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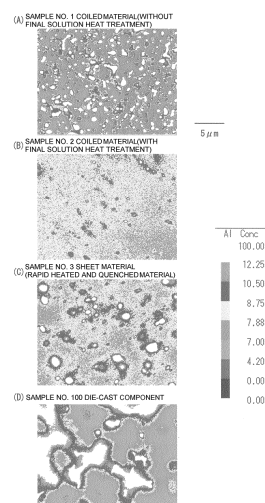
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(54) **MAGNESIUM ALLOY MATERIAL**

(57) A magnesium alloy material having high corrosion resistance is provided. The magnesium alloy material contains a magnesium alloy containing 7.3% to 16% by mass Al, wherein a region having an Al content of 0.8x% by mass or more and 1.2x% by mass or less occupies 50% by area or more, a region having an Al content of 1.4x% by mass or more occupies 17.5% by area or less, wherein x% by mass denotes the Al content of the entire magnesium alloy material, and there is substantially no region having an Al content of 4.2% by mass or less. The magnesium alloy material has small variations in Al concentration and includes a few regions having a very low Al content, thereby effectively preventing and retarding local corrosion. Thus, the magnesium alloy material has higher corrosion resistance than die-cast components having the same Al content. The magnesium alloy material may be a sheet, a coiled long sheet, or a formed product.

FIG. 1



Description

Technical Field

5 **[0001]** The present invention relates to a magnesium alloy material suitable for various components, such as housings for electronic and electrical devices and parts of automobiles, and materials of these components. In particular, the present invention relates to a magnesium alloy material having high corrosion resistance.

Background Art

10 **[0002]** Magnesium alloys containing various additive elements added to magnesium are used in constituent materials for various components, such as housings for mobile electronic and electrical devices, for example, mobile phones and laptop computers, and parts of automobiles.

15 **[0003]** Magnesium alloy components are mainly die-cast components and thixomold components (AZ91 alloys as defined in the American Society for Testing and Materials standards). In recent years, components manufactured by press forming of a sheet made of a wrought magnesium alloy exemplified by an AZ31 alloy as defined in the American Society for Testing and Materials standards have been used. Patent Literature 1 proposes a magnesium alloy sheet made of an alloy equivalent to an AZ91 alloy as defined in the American Society for Testing and Materials standards. The magnesium alloy sheet has excellent press workability.

20 **[0004]** Since magnesium is an active metal, surfaces of the components and magnesium alloy sheets serving as the materials of the components need corrosion protection, such as anodic oxidation treatment or chemical conversion treatment, to increase corrosion resistance.

Citation List

25 Patent Literature

[0005] PTL 1: Japanese Unexamined Patent Application Publication No. 2007-098470

30 Summary of Invention

Technical Problem

35 **[0006]** Al-containing magnesium alloys, such as AZ31 alloys and AZ91 alloys, tend to have higher corrosion resistance with increasing Al content. For example, AZ91 alloys are considered to have high corrosion resistance among magnesium alloys. Even components made of AZ91 alloys (mainly die-cast components and thixomold components), however, require the corrosion protection as described above. This is because die-cast components of AZ91 alloys without corrosion protection may suffer from local corrosion in a corrosion test as described below. Thus, it is desirable to increase the corrosion resistance of magnesium alloy materials.

40 **[0007]** Accordingly, it is an object of the present invention to provide a magnesium alloy material having high corrosion resistance.

Solution to Problem

45 **[0008]** As described above, the corrosion resistance increases with increasing Al content. The present inventors studied corrosion resistance of various forms of magnesium alloy materials containing 7.3% by mass or more Al. Even at the same Al content, the corrosion resistance depended on the form of a magnesium alloy material. In order to clear up the cause of this, the structure of each form was examined. Magnesium alloy materials having low corrosion resistance contained coarse precipitates (based on an additive element in an alloy; typically an intermetallic compound containing at least one of Al and Mg). Magnesium alloy materials having high corrosion resistance contained substantially uniformly dispersed fine precipitates or substantially no precipitate.

50 **[0009]** An additive element, such as Al, in a magnesium alloy is present principally as at least one of precipitates (typically intermetallic compounds), impurities in crystal and precipitated impurities, and solid solution. When Al is used in precipitates, this decreases the Al content of the main phase of a magnesium alloy in a region distant from the precipitates and their surroundings.

55 **[0010]** A structure containing the coarse precipitates has a higher Al concentration than its surroundings and is a structure in which a region having a relatively large area of the high Al concentration portion (a region mainly composed of the precipitates and their surroundings) is locally present. In other words, the structure includes many local regions

having a relatively low Al concentration. The regions having a low Al concentration often suffer from corrosion, and local corrosion, such as pitting corrosion, may occur and advance.

[0011] A structure containing substantially uniformly dispersed fine precipitates has a higher Al concentration than its surroundings and is a structure in which micro regions composed of high Al concentration portions are substantially uniformly dispersed. In other words, the structure includes substantially uniformly dispersed fine precipitates, and a large amount of Al remaining in the main phase is substantially uniformly dispersed. A structure containing substantially no precipitate is substantially composed of the main phase containing substantially uniformly dispersed Al and a small number of or no very fine precipitates. Substantially uniform dispersion of Al can prevent or retard local corrosion. A magnesium alloy material having such a structure can have high corrosion resistance.

[0012] In order to measure the Al concentration over the coarse to micro regions, an electron probe micro analyzer (EPMA) can be suitably utilized. The Al concentration of various forms of magnesium alloy materials was analyzed with an EPMA. It was found that, as described below in the examples, in a magnesium alloy material having high corrosion resistance a region satisfying $x\% \pm \alpha$ wherein $x\%$ by mass denotes the Al content of the entire alloy material occupies half, and there are substantially no portion having a very low Al content and a relatively few portions having a very high Al content. Thus, the present inventors found that high corrosion resistance can be quantitatively defined with a parameter, such as the area percentage of Al concentration. This quantitative definition can be applied to any form of Al.

