and mechanical properties such as strength and proof stress because of dispersion strengthening by the particles of the Al-Mn crystallized phases that are generally harder than the magnesium alloy serving as the matrix phase. In addition, with the above magnesium alloy production method, the particles of the Al-Mn crystallized phases are fine, and these fine particles are unlikely to serve as starting points of cracking etc. Therefore, the magnesium alloy produced can also be excellent in toughness such as elongation, impact resistance, and plastic formability.

[0025] In the above magnesium alloy production method, since the temperature of the melt is relatively low, the following can be achieved. (α') The oxidation of the melt can be easily suppressed, so that a reduction in yield due to oxide can be reduced. (β') Workability is excellent. (γ') The energy required to maintain the temperature of the melt can be reduced. (δ') Thermal degradation of the production facility can be reduced. In addition, in the above magnesium alloy production method, since continuous casting is performed, the magnesium alloy can be mass-produced. Since the cooling rate is high, a fine crystalline structure can be easily obtained. Therefore, a magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability can be easily produced. In view of the above, with the above magnesium alloy production method, a magnesium alloy excellent in impact resistance, mechanical properties, and plastic formability can be produced with high productivity.

[Details of embodiment of the present invention]

[0026] A magnesium alloy, a magnesium alloy sheet, a magnesium alloy structural member, and a magnesium alloy production method according to an embodiment of the present invention will be described one by one. The unit of the content of each element is percent by mass.

(Magnesium alloy, magnesium alloy sheet, and magnesium alloy structural member)

- Composition

[0027] One feature of the magnesium alloy in the embodiment is that the magnesium alloy has a composition containing at least both Al and Mn as additive elements. The magnesium alloy may contain, in addition to the composition containing A1 and Mn, a second additive element described later, so long as a specific amount of compounds containing Al and Mn (Al-Mn crystallized phases) having a specific size can be formed in the production process. In any of these compositions, the balance is Mg and inevitable impurities, and the content of Mg is more than 50%.

[0028] The content of Al is from 1% to 12% inclusive. When Al is contained within the above range, excellent mechanical properties such as strength and excellent corrosion resistance, in particular, are obtained. The larger the content of Al within the above range, the higher the strength and the corrosion resistance. Therefore, the content of Al may be 3% or more, 5% or more, 5.5% or more, and 7% or more. A magnesium alloy containing Al in an amount of from 8.3% to 9.5% inclusive, e.g., an ASTM standard AZ91 alloy, has mechanical properties and corrosion resistance superior to those of a magnesium alloy containing Al in an amount of about 3%, e.g., an ASTM standard AZ31 alloy. The lower the content of Al within the above range, the more easily plastic forming such as bending can be performed. Therefore, the content of Al may be 7% or less and particularly 4% or less. The content of Al that provides a good balance between strength and workability may be from 5.5% to 12% inclusive. Part of Al in the alloy is present as compounds such as intermetallic compounds typified by compounds containing Al and Mn and compounds containing Al and Mg, and the other part is dissolved in Mg to form a solid solution.

[0029] The content of Mn is from 0.1% to 5% inclusive. When Mn is contained within the above range, excellent corrosion resistance is obtained. The larger the content of Mn within the above range, the higher the corrosion resistance. Therefore, the content of Mn may be 0.15% or more. The larger the content of Mn, the more easily the compounds containing Al and Mn are formed and grow. In this case, the amount of solute Al tends to decrease, and coarse compound particles tend to be present. Therefore, the content of Mn may be 2% or less, 1.5% or less, and particularly 1% or less. A Mn content of from 0.2% to 0.5% inclusive is expected to effectively suppress excessive formation and growth of the above compounds.

[0030] The second additive element may be at least one element selected from Zn (zinc), Ca (calcium), Si (silicon), Be (beryllium), Sr (strontium), Y(yttrium), Ag (silver), Sn (tin), Zr (zirconium), Ce (cerium), Au (gold), and rare-earth elements (excluding Y and Ce). The specific content of Zn may be from 0.2% to 7.0% inclusive, and the specific content of Ca may be from 0.2% to 6.0% inclusive. The specific content of Si may be from 0.2% to 1.0% inclusive, and the specific content of Be may be from 0.0001% to 0.002% inclusive. The specific content of Sr may be from 0.2% to 7.0% inclusive, and the specific content of Y may be from 1.0% to 6.0% inclusive. The specific content of Ag may be from 0.5% to 3.0% inclusive, and the specific content of Sn may be from 0.01% to 2.0% inclusive. The specific content of Zr may be from 0.1% to 1.0% inclusive, and the specific content of Ce may be from 0.05% to 1.0% inclusive. The specific contents of rare-earth elements (excluding Y and Ce) may be from 1.0% to 3.5% inclusive.

[0031] When the second additive element is contained, only one of the listed elements may be contained, or a combination of two or more elements may be contained. The second additive element contained can provide the following effects: various excellent properties including mechanical properties such as strength and elongation (e.g., Zn, Zr, etc.), high-temperature strength and creep resistance (e.g., Si, rare-earth elements, Ag, etc.), and flame resistance (e.g., Ca etc.); a reduction in crystal size; and suppression of hot cracking (e.g., Zr etc.). Specific production conditions described later may be used to produce a magnesium alloy having a composition including Al and Mn in amounts within the above specific ranges and further including the second additive element. Also in this magnesium alloy, the compounds containing Al and Mn and having a specific size are contained in a specific amount, and the particles of these compounds are uniformly distributed.

[0032] More specific examples of the composition of the magnesium alloy containing Al and Mn include the following.

- ASTM standard AM-based alloys (AM60 alloy, AM100 alloy, etc.)
- ASTM standard AZ-based alloys (AZ61 alloy, AZ80 alloy, AZ81 alloy, AZ91 alloy, etc.)

[0033] The AZ-based alloys contain, in addition to Al and Mn, from 0.2% to 1.5% inclusive of Zn as the second additive element. As the Al content in the AZ-based alloys increases, the mechanical properties such as strength and proof stress and corrosion resistance tend to be improved. As the Al content decreases, the plastic formability tends to be improved.

- Structure

[0034] One feature of the magnesium alloy in the embodiment is that the magnesium alloy has a structure in which relatively fine particles formed of compounds containing Al and Mn are uniformly dispersed. The compounds containing Al and Mn are crystallized phases that are formed mainly during casting. These crystallized phases have high hardness. When the crystallized phases are once formed, it is difficult to change their size and content during a production process after the casting. Therefore, in the magnesium alloy in the embodiment, specific casting conditions described later, for example, are used to control the size and content of the above-described compounds (crystallized phases).

- Compositions of compounds

[0035] Examples of the compounds containing Al and Mn include intermetallic compounds containing only Al and Mn and intermetallic compounds containing iron (Fe) etc. in addition to Al and Mn. Fe contained in the latter intermetallic compounds is an inevitable impurity. The compositions of these compounds can be examined by component analysis using energy dispersive X-ray analysis (EDX) or Auger electron spectroscopy (AES).

- Size of compounds

[0036] The compounds containing Al and Mn are present as particles in the matrix of the magnesium alloy in the embodiment. The average diameter of the particles of the compounds is from 0.3 μm to 1 μm inclusive. When the average particle diameter is within the above range, the particles of the compounds can well function as a dispersion strengthening material for the structure and are less likely to serve as starting points of cracking, so that the magnesium alloy is excellent in impact resistance, mechanical properties, and plastic formability. The average particle diameter can be from 0.3 μm to 0.9 μm inclusive and particularly from 0.35 μm to 0.8 μm inclusive.

[0037] Preferably, the maximum diameter of the compounds containing Al and Mn is less than 2.5 μm. When coarse particles of 2.5 μm or more are not present, cracking originating from such coarse particles is unlikely to occur, and deterioration of impact resistance, mechanical properties, and plastic formability caused by such coarse particles can be suppressed. In addition, a reduction in the amount of fine particles due to the presence of these coarse particles can be suppressed, so that an appropriate amount of fine particles can be contained. Therefore, the magnesium alloy can be excellent in impact resistance, mechanical properties, and plastic formability. The smaller the compounds, the smaller the number of coarse particles serving as the starting points of cracking, and the more easily a structure containing an appropriate amount of fine particles is obtained. Therefore, the maximum diameter is preferably 2 μm or less, more preferably 1.5 μm or less, still more preferably 1.2 μm or less, and yet more preferably 1 μm or less. When the average particle diameter of the above compounds is within the above range and the maximum diameter of the above compounds is less than 2.5 μm and preferably 2 μm or less, the variations in size of the above compounds are small, and the size is uniform. Therefore, in this form, variations in characteristics due to the variations in size of the above compounds can also be suppressed, and good characteristics can be achieved.

- Content of compounds

[0038] The content of the compounds containing Al and Mn is determined by the area ratio of the compounds in a cross section of the magnesium alloy, and the area ratio is from 3.5% to 25% inclusive. When the area ratio is 3.5% or more, a sufficient amount of the above compounds is present in the magnesium alloy, and the dispersion strengthening effect of the particles of the compounds can be preferably obtained. When the area ratio is 25% or less, an appropriate amount of the above compounds is present, and the embrittlement of the alloy due to the presence of an excessive amount of the above compounds, a reduction in corrosion resistance due to a reduction in the amount of solute Al, etc. are suppressed, so that the magnesium alloy is excellent in impact resistance, mechanical properties, and plastic formability.