[0013] The present invention is based on such findings and defines a magnesium alloy material having high corrosion resistance using the Al concentration and the area percentage thereof.

[0014] The present invention relates to a magnesium alloy material made of a magnesium alloy containing 7.3% by mass or more and 16% by mass or less Al. This magnesium alloy material satisfies the following (1) to (3), wherein $x\%$ by mass denotes the Al content of the entire magnesium alloy material:

(1) a region having an Al content of $(x \times 0.8)\%$ by mass or more and $(x \times 1.2)\%$ by mass or less occupies 50% by area or more,

(2) a region having an Al content of $(x \times 1.4)\%$ by mass or more occupies 17.5% by area or less, and

(3) there is substantially no region having an Al content of 4.2% by mass or less.

[0015] As described above, a magnesium alloy material according to the present invention includes substantially no region having low corrosion resistance, such as a region having an Al content of 4.2% by mass or less, and a region having a high Al concentration (a region having an Al concentration in the range of $0.8x\%$ to $1.2x\%$ by mass) occupies 50% or more, and a region having a very high Al concentration (a region having an Al concentration of $1.4x\%$ by mass or more) is present in a small amount. Thus, a magnesium alloy material according to the present invention includes substantially no region having a low Al concentration and can therefore effectively prevent local corrosion. Furthermore, a magnesium alloy material according to the present invention includes few or substantially no regions having a very high Al concentration (typically includes a small amount of fine precipitates containing Al (substantially no precipitates of some form)), and Al is sufficiently and widely dispersed in the magnesium alloy main phase. Thus, a magnesium alloy material according to the present invention has a substantially uniformly high Al concentration in at least the entire surface side region. A magnesium alloy material according to the present invention having such a structure has high corrosion resistance.

[0016] In accordance with one aspect of the present invention, a region having an Al content of $(x \times 0.8)\%$ by mass or more and $(x \times 1.2)\%$ by mass or less occupies 70% by area or more, and a region having an Al content of $(x \times 1.4)\%$ by mass or more occupies 5% by area or less.

[0017] In accordance with this aspect, a region having a high Al concentration (a region having an Al concentration in the range of $0.8x\%$ to $1.2x\%$ by mass) occupies 70% or more, and a region having a very high Al concentration (a region having an Al concentration of $1.4x\%$ by mass or more) occupies 5% by area or less or, in some instances, as small as 3% by area or less. Thus, Al is more uniformly dispersed, and the corrosion resistance is further improved.

[0018] In accordance with one aspect of the present invention, a region having an Al content of $(x \times 0.9)\%$ by mass or more and $(x \times 1.2)\%$ by mass or less occupies 50% by area or more.

[0019] In accordance with this aspect, a region having a higher Al concentration (a region having an Al concentration in the range of $0.9x\%$ to $1.2x\%$ by mass) occupies half or more. Thus, because of many regions having high corrosion resistance, the corrosion resistance is further improved.

[0020] In accordance with one aspect of the present invention, the total area of an intermetallic compound containing at least one of Al and Mg is 3% by area or less in a cross section in a surface side region of the magnesium alloy material.

[0021] This aspect includes a small amount of or no very fine intermetallic compound containing Al or Mg in at least the entire surface side region and has high corrosion resistance. Furthermore, in the presence of a very small amount of or no intermetallic compound containing Al, the main phase has a substantially uniformly high Al concentration, resulting in high corrosion resistance.

[0022] In accordance with one aspect of the present invention, the magnesium alloy material is a sheet.

[0023] This aspect can be suitably utilized in a material for a plastic worked component subjected to plastic working, such as press forming, forging, or bending. In particular, under the specific plastic working conditions described below, the resulting plastic worked component can have an Al concentration distribution similar to that of the sheet described above and high corrosion resistance.

[0024] In accordance with one aspect of the present invention, the magnesium alloy material is a coiled long sheet.

[0025] Since the coiled material is composed of a sheet having high corrosion resistance, the coiled material can be used as a material for a plastic worked component subjected to plastic working, such as press forming, forging, or bending, thereby contributing to the mass production of the plastic worked component. In particular, under the specific plastic working conditions described below, the resulting plastic worked component can have an Al concentration distribution similar to that of the coiled material and high corrosion resistance. The coiled material can be unwound and punched or cut to form a sheet having a desired shape, thereby contributing to the mass production of such a sheet. The resulting sheet substantially retains the Al concentration distribution of the coiled material and therefore has high corrosion resistance. The sheet can be used directly or as a material for the plastic worked component.

[0026] In accordance with one aspect of the present invention, the magnesium alloy material is a plastic worked component of a sheet.

[0027] A magnesium alloy material according to the present invention may have various forms as described below. In particular, a plastic worked component (formed product) having a desired shape as described above can be suitably used in various components and housings. When the sheet is subjected to solution heat treatment (in particular, final solution heat treatment) as described below, the sheet has high elongation. Thus, when such a sheet is subjected to plastic working, such as press forming or forging possible, the sheet has higher corrosion resistance and toughness than die-cast components and thixomold components. When the sheet is subjected to plastic working (primary processing), such as rolling, or the primary processed sheet is further subjected to final solution heat treatment, this reduces or substantially eliminates internal defects, such as voids (cavities), in processing, such as rolling, thereby improving toughness, or the rolling reduces the size of crystal grains and thereby improves strength. When such a sheet is subjected to plastic working (secondary processing), such as press forming or forging possible, the sheet has higher corrosion resistance and better mechanical characteristics, such as toughness and strength, than die-cast components and thixomold components. Advantageous Effects of Invention

[0028] A magnesium alloy material according to the present invention has high corrosion resistance.

Brief Description of Drawings

[0029]

[Fig. 1] Figures 1(A) to 1(D) are FE-EPMA composition mapping images of magnesium alloy materials. Figure 1(A) shows a sample No. 1: coiled material (without final solution heat treatment). Figure 1(B) shows a sample No. 2: coiled material (with final solution heat treatment). Figure 1(C) shows a sample No. 3: sheet material (rapid heated and quenched material). Figure 1(D) shows a sample No. 100: die-cast component.

[Fig. 2] Figures 2(A) to 2(D) are bar graphs of the relationship between Al concentration and area percentage (%) in the magnesium alloy material. Figure 2(A) shows the sample No. 1: coiled material (without final solution heat treatment). Figure 2(B) shows the sample No. 2: coiled material (with final solution heat treatment). Figure 2(C) shows the sample No. 3: sheet material (rapid heated and quenched material). Figure 2(D) shows the sample No. 100: die-cast component.

[Fig. 3] Figures 3(A) to 3(D) are photomicrographs (x 5000) of magnesium alloy materials. Figure 3(A) shows the sample No. 1: coiled material (without final solution heat treatment). Figure 3(B) shows the sample No. 2: coiled material (with final solution heat treatment). Figure 3(C) shows the sample No. 3: sheet material (rapid heated and quenched material). Figure 3(D) shows the sample No. 100: die-cast component.

[Fig. 4] Figure 4 is a graph of the relationship between Al concentration (% by mass) measured by ICP spectroscopy and EPMA X-ray intensity in magnesium alloy materials having different Al contents.

Description of Embodiments

[0030] The present invention will be described in detail below.

[Magnesium Alloy Material]

(Composition)

[0031] A magnesium alloy constituting a magnesium alloy material according to the present invention may have a

composition in which Mg is combined with an additive element (the remainder: Mg and impurities, Mg: 50% by mass or more). In particular, in the present invention, the magnesium alloy is a high-concentration alloy in which an additive element constitutes 7.3% by mass or more, particularly a Mg-Al alloy containing at least Al as an additive element. A higher Al content tends to result in higher corrosion resistance as well as excellent mechanical characteristics, such as strength and hardness. Thus, an alloy having a high Al content, for example, of 7.3% by mass or more as in the present invention has higher corrosion resistance and better mechanical characteristics than alloys having a low Al content. An Al content of more than 16% by mass, however, results in poor plastic formability. Thus, the upper limit is 16% by mass. The Al content is preferably 12% by mass or less because of further improved plastic formability, particularly preferably 11% by mass or less, more preferably 8.3% to 9.5% by mass.

[0032] The additive element other than Al may be one or more elements selected from the group consisting of Zn, Mn, Si, Be, Ca, Sr, Y, Cu, Ag, Sn, Li, Zr, Ce, Ni, Au, and rare-earth elements (except Y and Ce). Each of these elements may constitute 0.01% by mass or more and 10% by mass or less, preferably 0.1% by mass or more and 5% by mass or less, of the magnesium alloy. Among the additive elements, 0.001% by mass or more in total, preferably 0.1% by mass or more and 5% by mass or less in total, of at least one element selected from Si, Ca, Sn, Y, Ce, and rare-earth elements (except Y and Ce) can improve heat resistance and flame resistance. When a magnesium alloy contains a rare-earth element, the rare-earth element content is preferably 0.1% by mass or more in total. In particular, when a magnesium alloy contains Y, the Y content is preferably 0.5% by mass or more. Examples of the impurities include Fe.

[0033] Examples of more specific compositions of the Mg-Al alloy include AZ alloys (Mg-Al-Zn alloys, Zn: 0.2% to 1.5% by mass), AM alloys (Mg-Al-Mn alloys, Mn: 0.15% to 0.5% by mass), Mg-Al-rare-earth element (RE) alloys, AX alloys (Mg-Al-Ca alloys, Ca: 0.2% to 6.0% by mass), AS alloys (Mg-Al-Si alloys, Si: 0.2% to 6.0% by mass), and AJ alloys (Mg-Al-Sr alloys, Sr: 0.2% to 7.0% by mass) as defined in the American Society for Testing and Materials standards. In particular, Mg-Al alloys containing 8.3% to 9.5% by mass Al and 0.5% to 1.5% by mass Zn, typically AZ91 alloys, are preferred because of their high corrosion resistance and excellent mechanical characteristics.

[0034] In the present invention, the Al content of the entire magnesium alloy material (hereinafter referred to as an Al overall average) x% by mass refers to the total amount of Al in the magnesium alloy material, irrespective of the state of Al in the magnesium alloy material (principally, at least one of precipitates, impurities in crystal and precipitated impurities, and solid solution). Typically, the total amount can be suitably measured by ICP spectroscopy (inductively coupled plasma atomic emission spectroscopy: ICP-AES).

(Al Concentration and Area Percentage (Area Ratio))

[0035] A magnesium alloy material according to the present invention is most characterized by Al concentration distribution. More specifically, an analysis of the Al concentration on the surface of the alloy material shows that (1) a region having an Al content of Al overall average (x% by mass) $\pm$ 20% occupies 50% by area or more (wherein $7.3 \leq x \leq 16$). A region having an Al content of less than 0.8x% by mass (a minimum of 5.84% by mass) has low corrosion resistance. A region having an Al content of more than 1.2x% by mass (a maximum of 19.2% by mass) has high corrosion resistance, but the concentration of Al in this region makes it relatively easy for a region having low corrosion resistance to be present. In contrast, the region having an Al content in the range of 0.8x% to 1.2x% by mass (hereinafter referred to as a central composition region) has small variations in Al concentration. Thus, when the region having such a uniform Al concentration occupies 50% by area or more, regions having large variations in Al concentration, such as the region having an Al content of less than 0.8x% by mass and the region having an Al content of more than 1.2x% by mass, are difficult to be present. Thus, a magnesium alloy material according to the present invention includes few or substantially no regions having low corrosion resistance, and at least the surface side region of the alloy material is composed of a region having a relatively high Al concentration. This can prevent local corrosion and improve corrosion resistance. A higher area percentage of the central composition region tends to result in a wider region having a uniform Al concentration and a more uniform Al concentration. In other words, this tends to result in a decrease in Al concentration distribution width. Thus, the area percentage of the central composition region is preferably 55% by area or more, more preferably 70% by area or more, still more preferably 90% by area or more, particularly preferably 95% by area or more. When a region having a higher Al concentration, more specifically a region having an Al concentration in the range of 0.9x% to 1.2x% by mass occupies 30% by area or more, more preferably 50% by area or more, the corrosion resistance is further improved because of the high Al concentration and uniform presence of the region having such a high concentration. A method for measuring the Al concentration and a method for measuring the area percentage are described in detail below.