[0039] The area ratio is measured as follows. A cross section of the magnesium alloy is taken, and an observation field described below (e.g., a square region of 195 μm × 195 μm) is selected in the cross section. A compositional mapping by FE-EPMA is performed on the observation field to determine the distribution of the concentration of Mn. Assume that substantially all the Mn in the observation field is present as the compounds containing Al and Mn. Then the area ratio of Mn in the observation field is regarded as the area ratio of the compounds containing Al and Mn. Specifically, the distribution of the Mn concentration determined by the compositional mapping is used to determine the area ratio of the above compounds. A specific computation method will be described later.

[0040] A region of the magnesium alloy that extends inwardly from its surface to a depth of 30% of the thickness of the magnesium alloy is referred to as a surface layer region, and the above-described observation field is selected in this surface layer region. The reason that the observation field is selected in the surface layer region is that a region that undergoes cracking and directly receives an impact of, for example, dropping may generally be the surface layer region.

[0041] The distribution of the Mn concentration varies depending on the acceleration voltage of an electron gun used in the FE-EPMA. As the acceleration voltage increases, the amount of information obtained tends to increase, and the concentration (level) of Mn tends to increase. Specifically, the value of the area ratio may vary depending on the magnitude of the acceleration voltage. To measure the area ratio, the acceleration voltage of the electron gun is 15 kV or less.

[0042] For example, the area ratio when the compositional mapping by the FE-EPMA is performed on the observation field in the cross section using an electron gun acceleration voltage of 15 kV is 9.5% or more, from 10% to 25% inclusive, and particularly from 15% to 24% inclusive.

[0043] For example, the area ratio when the compositional mapping by the FE-EPMA is performed on the observation field in the cross section using an electron gun acceleration voltage of 5 kV is from 3.5% to 15% inclusive, from 4.0% to 12% inclusive, and particularly from 5.0% to 10% inclusive.

- Crystal grain size

[0044] In one exemplary form of the magnesium alloy in the embodiment, the magnesium alloy has a fine crystalline structure. One example of such a structure is a structure in which the average crystal grain size satisfies 10 μm or less.

When the average crystal grain size is 10 μm or less, substantially no coarse crystal grains are present, and the occurrence of cracking due to coarse crystal grains can be reduced. Therefore, in this form, the magnesium alloy is more excellent in impact resistance, mechanical properties such as strength and elongation, and plastic formability. The smaller the crystal grains, the more effectively the occurrence of cracking due to coarse crystal grains can be reduced. The average crystal grain size may be, for example, 6 μm or less and particularly 4 μm or less. The lower limit of the average crystal grain size may be, for example, 2 μm and particularly 1 μm. To reduce the crystal grain size, it is effective to perform plastic forming such as rolling after casting. Representative examples of the magnesium alloy having a fine crystalline structure include rolled sheets and press-formed sheets obtained by subjecting the rolled sheets to press forming. It is expected that the crystal grain size can be further reduced easily by increasing the cooling rate in the casting step (560°C/second or higher and particularly 600°C/second or higher) or adding the second additive element described above.

- Forms classified by production process

[0045] Specific forms of the magnesium alloy in the embodiment are classified by their production process as follows. (1) Cast material. (2) Primary-processed material (such as a rolled material) prepared by subjecting the cast material to plastic forming (primary processing) such as rolling. (3) Treated material prepared by subjecting the primary-processed material to various types of treatment such as polishing, leveling, heat treatment performed for the purpose of, for example, removal of strain, anticorrosive treatment (chemical conversion treatment, anodic oxidation treatment), treatment for decoration purposes (cutting such as diamond cut finishing and hairline finishing, etching, shot blasting, etc.), and coating treatment. (4) Secondary-processed material (a magnesium alloy structural member in the embodiment) prepared by subjecting the primary-processed material or the above treated material to plastic forming (secondary processing) such as press forming. (5) Surface-treated material (a magnesium alloy structural member in the embodiment) prepared by subjecting the secondary-processed material to surface treatment such as anticorrosive treatment, coating, or processing for decoration. In the primary-processed material such as the rolled material and the above treated material, their average crystal grain size is smaller than that of the cast material as described above, and cracking etc. are less likely to occur. Therefore, they can be used as raw materials for secondary-processed materials such as press-formed materials. Typically, the entire portion of the primary-processed material is subjected to plastic forming and is therefore a plastically formed portion. The secondary-processed material may be in such a form that only part of the raw material is subjected to plastic forming to form a plastically formed portion (e.g., a press-formed material having a bent portion) or may be in such a form that the entire portion of the raw material is subjected to plastic forming (e.g., a processed material bent into a cylindrical shape).

- Shape

[0046] Specific examples of the shape of the magnesium alloy in the embodiment include a sheet having first and second surfaces parallel to each other (a magnesium alloy sheet in the embodiment). The first and second surfaces are typically flat surfaces but may be subjected to, for example, bending to form bent surfaces. The planar shape of the sheet is typically rectangular, but the sheet may be punched into a circular shape or any other shape. The sheet may have any of the following forms classified by their production process described above: (1) a cast material, (2) a primary-processed material (such as a rolled sheet), (3) a treated material, (4) a secondary-processed material, and (5) a surface-treated material. Specific examples of the shape of the secondary-processed material include a member including a bottom portion and side wall portions extending from the bottom portion and having a rectangular U-shaped cross section (a member having a sheet portion).

- Size

[0047] When the magnesium alloy in the embodiment is in the form of a sheet (a magnesium alloy sheet in the embodiment) or a member prepared by subjecting at least part of the sheet to plastic forming such as press forming (a magnesium alloy structural member in the embodiment), the thickness of the sheet may be 5 mm or less. The thickness of the sheet is the average distance between the first and second surfaces. When the sheet has been subjected to plastic forming such as rolling, i.e., is a primary-processed material or a secondary-processed material, the thickness can be easily made uniform over the entire sheet and can be further reduced easily. In one exemplary form, the thickness may be about 3 mm or less and particularly 2.5 mm or less. The larger the thickness of the sheet, the higher the strength and stiffness. When the thickness of the sheet is small (preferably 2 mm or less, more preferably 1.5 mm or less, and still more preferably 1.2 mm or less), a thin and lightweight primary-processed material and secondary-processed material can be formed. The lower limit of the thickness of the sheet may be 0.1 mm or more and particularly 0.3 mm or more. The thickness of the final sheet may be selected by controlling the casting conditions, the rolling conditions, etc. according to its desired application purpose. In forms other than the forms in which the thickness is uniform over the entire sheet and the entire member, portions with different thicknesses may be present (e.g., a form in which a through hole is provided and a form in which a groove or a protrusion is provided).

- Characteristics

[0048] The magnesium alloy in the embodiment is excellent in mechanical properties such as strength, proof stress, and elongation. In one exemplary form of the magnesium alloy in the embodiment, at least one of a tensile strength (room temperature) of 270 MPa or more, a 0.2% proof stress (room temperature) of 200 MPa or more, and a rupture elongation (room temperature) of 5% or more is satisfied. Preferably, all the three are satisfied. Examples of such a form include the magnesium alloy subjected to the above-described plastic forming such as rolling, i.e., the primary-processed material and the secondary-processed material. When Al is contained in an amount of 5% or more or plastic forming such as rolling is performed, at least one of a tensile strength of from 280 MPa to 450 MPa inclusive, a 0.2% proof stress of from 230 MPa to 350 MPa inclusive, and a rupture elongation of from 5% to 15% inclusive can be satisfied, and preferably all the three can be satisfied. However, this depends on the composition, the production process, etc.

[0049] The magnesium alloy in the embodiment is less likely to be dented when the alloy receives an impact of, for example, dropping. For example, when a shock resistance test described later is performed, the amount of dent is small and is less than 0.63 mm. When the magnesium alloy in the embodiment has been subjected to the above-described plastic forming such as rolling, i.e., is a primary-processed material or a secondary-processed material, the amount of dent is further small and is 0.6 mm or less and particularly 0.55 mm or less.

(Magnesium alloy production method)

[0050] One feature of the magnesium alloy production method in the embodiment is that the method includes a specific casting step in order to form a structure in which compounds having specific compositions, i.e., compounds containing Al and Mn, are contained in a specific amount and have a specific size. Specifically, this casting step includes the following three conditions: (1) Continuous casting is performed. (2) The temperature of the melt is set to be relatively low. (3) The cooling rate of the melt is set to be very high. The casting step will next be described in detail, and then steps after the casting will be described.

- Casting step

- Continuous casting

[0051] In the magnesium alloy production method in the embodiment, a melt of a magnesium alloy having a specific composition containing Al and Mn within the specific ranges described above is prepared, and then continuous casting is performed. In the continuous casting, rapid solidification can be performed. Therefore, the amount of oxide and the amount of segregation can be reduced, and the formation of coarse crystallized phases can be easily reduced. In addition, the size of the compounds containing Al and Mn can be easily controlled to the above-described specific value. Specific examples of the continuous casting process include a twin-roll process. The twin-roll process is suitable for production of a cast sheet. In the twin-roll process, the cooling rate can be increased by reducing the thickness of the cast sheet (to preferably 5 mm or less), reducing the temperature of the rolls (to preferably 100°C or lower), changing the material of the rolls, etc.