[0036] The Al concentration can be measured in any point in any cross section of a magnesium alloy material. A region most closely involved in corrosion is a surface of the alloy material. Thus, at least a surface of a magnesium alloy material according to the present invention satisfies the Al concentration distribution specified above. In accordance with the present invention, the Al concentration distribution in the inside of a magnesium alloy material (for example, a region located at a depth of more than a quarter of the thickness from a surface) may be equivalent to the Al concentration distribution on the surface, or the Al concentration distribution in the inside may be different from the Al concentration

distribution on the surface.

[0037] A magnesium alloy material according to the present invention includes (2) few regions having an Al content of Al overall average ($x\%$ by mass) $\times 140\%$ or more (wherein $7.3 \leq x \leq 16$). A region having an Al content of $1.4x\%$ by mass (a maximum of 22.4% by mass) or more has high corrosion resistance, but the concentration of Al in this region makes it easy for a region having a relatively low Al concentration and low corrosion resistance to be present. In contrast, in a magnesium alloy material according to the present invention, a region having an Al content of $1.4x\%$ by mass or more (hereinafter referred to as an ultra-high concentration region) occupies as little as 17.5% by area or less. Thus, a region having low corrosion resistance is difficult to be present, and the corrosion resistance is improved. A decrease in the area percentage of the ultra-high concentration region results in fewer regions having a relatively low Al concentration and fewer regions having low corrosion resistance. In other words, this tends to result in a decrease in Al concentration distribution width. Thus, the area percentage of the ultra-high concentration region is preferably 15% by area or less, more preferably 14% by area or less, particularly preferably 5% by area or less, still more preferably 3% by area or less, still more preferably 1% by area or less. The area percentage of the ultra-high concentration region is still more preferably 0.15% by area or less, ideally zero.

[0038] In accordance with a magnesium alloy material according to the present invention, (3) there is substantially no region having an Al content of 4.2% by mass or less (hereinafter referred to as a low-concentration region), that is, substantially no region having low corrosion resistance. In the presence of a portion having a relatively high Al content, corrosion may occur or advance preferentially in a portion having a relatively low Al content. In contrast, a magnesium alloy material according to the present invention includes substantially no portion having a very low Al concentration, that is, substantially no portion in which corrosion is likely to occur or advance, and therefore has high corrosion resistance. The term "substantially no", as used herein, means that a point having an Al content of 4.2% by mass or less is not observed by EPMA.

(Structure)

[0039] It is desirable that a structure having high corrosion resistance include smaller and fewer, preferably substantially no, regions having a very high Al concentration. Thus, a structure containing substantially no Al-rich precipitates exemplified by Al-rich intermetallic compounds, such as $\text{Al}_{12}\text{Mg}_{17}$, and those in combination with some additive element, such as Al_2Ca , Al_4Ca , and Al_3Ni , is expected to have highest corrosion resistance. The corrosion resistance is excellent when the area percentage of the ultra-high concentration region satisfies a particular range and when there is substantially no low-concentration region. Thus, the present invention allows Al-rich precipitates, such as the intermetallic compounds described above, to be present, provided that the area percentage is satisfied. In particular, in the presence of an Al-rich intermetallic compound, a structure containing a substantially uniformly dispersed (the total area percentage: 11% or less) small intermetallic compound (average particle size: $3.0\text{ }\mu\text{m}$ or less, preferably $0.5\text{ }\mu\text{m}$ or less) tends to have a substantially uniform Al concentration and is therefore preferred. Uniform presence of an Al-rich precipitate, such as the intermetallic compound, is expected to function as a barrier to corrosion.

[0040] With some additive element in the alloy, in addition to the Al-rich intermetallic compound, another intermetallic compound containing Mg, such as Mg_2Si , Mg_2Ca , Mg_2Sn , or $\text{Mg}_{17}\text{Sr}_2$, may be formed. The intermetallic compound containing Mg or Al as described above in at least the surface side region of a magnesium alloy material preferably constitutes 3% by area or less in terms of corrosion resistance. Thus, the present invention has no lower limit of the intermetallic compound. In the present invention, the surface side region in which the area percentage of the intermetallic compound is to be measured refers to a region located at a depth of $100\text{ }\mu\text{m}$ or less from a surface of the magnesium alloy material. When the magnesium alloy material has a thickness of less than $100\text{ }\mu\text{m}$, the surface side region refers to a region located at a depth of not more than a quarter of the thickness from a surface of the magnesium alloy material. A method for measuring the area ratio of the intermetallic compound will be described below.

(Form)

[0041] From the perspective of manufacturing process, examples of the form of a magnesium alloy material according to the present invention include wrought materials (with solution heat treatment during manufacture), such as rolled sheets and extruded materials; straightened materials manufactured by straightening of wrought materials; heat-treated materials manufactured by heat treatment of wrought materials in order to remove strain; solution-heat-treated materials manufactured by final solution heat treatment of various forms, including die-cast components, thixomold components, wrought materials, straightened materials, and cast materials (for example, materials manufactured by a twin-roll continuous casting process); wrought materials (after solution heat treatment) manufactured by flatting, such as rolling or extrusion, of solution-heat-treated materials; straightened materials (after solution heat treatment) manufactured by straightening of solution-heat-treated materials; heat-treated materials (after solution heat treatment) manufactured by flatting, such as rolling, and subsequently the heat treatment of solution-heat-treated materials; and polished components

manufactured by grinding wrought materials, straightened materials, heat-treated materials, and solution-heat-treated materials. Other examples include worked components manufactured by plastic working, such as drawing, bending, forging, or press forming, or machining, such as cutting or punching, of sheets in the form of a wrought material, a straightened material, a heat-treated material, a solution-heat-treated material, or a polished component.

[0042] Among the wrought materials, the rolled sheets may have small crystal grains because of rolling and have a fine structure having an average grain size of 10 μm or less or even 5 μm or less or have a structure containing few, small, or substantially no internal defects, such as voids (cavities) (a structure having an actually measured density of 99% or more of the density of a theoretical density material as determined from the material composition). The presence of such a fine structure or a structure having a high actually measured density can be indicative of a rolled sheet. A rolled sheet having few, small, or preferably substantially no internal defects as described above has excellent mechanical characteristics, such as tensile strength, elongation, and rigidity and can be suitably used in a structural component or as a material for a structural component.

[0043] Straightening may be performed by leveler roller processing. Depending on the degree of straightening, a straightened material manufactured by leveler roller processing may have a shear band and may have a structure having a grain boundary that is difficult to clearly observe even in microscopic observation. In this case, the structure is not even a non-amorphous structure because a monochromatic X-ray diffraction peak can be obtained. Thus, the fact that a monochromatic X-ray diffraction peak can be obtained and that no grain boundary can be observed can be indicative of a straightened material manufactured by leveler roller processing. A straightened material, particularly a straightened material manufactured by leveler roller processing, tends to cause recrystallization during plastic working, such as press forming, thereby having excellent plastic formability. At a low degree of straightening, the appearance, structure, and mechanical properties may be similar to those of the rolled sheets.

[0044] Since solution-heat-treated materials have been subjected to solution heat treatment, which produces a supersaturated solid solution, an additive element, such as Al, is mainly present as a solid solution, and a precipitate, such as an Al-containing intermetallic compound, for example, $\text{Al}_{12}\text{Mg}_{17}$, $\text{Al}(\text{MnFe})$, Al_2Ca , Al_4Ca , or Al_3Ni , is rarely present and, if present at all, is present in a small amount. Thus, a low abundance of an Al-containing intermetallic compound can be indicative of a solution-heat-treated material. More specifically, when the percentage of the total area of an intermetallic compound containing at least one of Al and Mg in a cross section in the surface side region of a magnesium alloy material (typically a region located at a depth of 100 μm or less from the surface) is 3% or less or 1% or less, the magnesium alloy material is a solution-heat-treated material. Solution-heat-treated materials tend to substantially retain their hardness or elongation after heat treatment at 400°C for 30 hours or more (the surface of a test specimen has been ground). Thus, a variation in mechanical characteristics due to heat treatment can be utilized as an indicator of a solution-heat-treated material.

[0045] As described above, in solution-heat-treated materials, a supersaturated solid solution is entirely formed, and Al can be substantially uniformly dispersed. More specifically, a solution-heat-treated material that has been subjected to final solution heat treatment has an Al concentration distribution such that the central composition region constitutes 90% by area or more and the ultra-high concentration region constitutes 3% by area or less or even 1% by area or less. Thus, the solution-heat-treated material has still higher corrosion resistance. Solution-heat-treated materials contain substantially no defect that can be a starting point of cracking, such as a coarse precipitate (typically an intermetallic compound), in plastic working and therefore have excellent plastic formability. Thus, such solution-heat-treated materials can be suitably used as materials for plastic worked components.

[0046] Polished components have a smooth surface and have excellent surface texture. Thus, surface smoothness (for example, a maximum height R_z of 20 μm or less) or polishing marks are indicative of polished components.

[0047] In the case of heat-treated materials, for example, the fact that (1) no shear band is observed in the inside of a magnesium alloy material or (2) particles having a crystal grain size of 0.1 μm or less constitute 5% by area or less in a cross section is indicative of heat-treated materials, although it depends on the heat treatment conditions.

[0048] In the case that the worked components are plastic worked components, when a sheet of a magnesium alloy material according to the present invention is used as a material and is subjected to plastic working under particular conditions, the plastic worked component has an Al concentration distribution such that the central composition region constitutes 50% by area or more, the ultra-high concentration region constitutes 17.5% by area or less, and there is substantially no low-concentration region, and the plastic worked component has high corrosion resistance. Thus, the plastic worked component can substantially retain the Al concentration distribution of the material. The machined materials can also substantially retain the Al concentration distribution of the material.

[0049] From the perspective of shape, examples of the form of a magnesium alloy material according to the present invention include sheets (composed of substantially flat front and back sides parallel to each other and side surfaces between the front and back sides; the distance (= thickness) between the front and back sides is substantially constant on the whole; as viewed from the top, the sheets can assume various planar shapes, such as rectangular, circular, elliptical, and polygonal), coiled materials of a long sheet, and various special-shaped materials other than the sheets. Sheets can assume various shapes by cutting or punching, for example, various planar shapes, such as circular, elliptical,

polygonal, and shapes having a through-hole (including a large through-hole, such as a window). Sheets may have a portion having a different thickness by using a profile roller as described below; for example, a sheet partly has a recessed portion or a rib (a raised portion). Examples of the special-shaped materials include three-dimensionally shaped materials formable by a die-casting process or a thixomold process and three-dimensionally shaped materials formable by plastic working, such as press forming. Examples of the three-dimensionally shaped materials include sheets having a projection, such as a rib, or a recessed portion and partly having a different thickness; boxes having a J-shaped cross section or J-shaped frames for use in housings for various apparatuses; closed-end tubes; and those having a relatively simple shape, for example, spheres, ellipsoids, and polygonal prisms, such as triangular prisms. Special-shaped materials may have a through-hole (including a large through-hole, such as a window). Such forms having recessed and raised portions or a through-hole can be easily formed by a die-casting process. A material having a desired shape manufactured by cutting or polishing of an ingot may also be used. Special-shaped materials may have a plastic worked portion that has been subjected to plastic working, such as press forming.