- Temperature of melt

[0052] The temperature of the melt before it comes into contact with a mold is from 630°C to 690°C inclusive. The reason that the lower limit is defined as above is that, when the temperature of the melt is lower than 630°C, the compounds containing Al and Mn are very easily formed. The reason that the upper limit is defined as above is that, when the temperature is higher than 690°C, productivity becomes low because the temperature of the melt is excessively high. By setting the temperature of the melt within the above range, the compounds containing Al and Mn can be preferably formed during the solidification process and contained in an appropriate amount (the specific amount described above). To form the above compounds sufficiently, it is preferable that the temperature of the melt is as low as possible. The temperature of the melt is preferably 685°C or lower, more preferably 680°C or lower, and still more preferably 675°C or lower. When the temperature of the melt is 635°C or higher, 640°C or higher, and particularly 645°C or higher, excessive formation and coarsening of the above compounds can be easily suppressed, and the amount and size of the above compounds can be easily controlled. Therefore, it is expected that the productivity can be improved. As the content of A1 decreases, the melting temperature tends to increase. The temperature of the melt is controlled within the above range according to the composition.

[0053] Before the melt comes into contact with the mold, the melt is held in facilities such as a melting furnace, a conveying launder, and a holding furnace. When the temperature of the melt in these facilities for holding the melt is set to be uniform, i.e., to a temperature selected within the range of from 630°C to 690°C inclusive, the temperature can be easily controlled. Since this temperature range is relatively lower than the conventional range, thermal damage to the facilities can be easily reduced, and the service life of the facilities can be extended. From this point of view, it is expected to improve the productivity and reduce the cost.

- Cooling rate

[0054] The above melt having a relatively low temperature is rapidly cooled at a cooling rate of 560°C/second or higher. In this rapid cooling, retention time at around 630°C that is within a temperature range in which the compounds containing Al and Mn are easily formed in the solidification process is sufficiently short. In this case, excessive formation and coarsening of the above compounds can be effectively suppressed, and a structure in which the above compounds are present in a certain amount and are relatively fine can be preferably formed. The higher the cooling rate, the more preferable. The cooling rate may be 600°C/second or higher, 620°C/second or higher, and particularly 650°C/second or higher. The cast material obtained by the above-described rapid solidification has a dispersion strengthened structure in which the above compounds having the above-described specific size are uniformly dispersed in at least the surface layer region of the cast material. In this structure, the crystals are also fine.

[0055] The cooling rate is computed using a DAS (dendrite arm spacing). Let α and β be constants based on the composition of the magnesium alloy, d (μm) be the DAS, and V (°C/second) be the cooling rate. Then the following relation (1) can be used:

$$d = \alpha \times V^{-\beta}. \quad \text{relation (1)}$$

[0056] For example, in an ASTM standard AZ-based alloy, α in relation (1) above is 35.5, and $\beta = 0.31$. The DAS is denoted by d_{AZ}, and the cooling rate V_{AZ} is represented as follows:

$$d_{AZ} = 35.5 \times V_{AZ}^{-0.31}.$$

[0057] Test pieces with different compositions and sizes (thicknesses, widths, etc.) are used to determine the relation between the DAS and the cooling rate in advance, and correlation data is produced. Good workability is obtained when the cooling conditions are controlled using this correlation data such that a desired cooling rate is achieved.

[0058] Examples of the method for achieving a cooling rate of 560°C/second or higher include the following. (1) The surface temperature of the mold is reduced (e.g., to 100°C or lower and particularly 80°C or lower). For example, a forced cooled mold such as a water-cooled mold is used. In this case, the surface temperature of the mold can be maintained low. (2) The size of the cast material is reduced. For example, when the cast material is a cast sheet, its thickness is 5 mm or less, 4.5 mm or less, and particularly 4 mm or less. (3) A mold formed of a material having high cooling ability is used. For example, when a mold formed of a material with high thermal conductivity is used, the cooling rate can be increased because of the high heat radiation performance of the mold.

[0059] Preferably, the casting step (including the cooling step) is performed in an inert gas atmosphere in order to prevent, for example, oxidation of the magnesium alloy.

- Steps after casting

- Rolling step

[0060] When the magnesium alloy in the embodiment is formed into a rolled material (typically a rolled sheet), the above-described cast material (typically a cast sheet) is subjected to at least one rolling pass. Specifically, one exemplary form of the magnesium alloy production method in the embodiment includes the casting step described above and the step of subjecting the cast material obtained by the continuous casting to at least one rolling pass (this step may be hereinafter referred to as a rolling step). Preferably, the at least one rolling pass is warm rolling at a rolling temperature of from 200°C to 400°C inclusive. The number of passes in the rolling step, a rolling reduction per pass, the total rolling reduction, etc. may be appropriately selected such that a rolled sheet with a desired thickness is obtained. By subjecting the cast material to rolling, a rolled structure (typically a recrystallized structure) can be obtained instead of a cast structure. As a result of the rolling, the following effects are expected. (1) A fine structure having an average crystal grain size of 20 μm or less and particularly 10 μm or less is easily obtained. (2) The occurrence of internal defects and surface defects such as segregation, shrinkage cavities, and pores during casing can be reduced, and a good surface texture can be obtained. (3) The formation of a fine recrystallized structure easily allows the strength and corrosion resistance to be further improved. The rolled sheet obtained through the above-described rolling step has a dispersion strengthened structure in which at least its surface layer region has a finer crystalline structure and the compounds containing Al and Mn having the above-described specific size are uniformly dispersed. The production method may further include, after the rolling step, the step of performing at least one additional process such as the above-described polishing, leveling, anticorrosive treatment, coating, processing for decoration purposes, and heat treatment for the purpose of, for example, removal of strain.

- Secondary processing step

[0061] When the magnesium alloy in the embodiment is processed into a plastically formed member, at least part of the above rolled sheet (which may have been subjected to an additional process such as polishing or leveling) is subjected to plastic forming. Specifically, one exemplary form of the magnesium alloy production method in the embodiment includes the above-described casting step, the above-described rolling step, and the step of subjecting at least part of the raw material subjected to the rolling step to plastic forming (secondary processing).

[0062] Specific examples of the plastic forming (secondary processing) include press forming (deep drawing, punching, upsetting, etc.), forging, and bending. Preferably, the plastic forming is performed as warm working at a processing temperature of from 200°C to 280°C inclusive. This is because since the plastic formability of the raw material (typically the above rolled sheet) is improved, the plastic forming (secondary processing) can be performed with high precision. With the warm working, the amount of a coarse recrystallized structure in the structure of the raw material can be reduced, so that the deterioration of the mechanical properties and corrosion resistance can be reduced. The plastic forming (secondary processing) may be performed on only part of the raw material or on the entire raw material. The production method may further include, after the secondary processing step, the step of performing at least one additional process such as the above-described polishing, anticorrosive treatment, coating, processing for decoration purposes, and heat treatment for the purpose of, for example, removal of strain.

[0063] The magnesium alloy in the embodiment and its production method will be described more specifically by way of a Test Example.

[Test Example 1]

[0064] Magnesium alloys having different compositions shown in Table 1 were used to produce magnesium alloy sheets under various conditions, and these magnesium alloy sheets were subjected to press forming to produce press-formed materials. For each of the magnesium alloy sheets obtained, structural observation, a tensile test (ordinary temperature), an impact resistance test (ordinary temperature), a pass/fail check of press formability, and a pass/fail determination of productivity were performed.

[0065] The content of each element is represented by percent by mass (mass%).

- AZ91 shown in Table 1 is a magnesium alloy containing Al, Mn, and Zn in amounts corresponding to those in an ASTM standard AZ91 alloy. The alloy contains 9.1% of Al, 0.16% of Mn, and 0.72% of Zn.
- AZX911 shown in Table 1 is a magnesium alloy containing Al, Mn, and Zn in amounts corresponding to those in the ASTM standard AZ91 alloy and further containing Ca. The alloy contains 9.0% of Al, 0.16% ofMn, 0.74% of Zn, and 1.0% of Ca.
- AZ61 shown in Table 1 is a magnesium alloy containing Al, Mn, and Zn in amounts corresponding to those in an ASTM standard AZ61 alloy. The alloy contains 6.1% of Al, 0.22% of Mn, and 0.70% of Zn.
- AM60 shown in Table 1 is a magnesium alloy containing Al and Mn in amounts corresponding to those in an ASTM standard AM60 alloy. The alloy contains 6.2% of Al and 0.20% of Mn.

[0066] In this Example, cast sheets (magnesium alloy sheets), rolled sheets (magnesium alloy sheets), and press-formed materials (magnesium alloy structural members) were produced using a production process including twin-roll continuous casting, rolling, and press forming in this order. Specifically, an ingot of a magnesium alloy having one of the compositions shown in Table 1 was melted in an inert atmosphere to prepare a melt of the alloy. The temperature of the melt immediately before it comes into contact with the mold (hereinafter referred to as molten alloy temperature, °C) is shown in Table 1. In this case, a facility including a melting furnace, a holding furnace for holding the melt, and a conveying unit for conveying the melt from the holding furnace to the mold (a pair of rolls) was used, and the temperature of the melt in the conveying unit is used as the "molten alloy temperature." The temperature of the melt in the conveying unit is the temperature setting of the facility. The melt was brought into contact with the mold (rolls) and thereby solidified to produce a cast sheet having a thickness of 5.0 mm.

[0067] The cooling rate (°C/second) in the casting step is shown in Table 1. In samples Nos. 1-1 to 1-5, 1-101, and 1-201, the cooling rate was changed by controlling the temperature of the rolls, the peripheral speed of the rolls, the rate of casting, etc. In samples Nos. 1-1 to 1-5, and 1-101, a water-cooled mold was used, and the casting was performed while the rolls were cooled such that the roll temperature was 100°C or lower.

[0068] Each of the cast sheets obtained was subjected to a plurality of warm rolling passes to produce a rolled sheet with a thickness of 0.7 mm. The conditions of the warm rolling were a rolling temperature of from 200°C to 400°C inclusive, a rolling reduction per pass of from 5% to 20% inclusive, and a total rolling reduction of 86%.

[0069] Each of the rolled sheets obtained was cut into a 200 mm x 30 mm piece, and the cut piece was used as a raw material for pressing. The raw material was subjected to press forming (square cup drawing) to produce a press-formed material having a rectangular U-shaped cross section and including a top portion and leg portions extending from the top portion. The press conditions were a heating temperature of 250°C, and a corner R connecting the top portion and a leg portion was 2 mm.

[0070] After the continuous casting, each of the cast sheets may be subjected to heat treatment (solution treatment) for homogenization of the structure or aging treatment, subjected to intermediate heat treatment during rolling, or subjected to final heat treatment after final rolling. The rolled sheet may be subjected to leveling to improve flatness or may be subjected to polishing to further smoothen the surface.

- Structural observation

[0071] Metallographic observation was performed on each of the rolled sheets of the obtained samples as follows. Each rolled sheet was cut along a plane parallel to its thickness direction to obtain a cross section (a vertical cross section). This cross section is a CP cross section prepared using a commercial cross section polisher (CP). In the CP cross section, a region extending in a thickness direction from the surface of the sheet to a depth of 30% of the thickness of the sheet was used as a surface layer region (0.7 mm x 0.3 = 0.21 mm in this case), and an observation field was arbitrarily selected in the surface layer region. An upper part of Figure 1 shows a secondary electron image obtained by SEM observation of the selected observation field in the rolled sheet of sample No. 1-1, and the lower part shows a binary image obtained by binarizing the secondary electron image. Figure 2 is a backscattered electron image obtained by SEM observation of the selected observation field.

[0072] As can be seen from the upper part of Figure 1, many small and large particles are dispersed in a fine crystalline structure. Specifically, relatively large particles shown in light grey (maximum length: about 0.1 μm to about 1 μm) and relatively small particles shown in white were found to be present. Component analysis was performed on these particles. The relatively large particles (light grey) were found to be a compound containing Al and Mg (a β phase, mainly precipitates), and particles (white) smaller than the β phase were found to be compounds containing Al and Mn (Al-Mn crystallized phases). To facilitate the clarification of the presence of the white particles, the contrast was changed as shown in the lower part of Figure 1. As can be seen, the white particles are uniformly dispersed in the crystalline structure. As also can be seen, a certain amount of the white particles is present, although the white particles are smaller than the β phase and the amount of the white particles is smaller than the amount of the β phase. This can also be seen from Figure 2. As can also be seen in the SEM backscattered electron image shown in Figure 2, light grey particles and white particles are present. A certain amount of the white particles is present, although the white particles are smaller than the light grey particles and the amount of the white particles is smaller than the amount of the light grey particles. It was therefore found that, in the rolled sheet of sample No. 1-1, a certain amount of the compounds containing Al and Mn (Al-Mn crystallized phases) was present although they were relatively small and their amount was relatively small. It was also found that these compounds were uniformly dispersed. The rolled sheets of samples Nos. 1-2 to 1-5 have the same structure as the rolled sheet of sample No. 1-1, i.e., have a fine crystalline structure in which the relatively small Al-Mn crystallized phases are present in a certain amount and are uniformly distributed.

[0073] In the rolled sheet of sample No. 1-101, the amount of the compounds containing Al and Mn (Al-Mn crystallized phases) was very small. In the rolled sheet of sample No. 1-201, although the amount of the compounds containing Al and Mn was very small, coarse particles were present.

[0074] For each of the rolled sheets of the samples, an image observed under an optical microscope was used to measure an average crystal grain size. The results are shown in Table 1. The average crystal grain size was measured according to "Steels-Micrographic determination of the apparent grain size, JIS G 0551 (2005), an intercept method using linear test lines." Straight lines parallel to the thickness direction of the rolled sheet were drawn in the image observed, and line segments intersecting crystal grains were used as grain sizes. The average crystal grain sizes of the rolled sheets of samples Nos. 1-1 to 1-5 were 10 μm or less. This shows that the crystal grains in each of the rolled sheets of samples Nos. 1-1 to 1-5 are fine.

[0075] For each of the rolled sheets of the samples obtained, the above-described white particles in the SEM image (the binary image converted from the secondary electron image) were extracted as the compounds containing Al and

Mn (Al-Mn crystallized phases), and the average diameter (μm) and the maximum diameter (μm) of the extracted particles of the Al-Mn crystallized phases were examined. The results are shown in Table 1. The diameters of the particles of the Al-Mn crystallized phases were determined as follows. The diameters of circles having the same areas as the extracted particles were determined. The average of the diameters of all the particles present in the observation field (a 195 μm × 195 μm square region selected in the above-described surface layer region) was used as the average particle diameter of the Al-Mn crystallized phases. The largest value among the diameters of all the particles was used as the maximum diameter of the Al-Mn crystallized phases.

[0076] For each of the rolled sheets of the samples obtained, a compositional mapping by FE-EPMA was produced in the observation field selected in the CP cross section to examine the distribution of the Mn concentration. The concentration of Mn was analyzed under two different conditions with different electron gun acceleration voltages. These conditions are shown below.

(1) The acceleration voltage of the electron gun: 15 kV, irradiation current: 100 nA, measurement time: 50 ms, measurement element: Mn (LiFH), measurement area: 195 μm × 195 μm square region
(2) The acceleration voltage of the electron gun: 5 kV, irradiation current: 100 nA, measurement time: 500 ms, measurement element: Mn (TAPH), measurement area: 24 μm × 24 μm square region

[0077] In conditions (2) with a smaller acceleration voltage, the measurement area was smaller than that in conditions (1). However, it had been checked that, even when the measurement area in conditions (2) was the same as that in conditions (1), no significant difference was found in the measurement results (the distribution of the Mn concentration).

[0078] Figure 3 shows an FE-EPMA compositional mapping of Mn in the rolled sheet of sample No. 1-1 under conditions (1) with an acceleration voltage of 15 kV. A color scale is shown on the right side of Figure 3. In this compositional mapping, the concentration of Mn is represented by a color shade changing from white, pink, red, orange, yellow, green, light blue, blue, to black. A color close to white means a high Mn concentration, and a color close to black means a low Mn concentration. In Figure 3, the level of Mn at a point with the highest Mn concentration is set to 135, and the level of Mn at a point with no Mn is set to 0. Then the concentration of Mn at each point is represented by a value relative to the level 135. The percentage of each level is represented as an area ratio (Area %). As shown in the compositional mapping in Figure 3, a large number of regions composed of red-to-blue particle-like clusters are present in a black background. By comparing the positons of the red-to-blue particle-like regions present in the compositional mapping in Figure 3 with the positions of the white particles present in the SEM image (backscattered electron image) in the same observation field (see Figure 2), the red-to-blue particle-like regions in the compositional mapping were found to be included in the compounds containing Al and Mn (Al-Mn crystallized phases). This may show that Mn in the rolled sheet of sample No. 1-1 is present as the Al-Mn crystallized phases. Therefore, in this case, all the Mn present is treated as compounds with Al.

[0079] Figure 4 is a graph of the frequency of the level of Mn (the number of Mn counts) and the cumulative frequency produced using the compositional mapping (15 kV) of Mn shown in Figure 3. In the graph in Figure 4, the horizontal axis represents the level of Mn (0 to 135, the level is shown up to 110 in Figure 4). The left vertical axis represents the frequency of the level of Mn, and the right vertical axis represents the cumulative frequency (%) of the level of Mn.

[0080] The cumulative frequency at a level of Mn is equivalent to the area ratio (Area %) at this level. The average S_{Level} of the levels of Mn was computed and found to be $S_{Level} = 10$, and the overall concentration of Mn was found to be very small. Therefore, when regions in which the level of Mn is about the average S_{Level} are treated as noise, Mn may be more suitably extracted. Specifically, the compounds containing Al and Mn (Al-Mn crystallized phases) may be more suitably extracted. The standard deviation σ_{Level} of the levels of Mn was determined. Then the average $S_{Level} + 3\sigma_{Level}$ was used as a threshold value, and regions in which the level of Mn was equal to or larger than the average $S_{Level} + 3\sigma_{Level}$ were treated as the Al-Mn crystallized phases. The cumulative frequency (%) in a portion in which the level was equal to or larger than the average $S_{Level} + S\sigma_{Level}$ (11.3 in this case) was treated as the area ratio (%, 15 kV) of the Al-Mn crystallized phases. The results are shown in Table 1.