[0050] A magnesium alloy material according to the present invention may have any of various shapes as described above. In particular, a coiled material can be suitably used as a material for a plastic worked component that has been subjected to plastic working, such as press forming, and contribute to the mass production of the plastic worked component. In the case that a magnesium alloy material according to the present invention is a coiled material, a more specific form may be a coiled rolled sheet, a coiled cast material, or a coiled solution-heat-treated material manufactured by final solution heat treatment of a coiled rolled sheet. The coiled material may have a thickness of 10 mm or less or 5 mm or less, a width of 100 mm or more, 200 mm or more, or particularly 250 mm or more, and a length of 30 m or more, 50 m or more, or particularly 100 m or more. Such long materials and wide materials are suitable as materials for plastic worked components. In particular, rolled sheets or rolled sheets that have been subjected to final solution heat treatment may be thinner or longer than the cast materials. For example, thin materials may have a thickness of 2 mm or less, particularly 1.5 mm or less, more particularly 1 mm or less, and long materials may have a length of 50 m or more, 100 m or more, particularly 200 m or more. Thin materials having a thickness of 2 mm or less can be suitably used as materials for low-profile light-weight plastic worked components. The thickness is preferably 0.1 mm or more, and thin materials having a thickness in the range of 0.3 to 1.2 mm are easy to use.

[0051] Because of its high corrosion resistance, a magnesium alloy material according to the present invention can be used without corrosion protection, such as chemical conversion treatment or anodic oxidation treatment, in some corrosive environment. This can obviate the necessity for a corrosion protection process, increase the productivity of the magnesium alloy material, and reduce wastes, thereby reducing environmental load. As a matter of course, a magnesium alloy material according to the present invention may be subjected to corrosion protection, such as chemical conversion treatment or anodic oxidation treatment, that is, may have an anticorrosive layer. In this case, the Al concentration can be measured by removing the anticorrosive layer from the surface by polishing or cutting to expose a substrate surface made of a magnesium alloy even without performing precise cross-sectional observation. In addition to the anticorrosive layer, a coating layer can further improve corrosion resistance or impart a color or a pattern to the magnesium alloy material, thereby improving commercial value. An anticorrosive layer or a coating layer may be formed on a desired portion.

[Manufacturing Method]

[0052] Manufacture of a magnesium alloy material according to the present invention involves at least one solution heat treatment before the completion of an end product. In particular, in a manufacturing method including a hot rolling process, in addition to a solution heat treatment process, the cooling rate of a material to a particular temperature can be controlled within a particular range in a cooling process after final hot rolling. Whether the hot rolling process is performed or not, the cooling rate in a particular temperature range can be controlled in a particular range in the final solution heat treatment process. For example, a method for manufacturing a magnesium alloy material according to the present invention may include a rolling process (manufacturing methods 1-1 to 1-5) or no rolling process (a manufacturing method 2). In the following manufacturing methods, at least one process may be omitted or the order of processes may be changed, provided that a magnesium alloy material according to the present invention has a particular Al concentration distribution that satisfies the conditions (1) to (3).

(Manufacturing Method 1-1)

[0053] In the case that a magnesium alloy material according to the present invention is a rolled sheet, for example, the magnesium alloy material can be manufactured by a method including the following preparation process, intermediate solution heat treatment process, and rolling process.

Preparation process: a process of preparing a cast material made of a magnesium alloy that contains 7.3% by mass or more and 16% by mass or less Al and manufactured by a continuous casting process.

Intermediate solution heat treatment process: a process of performing solution heat treatment of the cast material at a holding temperature of at least the following minimum holding temperature for a holding time of one hour or more and 25 hours or less to manufacture an intermediate-solution-heat-treated material.

Minimum holding temperature: a temperature 10°C lower than a temperature (solidus temperature) at which Al is dissolved in Mg in a Mg-Al binary phase diagram (% by mass)

Rolling process: a process of performing at least one pass of hot rolling to the intermediate-solution-heat-treated material to manufacture a rolled sheet.

In particular, in manufacturing processes from the intermediate solution heat treatment process, the thermal history of a material to be processed (typically a rolled sheet) is controlled such that the total time of holding the material at a temperature of 150°C or more and 300°C or less is 12 hours or less and that the material is not heated to a temperature of more than 300°C.

In the rolling process, after final hot rolling, the average cooling rate of the material from the starting temperature of cooling to a material temperature of 100°C or less is 0.8°C/min or more.

[0054] The minimum holding temperature, that is, the temperature 10°C lower than the solidus temperature in the Mg-Al binary phase diagram (% by mass) is typically represented by the following formula (the same applies to a manufacturing method 1-2 described below). When the Al overall average x% by mass of a magnesium alloy is 5% by mass or more and 13% by mass or less, the solidus temperature is in the range of 283°C to 437°C and increases with increasing Al overall average. The minimum holding temperature is expressed by the following linear expression.

$$(\text{Formula}) (\text{Minimum holding temperature}) = 20 \times x + (182 - 10) = 20x + 172$$

When the Al overall average is more than 13% by mass and 16% by mass or less, the minimum holding temperature is (437-10)°C = 427°C.

[0055] In the manufacturing method 1-1, in particular, the total time of holding a material at a temperature in the range of 150°C to 300°C in the processes from the intermediate solution heat treatment to preferably the completion of an end product is reduced to 12 hours or less. At a temperature in the range of 150°C to 300°C, an Al-rich intermetallic compound, such as Al₁₂Mg₁₇, is easy to grow. A relatively short holding time at this temperature range can suppress the growth of the intermetallic compound, suppress an increase in the area of an ultra-high concentration region or a low-concentration region, or reduce the area percentage of the intermetallic compound. After the final hot rolling, cooling in the cooling process is controlled at the particular cooling rate until the temperature reaches at least 100°C so as to substantially prevent Al diffusion. This can suppress the growth of the intermetallic compound and an increase in the area of an ultra-high concentration region or a low-concentration region. The cooling rate is preferably increased to suppress an increase in the area of an ultra-high concentration region or a low-concentration region. The growth of the intermetallic compound is also suppressed by heating the material to not more than 300°C.