[0081] A left part of Figure 5 shows an FE-EPMA compositional mapping of Mn in the rolled sheet of sample No. 1-1 when conditions (2) with an acceleration voltage of 5 kV were used, and the right part shows an SEM image (backscattered electron image) in the same observation field. Also in the compositional mapping in Figure 5, the concentration of Mn is represented by a color shade, as in Figure 3. In the compositional mapping in Figure 5, the level of Mn at a point with the highest Mn concentration is set to 55, and the level of Mn at a point with no Mn is set to 0. The percentage of each level is represented by an area ratio (Area %). In the compositional mapping in the left part of Figure 5, the irradiation energy of the electron gun is smaller than that of conditions (1), and the amount of information about Mn is smaller than that under conditions (1), so that the maximum level of Mn is small, i.e., 55. However, as shown in the left part of Figure 5, the color shade of Mn can be observed, and red-to-blue particle-like clusters are present, as in the compositional mapping in Figure 3. By comparing the positons of the red-to-blue particle-like regions present in the compositional mapping in the left part of Figure 5 with the positions of the white particles in the SEM image (backscattered electron image) in the right part of Figure 5, the red-to-blue particle-like regions in the compositional mapping were found to be the compounds containing Al and Mn (Al-Mn crystallized phases).

[0082] Figure 6 is a graph of the frequency of the level of Mn (the number of Mn counts) and the cumulative frequency produced using the compositional mapping (5 kV) of Mn shown the left part of Figure 5. In the graph in Figure 6, as in the graph in Figure 4, the horizontal axis represents the level of Mn (0 to 55, the level is shown up to 50 in Figure 6). The left vertical axis represents the frequency of the level of Mn, and the right vertical axis represents the cumulative frequency (%) of the level of Mn. Also in this case, the average S_{Level} of the levels of Mn and the standard deviation σ_{Level} were determined. Then the average $S_{Level} + 3\sigma_{Level}$ was used as a threshold value, and the cumulative frequency (%) in a portion in which the level was equal to or larger than the average $S_{Level} + 3\sigma_{Level}$ (12 in this case) was determined as the area ratio (%, 5 kV) of the compounds containing Al and Mn (Al-Mn crystallized phases). The results are shown in Table 1.

[0083] For each of the press-formed materials of samples Nos. 1-1 to 1-5, the metallographic structure of the top portion substantially free from bending etc. was observed in the same manner as in the rolled sheet. The top portion was found to have a fine crystalline structure as fine as that of the rolled sheet, and the compounds containing Al and Mn (Al-Mn crystallized phases) were dispersed in the structure. In the top portion, the average crystal grain size, the average diameter of the above compounds, their maximum diameter, and their area ratio were equivalent to those of the rolled sheet. Therefore, the top portion is considered to have substantially the same structure as that of the rolled sheet.

[0084] For each of the cast sheets of samples Nos. 1-1 to 1-5, the metallographic structure was observed in the same manner as in the rolled sheet. The cast sheet was found to have a fine crystalline structure although the crystal grains were larger than those in the rolled sheet. Also in the cast sheets of samples Nos. 1-1 to 1-5, at least their surface layer region was found to have a structure in which the compounds containing Al and Mn were uniformly dispersed. The average diameter of the above compounds, their maximum diameter, and their area ratios (15 kV and 5 kV) were examined and found to be equivalent to those of the rolled sheet. This shows that the above compounds present in the cast sheets are substantially maintained in the rolled sheets of samples Nos. 1-1 to 1-5.

- Tensile test (ordinary temperature, about 20°C)

[0085] JIS 13B plate-shaped test pieces (JIS Z 2201(1998)) were produced using the rolled sheets (thickness: 0.7 mm) of the samples obtained, and a tensile test (gage length GL = 50 mm) was performed according to a metallic material tensile test method in JIS Z 2241 (1998). The tensile strength (MPa), 0.2% proof stress (MPa), and rupture elongation (%) of each test piece were measured (the number of times of evaluation: n = 1 for all the cases). The results are shown in Table 2.

- Shock resistance test (room temperature, about 20°C)

[0086] Plate-shaped pieces of 30 mm x 30 mm were cut from the rolled sheets (thickness: 0.7 mm) of the samples obtained, and the cut plate-shaped pieces were used as test pieces. In this test, as shown in Figure 7, a support 20 having a circular hole 21 with a diameter d = 20 mm was prepared on a horizontal plane. The depth of the circular hole 21 was set such that a cylindrical rod 10 described layer could be inserted sufficiently into the circular hole 21. A test piece 1 was places so as to close the circular hole 21. While this state was maintained, the ceramic-made cylindrical rod 10 having a weight of 100 g and a forward end r = 5 mm was placed at a height of 200 mm from the test piece 1 such that the center axis of the cylindrical rod 10 was coaxial with the center axis of the circular hole 21. Then the cylindrical rod 10 was allowed to free-fall from the placement point (at a height of 200 mm) toward the test piece 1, and the amount of dent in the test piece 1 was measured. The amount of dent (mm) was measured as follows. A straight line connecting opposed sides of the test piece 1 was drawn, and the distance between this straight line and the most dented portion was measured using a point micrometer. The results are shown in Table 2.

- Formability

[0087] For each of the press-formed materials (materials subjected to square-cup drawing) of the samples obtained, the presence or absence of cracking in a rounded corner portion was visually checked. A press-formed material with no cracking was rated "Good," and a press-formed material with cracking was rated "Bad." The results are shown in Table 2.

- Productivity

[0088] When the temperature of the melt in the casting step was 690°C or lower, the productivity was rated "good."

[Table 1]

Sample No.	Composition	Casting conditions		Rolled sheet				
		Temperature ot melt (molten alloy temperature) °C	Cooling rate °C/sec	Average crystal grain size μm	Compound			
					Average particle diameter μm	Maximum diameter μm	Area ratio (15kV) %	Area ratio (5kV) %
1-1	AZ91	650	700	4.9	0.42	1.0	23	8.2
1-2	AZ91	670	560	5.1	0.35	0.8	19	6.1
1-3	AZ61	660	650	5.2	0.49	0.7	16	5.5
1-4	AM60	660	650	6.0	0.45	0.9	17	5.8
1-5	AZX911	650	700	5.0	0.55	1.1	20	6.9
1-101	AZ91	695	750	5.3	0.35	0.6	8	2.4
1-201	AZ91	700	545	5.5	1.2	2.6	9.4	3.2

[Table 2]

Sample No.	composition	Rolled sheet						
		Compound		Tensile strength MPa	0.2% Proof stress MPa	Rupture elongation %	Impact resistance Amount of dent mm	Formability
		Area ratio (15kV) %	Average particle diameter μm					
1-1	AZ91	23	0.42	343	260	11	0.35	Good
1-2	AZ91	19	0.35	345	262	10	0.36	Good
1-3	AZ61	16	0.49	320	241	12	0.48	Good
1-4	AM60	17	0.45	312	234	14	0.49	Good
1-5	AZX911	20	0.55	335	255	12	0.38	Good
1-101	AZ91	8	0.35	321	243	11	0.66	Good
1-201	AZ91	9.4	1.2	320	239	6	0.63	Bad

[0089] As shown in Table 1, in each of samples Nos. 1-1 to 1-5, the average diameter of the particles of the compounds containing Al and Mn was from 0.3 μm to 1 μm inclusive, and the area ratio of the particles of the compounds by FE-EPMA was from 3.5% to 25% inclusive. In samples Nos. 1-1 to 1-5, their strength, proof stress, elongation, and plastic formability were equivalent to those of sample No. 1-101 containing a very small amount of the above compounds. It was found that samples Nos. 1-1 to 1-5 had high strength and high toughness and were excellent in plastic formability irrespective of their composition. According to the above tests, the tensile strength of each of samples Nos. 1-1 to 1-5 was 300 MPa or more, their 0.2% proof stress was 230 MPa or more, and their rupture elongation was more than 6%. This shows that, even when these samples Nos. 1-1 to 1-5 are subjected to press forming such as square cup drawing, breakage and cracking are likely to occur. In samples Nos. 1-1 to 1-5, the area ratio of the particles of the compounds was larger than that in sample No. 1-101, and the amount of dent was 0.5 mm or less, so that the impact resistance was better than that of sample No. 1-101. One reason that samples Nos. 1-1 to 1-5 are excellent in impact resistance, mechanical properties, and plastic formability as described above may be as follows. Although a certain amount of the above compounds is present, the compounds are relatively fine. Therefore, 1. the dispersion strengthening effect is obtained preferably, and 2. the above compounds are unlikely to serve as the starting points of cracking etc.

[0090] The following was also found for samples Nos. 1-1 to 1-5.

[0091] The maximum diameter of the above compounds is 1.2 μm or less. This allows the occurrence of cracking etc.

originating from the above compounds to be effectively suppressed.

[0092] The crystals are also fine, and the average crystal grain size is 10 μm or less. This also allows the occurrence of cracking etc. originating from coarse crystal grains to be effectively suppressed. This may be the reason that excellent impact resistance, mechanical properties, and plastic formability are achieved.

[0093] Since the temperature of the melt during continuous casting is relatively low, thermal damage to the facility can be suppressed. Therefore, high productivity is achieved.

[0094] As can be seen from the above tests, the area ratio of the compounds containing Al and Mn in each of samples Nos. 1-1 to 1-5 was higher than that in each of samples Nos. 1-101 and 1-201, irrespective of whether the acceleration voltage of the electron gun for the analysis by the FE-EPMA was 5 kV or 15 kV. A sufficient amount of the compounds containing Al and Mn was found to be present.

[0095] In this test, when the acceleration voltage was 5 kV, the area ratio in samples Nos. 1-1 to 1-5 was 5% or more and was higher than that in samples Nos. 1-101 and 1-201. The area ratio in samples Nos. 1-101 and 1-201 was less than 3.5%.

[0096] In this test, when the acceleration voltage was 15 kV, the area ratio in samples Nos. 1-1 to 1-5 was 10% or more and was higher than that in samples Nos. 1-101 and 1-201. The area ratio in samples Nos. 1-101 and 1-201 was 9.4% or less.

[0097] It was found that a magnesium alloy excellent in impact resistance, mechanical properties, plastic formability, and also productivity can be produced by setting the temperature of the melt immediately before it comes into contact with the mold to be relatively low, i.e., from 630°C to 690°C inclusive, and then rapidly cooling the melt at a cooling rate of 560°C/second or higher, as described above. As can be seen from the above tests, even when the composition is changed, a magnesium alloy having impact resistance, mechanical properties, and plastic formability can be produced with high productivity by controlling the temperature of the melt and its cooling rate within the above ranges, so long as the compounds containing Al and Mn are contained in the above-described specific amount and have the specific average particle diameter.

[0098] In sample No. 1-201, although the temperature of the melt was very high, the cooling rate was very slow, i.e., less than 550°C/second. It was found that, in sample No. 1-201, although the amount of the compounds containing Al and Mn was smaller than that in sample No. 1-1, coarse particles (2.5 μm or more) were present. In sample No. 1-201, its impact resistance, mechanical properties, and plastic formability are worse than those of sample No. 1-1 having the same composition as sample No. 1-201. The reason for these results may be that the retention time in the temperature range of around 630°C in which the above compounds are easily formed and grow during solidification is long. As a result of growth of the particles the compounds, coarse particles are formed and serve as the starting points of cracking, and the dispersion strengthening effect by the fine compounds becomes insufficient. This may be the reason for the deterioration of the impact resistance, mechanical properties, and plastic formability deteriorate.

[0099] In sample No. 1-101, the temperature of the melt was high, and the cooling rate was also high. Therefore, the amount of the compounds containing Al and Mn was very small. In sample No. 1-101, the impact resistance, in particular, was worse than that of sample No. 1-1 having the same composition. This may be because the dispersion strengthening by the fine compounds was insufficient.

[0100] For each of the press-formed materials of samples Nos. 1-1 to 1-5, a test piece similar to that in the rolled sheet was produced from the top portion, and the same tensile test (room temperature) and the same shock resistance test (room temperature) as those for the rolled sheet were performed. The results were substantially the same as those for the rolled sheet. Therefore, the press-formed material was also excellent in impact resistance and mechanical properties. One of the reasons for this may be that at least part of the press-formed material substantially maintains the structure of the rolled sheet, i.e., the at least part of the press-formed material has a fine crystalline structure and the compounds containing Al and Mn having the specific size are uniformly dispersed in this structure.

[0101] The present invention is not limited to the above-described examples. The present invention is defined by the scope of the claims and is intended to include any modifications within the scope of the claims and meaning equivalent to the scope of the claims. For example, in the Test Example described above, the composition (the types of the additive elements and their contents), the shape and size (thickness, length, width, etc.) of the magnesium alloy sheet, the production conditions (the specifications of the mold, the temperature of the mold, the molten alloy temperature, the cooling rate, the thickness of the cast sheet, etc. in the casting conditions) may be appropriately changed.

Industrial Applicability

[0102] The magnesium alloy and magnesium alloy sheet of the present invention can be preferably used as raw materials for plastically formed members (magnesium alloy structural members) subjected to various types of plastic forming such as press forming, bending, and forging. Particularly, the magnesium alloy sheet can be preferably used as raw materials for members desirably having characteristics such as lightweight, small thickness, high strength, and vibration damping ability, and examples of such members include: exterior members such as housings and covers of various electronic-electric devices (personal computers (PCs), tablet PCs, cellular phones such as smartphones and folding cellular phones, digital cameras, etc.); structural members and constituent members of transportation apparatuses such as automobiles and aircrafts; bags; and various protective cases. The magnesium alloy and magnesium alloy structural member of the present invention can be preferably used for, for example, the above described exterior members such as housings, the structural members and constituent members of the transportation apparatuses, bags, and protective cases. The magnesium alloy production method of the present invention can be preferably used to produce magnesium alloys such as the above-described magnesium alloy sheet and the above-described magnesium alloy structural member.

Reference Signs List

[0103]

1 test piece, 10 cylindrical rod, 20 support, 21 circular hole

Claims

1. magnesium alloy comprising, in mass%, from 1% to 12% inclusive of Al and from 0.1% to 5% inclusive of Mn,
   wherein the magnesium alloy has a structure in which particles of a compound containing Al and Mn are dispersed,
   an average diameter of the particles of the compound is from 0.3 μm to 1 μm inclusive, and
   an area ratio of the particles of the compound is from 3.5% to 25% inclusive.

2. The magnesium alloy according to claim 1, wherein a maximum diameter of the particles of the compound is less than 2.5 μm.

3. The magnesium alloy according to claim 1 or 2, wherein an average crystal grain size of the magnesium alloy is 10 μm or less.

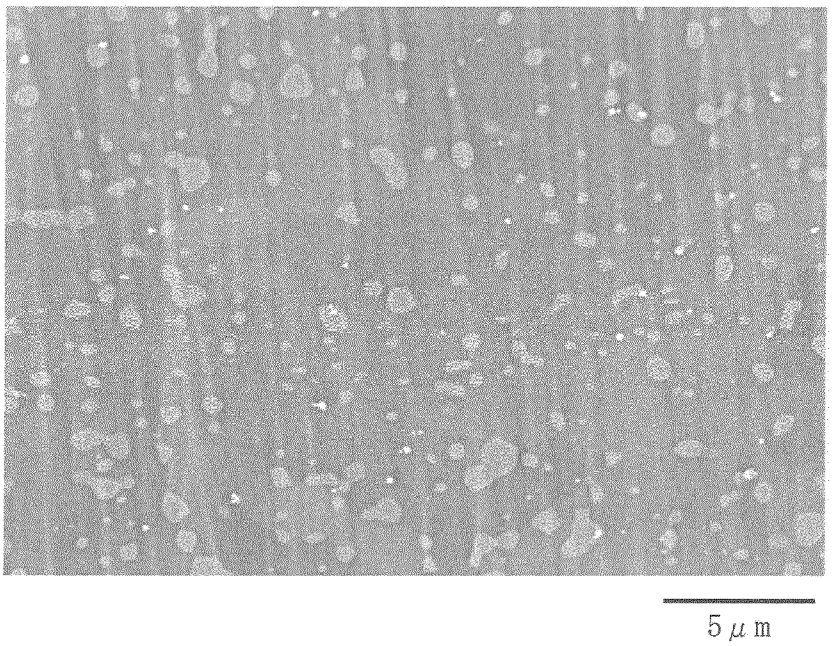
4. A magnesium alloy sheet formed from the magnesium alloy according to any one of claims 1 to 3.

5. A magnesium alloy structural member formed from the magnesium alloy according to any one of claims 1 to 3, the magnesium alloy structural member having, in at least a part thereof, a plastically formed portion subjected to plastic forming.

6. A method for producing a magnesium alloy, the method comprising the step of subjecting a melt of a magnesium alloy to continuous casting, the magnesium alloy containing, in mass%, from 1% to 12% inclusive of A1 and from 0.1% to 5% inclusive of Mn,
   wherein the temperature of the melt immediately before the melt comes into contact with a mold is from 630°C to 690°C inclusive, and
   a cooling rate of the melt is 560°C/second or higher.