(Manufacturing Method 1-2)

[0056] In the case that a magnesium alloy material according to the present invention is a solution-heat-treated material that has been subjected to a rolling process, the magnesium alloy material can be manufactured by a method including the following preparation process, intermediate solution heat treatment process, rolling process, and final solution heat treatment process, for example.

Preparation process: a process of preparing a cast material made of a magnesium alloy that contains 7.3% by mass or more and 16% by mass or less Al and manufactured by a continuous casting process.

Intermediate solution heat treatment process: a process of performing solution heat treatment of the cast material at a holding temperature of at least the following minimum holding temperature for a holding time of one hour or more and 25 hours or less to manufacture an intermediate-solution-heat-treated material.

Minimum holding temperature: a temperature 10°C lower than a temperature (solidus temperature) at which Al is dissolved in Mg in a Mg-Al binary phase diagram (% by mass)

Rolling process: a process of performing at least one pass of hot rolling to the intermediate-solution-heat-treated material to manufacture a rolled sheet.

Final solution heat treatment process: a process of performing final solution heat treatment of the rolled sheet at a holding temperature of at least the minimum holding temperature for a holding time of one hour or more and 40 hours or less.

In particular, in the final solution heat treatment process, the cooling rate at a temperature in the range of 330°C to 380°C satisfies the following.

A surface layer region, which is located at a depth of 10 μm or less from a surface of the rolled sheet, is cooled at 1°C/min

or more.

[0057] The final solution heat treatment performed after rolling as described above can form a solid solution of a precipitate, such as an Al-rich intermetallic compound, produced in the processes up to the rolling process and thereby effectively suppress an increase in the area of an ultra-high concentration region or a low-concentration region or reduce the area percentage of the intermetallic compound. The cooling rate after the final hot rolling in the rolling process of the manufacturing method 1-2 may be in a particular range in the same manner as in the manufacturing method 1-1. Also in the manufacturing method 1-2, from the final solution heat treatment process to the completion of an end product, the thermal history of the material is preferably controlled such that the total time of holding the material at a temperature of 150°C or more and 300°C or less is minimized and that the material is not heated to a temperature of more than 300°C. This can maintain the Al concentration distribution of the solution-heat-treated material manufactured through the final solution heat treatment process.

(Manufacturing Method 1-3)

[0058] A rolled sheet manufactured by the manufacturing method 1-1 may be subjected to final heat treatment in order to remove strain. More specifically, in the case that a magnesium alloy material according to the present invention is a heat-treated material that has been subjected to a rolling process, the magnesium alloy material can be manufactured by a method including a final heat treatment process described below, in addition to the preparation process, the intermediate solution heat treatment process, and the rolling process performed in the manufacturing method 1-1.

(Manufacturing Method 1-4)

[0059] The rolled sheet or the solution-heat-treated material manufactured by the manufacturing method 1-1 or 1-2 may be subjected to straightening (typically hot straightening) in order to improve its straightness or may be subjected to washing or polishing in order to improve its surface texture (remove an oxidized layer, surface defects, or a lubricant used in the rolling). In particular, in the case that a magnesium alloy material according to the present invention is a straightened material or a polished component, the magnesium alloy material can be manufactured by a method including at least one of a straightening process and a polishing process described below, in addition to the preparation process, the intermediate solution heat treatment process, the rolling process (specified in the manufacturing method 1-1 or 1-2), and the final solution heat treatment process (only specified in the manufacturing method 1-2).

(Form of Products of Manufacturing Methods 1-1 to 1-4)

[0060] A manufacturing method including a preparation process, an intermediate solution heat treatment process, and a rolling process and a manufacturing method further including at least one process selected from a final solution heat treatment process, a final heat treatment process, a straightening process, a polishing process, and a washing process can be used to manufacture a sheet having a predetermined length (a short sheet that is probably difficult to wind (for example, a length of 5 m or less, particularly 1 m or less); hereinafter referred to as a sheet material) or a long sheet.

[0061] For example, the sheet material can be manufactured by cutting a cast material into a cast material having a predetermined length (a cast sheet) in the preparation process and performing the subsequent processes using the cast material. Alternatively, the sheet material can also be manufactured by winding a long cast material to prepare a coiled cast material in the preparation process, manufacturing a coiled material also in each process, and finally cutting the coiled material into a predetermined length. Without the cutting, a long sheet is manufactured, and the long sheet can be wound to manufacture a magnesium alloy material according to the present invention in the form of a coiled material. In the manufacture of a coiled material, each process from the preparation process generally includes feeding and winding of the coiled material. In this case, a material subjected to each process is a coiled material of a long material or a wide material. Thus, a large amount of material can be transferred or heated and can be continuously treated in each process, thereby improving the productivity of a magnesium alloy material. A magnesium alloy material according to the present invention can be manufactured by using a sheet material or a coiled material as a material in each process.

(Manufacturing Method 1-5)

[0062] In the case that a magnesium alloy material according to the present invention is a plastic worked component manufactured by plastic working of a sheet of any one of the rolled sheet, the solution-heat-treated material, the heat-treated material, the straightened material, the polished component, and the washed material described above, the magnesium alloy material can be manufactured by any of the methods described above further including the following plastic working process.

Plastic working process: a process of preheating a sheet at a holding temperature of 350°C or less (preferably 300°C

or less) for a holding time of 8 hours or less (preferably 0.5 hours or less) and performing plastic working of the sheet during heating.

[0063] Each of the processes of the manufacturing methods 1-1 to 1-5 will be further described below.