FIG. 1

SEM (SECONDARY ELECTRON IMAGE)



BINARY IMAGE

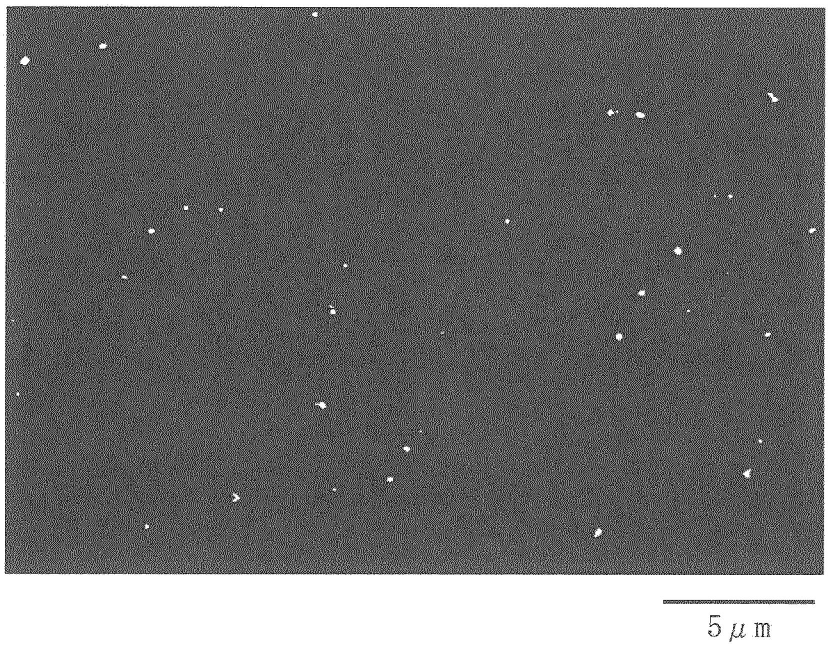


FIG. 2

SEM (BACKSCATTERED ELECTRON IMAGE)

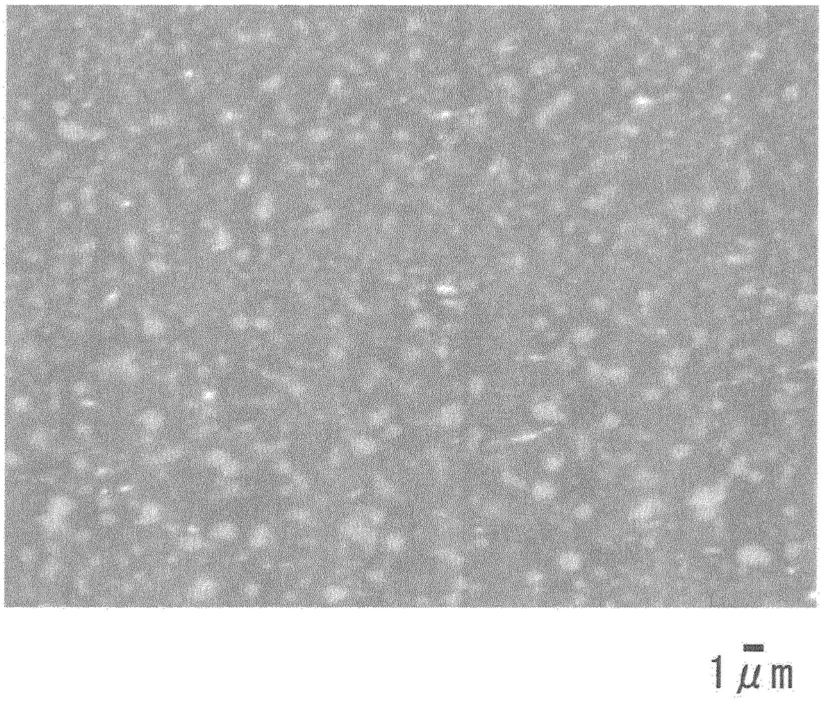


FIG. 3

ACCELERATION VOLTAGE: 15 kV

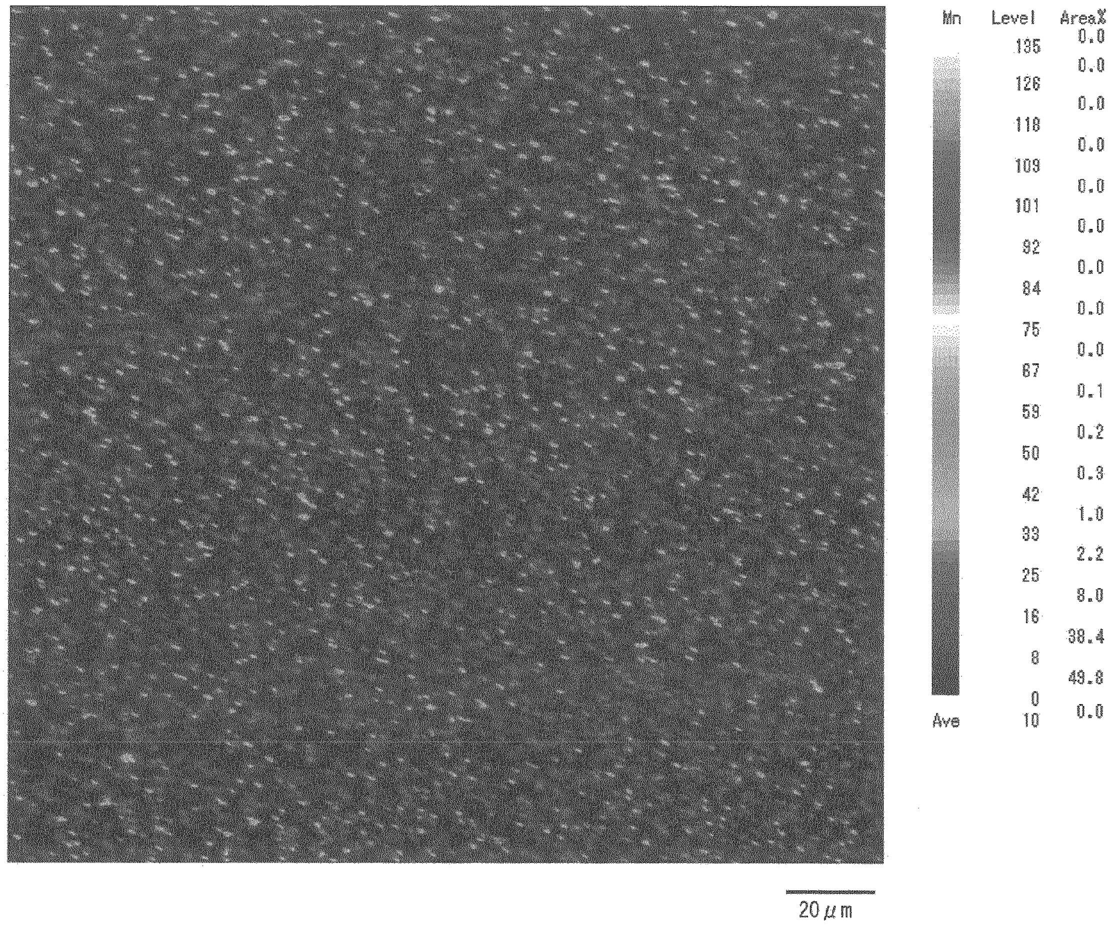


FIG. 4

ACCELERATION VOLTAGE: 15 kV

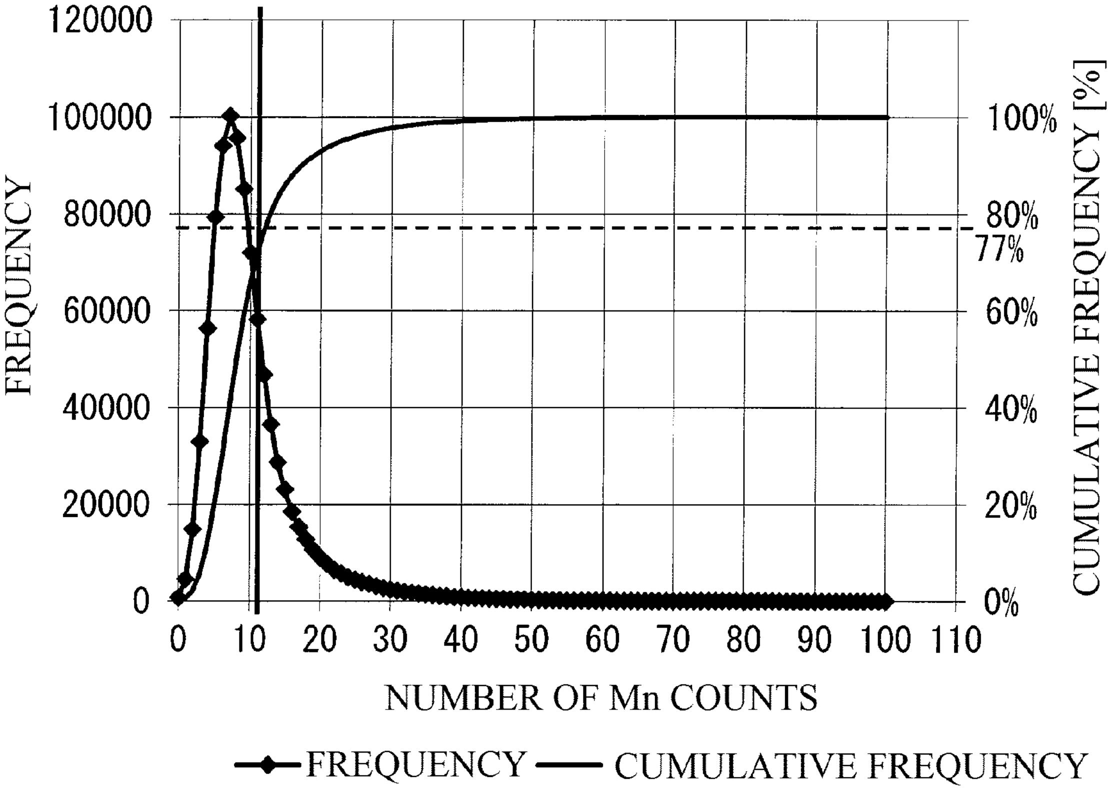


FIG. 5

ACCELERATION VOLTAGE: 5 kV

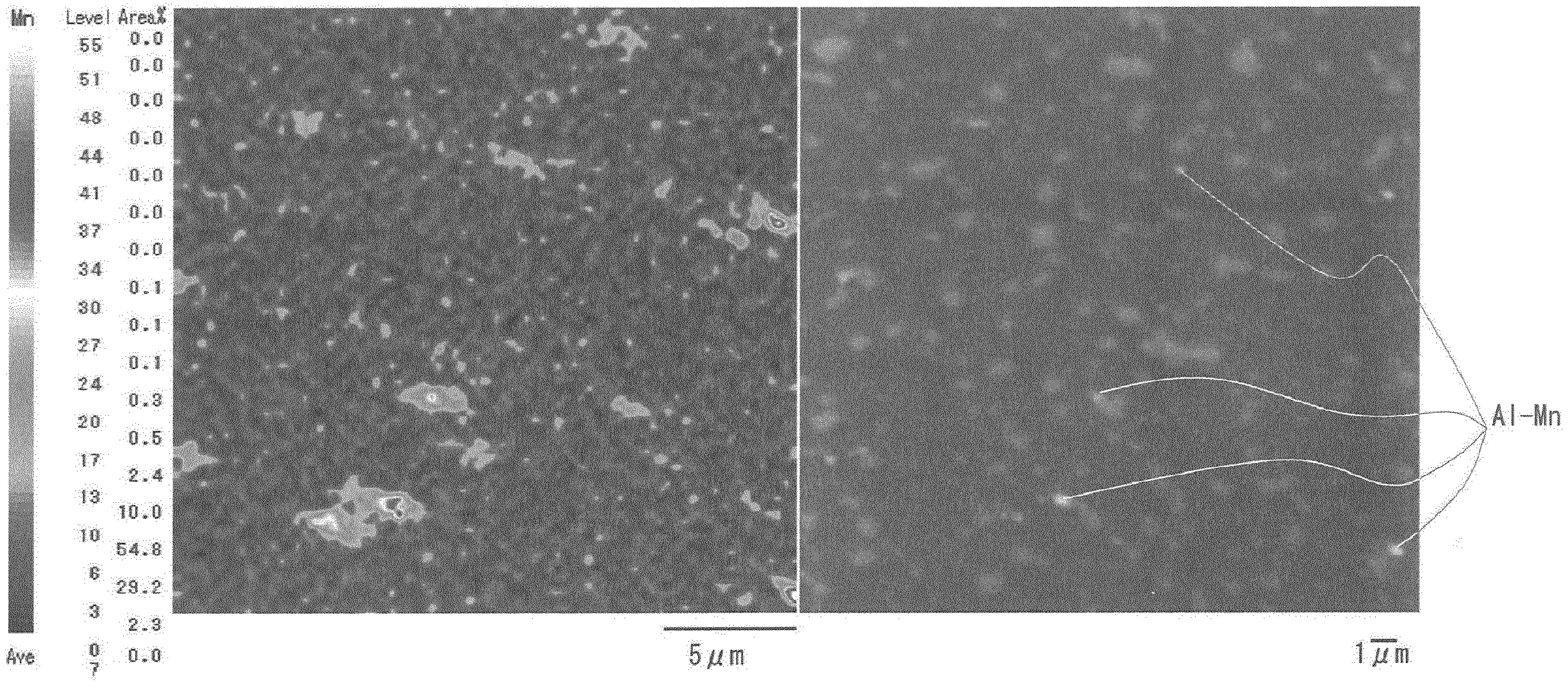
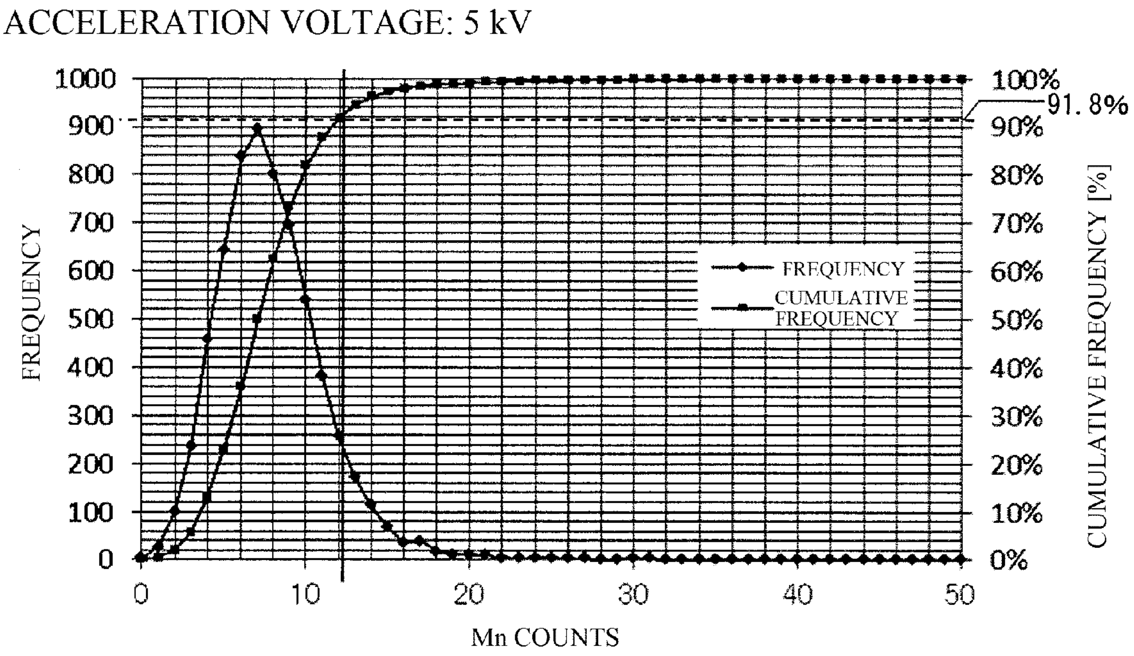


FIG. 6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90%
80%
70%
60%
50%
40%
30%
20%
10%
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10
20
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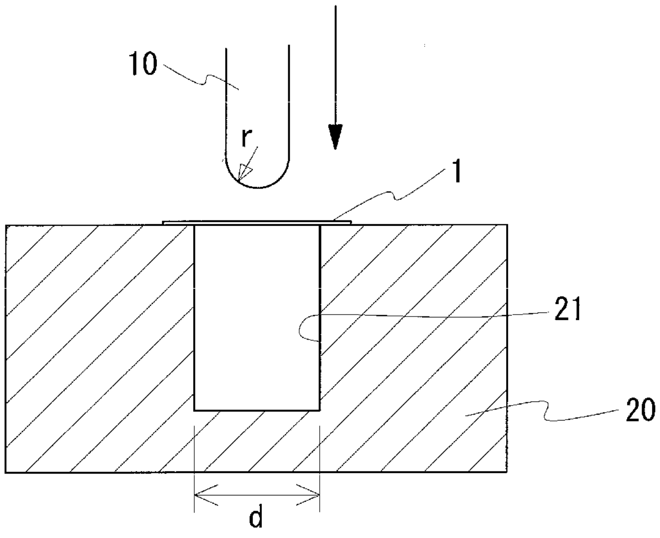
Mn COUNTS
FREQUENCY
CUMULATIVE FREQUENCY

FIG. 7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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/076885

A. CLASSIFICATION OF SUBJECT MATTER
C22C23/02(2006.01)i, *B21B3/00*(2006.01)i, *B22D11/06*(2006.01)i, *B22D21/04*(2006.01)i, *C22C23/00*(2006.01)i, *C22F1/06*(2006.01)i, *C22F1/00*(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C23/02, B21B3/00, B22D11/06, B22D21/04, C22C23/00, C22F1/06, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

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	JP 2010-156007 A (Mitsubishi Aluminum Co., Ltd.), 15 July 2010 (15.07.2010), entire text (Family: none)	1-6
A	JP 2011-006754 A (Sumitomo Electric Industries, Ltd.), 13 January 2011 (13.01.2011), entire text & US 2012/0100035 A1 entire text & WO 2010/150651 A1 & EP 2447381 A1	1-6

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

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"&" document member of the same patent family

Date of the actual completion of the international search
10 December 2015 (10.12.15)

Date of mailing of the international search report
22 December 2015 (22.12.15)

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) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/076885

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-077320 A (Mitsubishi Aluminum Co., Ltd.), 19 April 2012 (19.04.2012), entire text (Family: none)	1-6
A	JP 2011-236497 A (Sumitomo Electric Industries, Ltd.), 24 November 2011 (24.11.2011), entire text & US 2013/0031951 A1 entire text & WO 2011/129221 A1 & EP 2559780 A1	1-6

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2011006754 A **[0006]**