5 «Preparation Process»

[0064] The cast material is preferably manufactured by a continuous casting process. The continuous casting process can consistently yield cast materials having substantially uniform quality in the longitudinal direction. The continuous casting process allows rapid solidification and can thereby reduce oxides and segregation. The continuous casting process can also reduce the amount of coarse crystallized precipitate having a size of more than 10 μm , which can act as a starting point of cracking in rolling, and yield cast materials having excellent plastic formability, for example, in rolling or extrusion. In particular, a twin-roll continuous casting process can easily yield flat cast materials with little segregation. Although, the cast material may have any cross-sectional area, thickness, width, or length, an excessively large thickness may result in segregation. Thus, the thickness is preferably 10 mm or less, more preferably 7 mm or less, particularly preferably 5 mm or less. A long cast material having a length of 30 m or more, 50 m or more, particularly 100 m or more or a wide cast material having a width of 100 mm or more, 250 mm or more, particularly 600 mm or more can be used as a rolled sheet to manufacture a long rolled sheet or a wide rolled sheet. Depending on the desired form, the cast material may be wound to manufacture a coiled cast material or may be cut into a casted sheet material having a predetermined length. In the case that the cast material is wound to manufacture a coiled cast material having a small inner diameter, heating to 150°C or more immediately before winding the cast material can prevent cracking and allows the coiled cast material to be easily manufactured.

«Intermediate Solution Heat Treatment Process»

[0065] The cast material is subjected to intermediate solution heat treatment to make its composition uniform and produce a solid solution of an element, such as Al, thereby reducing the amount of coarse precipitates and yield a material having excellent plastic formability, for example, in rolling or extrusion. The holding temperature of the intermediate solution heat treatment is typically 350°C or more and 450°C or less, particularly 380°C or more, more particularly 390°C or more and 420°C or less. The holding time is one hour or more and 25 hours or less, particularly 10 hours or more and 25 hours or less. The holding time is preferably increased as the Al content increases. In a cooling process started from the holding temperature, the cooling rate is preferably increased, for example, by forced cooling, such as water cooling or air blast, in the same manner as in a final solution heat treatment described below (preferably 1°C/min or more, more preferably 50°C/min or more) to suppress the growth or precipitation of precipitates. In particular, it is easy to control the cooling rate of a casted sheet material.

[0066] The cast material may be directly subjected to intermediate solution heat treatment or, before intermediate solution heat treatment, may be subjected to rolling at a low rolling reduction (rolling reduction: approximately 1% to 15%/pass) or surface grinding.

«Rolling Process»

[0067] In rolling of a magnesium alloy, when the material temperature is room temperature, it is difficult to increase rolling reduction, thus resulting in low production efficiency. In terms of productivity, therefore, at least one pass of hot rolling is preferably performed. Heating a material (an intermediate-solution-heat-treated material or a rolled sheet during rolling) can improve plastic formability, for example, in rolling. The plastic formability is further improved as the material temperature is increased. An increase in material temperature, however, results in coarsening of a precipitate, such as an Al-containing intermetallic compound, which results in an increase in the area of an ultra-high concentration region or a low-concentration region. Coarse precipitates cause a deterioration in plastic formability. Thus, the material temperature is preferably 300°C or less, particularly preferably 150°C or more and 280°C or less. A material may be heated with heating means, such as an atmospheric furnace, in a preheating process. Any furnace that can house a material (a sheet material or a coiled material) can be used.

[0068] In particular, in the case that a rolled material (sheet) manufactured by rolling a casted sheet material is a magnesium alloy material according to the present invention having the particular Al concentration distribution, the holding time at the holding temperature in the preheating process is preferably reduced. As described above, the holding time of a material at the particular temperature range of 150°C to 300°C can be minimized (preferably 12 hours or less) principally in rolling to effectively suppress the growth of precipitates (an Al-rich intermetallic compound in particular) and prevent an increase in the area of an ultra-high concentration region or a low-concentration region or the area percentage of an intermetallic compound. When a coiled material of a long material or a wide material is entirely heated to a substantially uniform temperature, at least part of the coiled material tends to be held at the particular temperature

range for a longer time in preheating. In particular, when a material is densely wound to reduce a clearance between turns so as to manufacture a small coiled material even from a long material or a wide material, it takes a somewhat long time to substantially uniformly heat the entire coiled material. Thus, there may be a region that is held at the particular temperature range for a longer time. In order to suppress the growth of precipitates over the entire coiled material, it is desirable to control the size of the coiled material such that the preheating time is included in the total time or reduce the preheating time. The preheating time may be reduced by installing an in-line heater (typically a heater utilizing radiant heat, electric heating, or induction heating) immediately before a rolling apparatus to perform rapid heating. Use of the in-line configuration can also reduce the time between heating and rolling. The holding time of a material at a temperature in the range of 150°C to 300°C may be reduced by quenching a rolled sheet passing through a rolling apparatus (typically a rolling roller) with a refrigerant or a lubricant (preferably at a cooling rate of 1°C/sec or more). Performing the rapid heating and quenching can effectively reduce the holding time of a material at a temperature in the range of 150°C to 300°C in the rolling process. In particular, the rapid heating and quenching can be easily performed when the material to be rolled is a short material, such as a casted sheet material. Alternatively, the time for heating a material to a substantially uniform temperature can be relatively reduced by stacking a plurality of materials and heating them at the same time while the materials are placed at appropriate intervals. This method can also be easily performed when the material to be rolled is a short material, such as a casted sheet material. For example, when a rolled material (sheet) having a predetermined length and a particular Al concentration distribution that satisfies the conditions (1) to (3) is subjected to at least one pass of hot rolling, the total holding time of preheating before the rolling is preferably 0.01 hours or more and 8 hours or less, particularly preferably 0.01 hours or more and 0.3 hours or less. Thus, such preheating conditions can be controlled to manufacture a magnesium alloy material containing substantially no precipitate and having a narrow Al concentration distribution width, that is, a magnesium alloy material having improved corrosion resistance.

[0069] One or more passes of rolling including the hot rolling may be performed. A plurality of passes of rolling can yield a rolled sheet having a small thickness, reduce the average grain size of the structure of the rolled sheet (for example, 10 μm or less, preferably 5 μm or less), or improve plastic formability, for example, in press forming. The number of passes, the rolling reduction in each pass, and the total rolling reduction can be appropriately determined so as to manufacture a rolled sheet having a desired thickness. Known rolling conditions, for example, heating a reduction roll as well as a material may be employed.

[0070] In particular, in a cooling process after the final hot rolling in the manufacture of a rolled material (sheet) or a coiled rolled sheet having a particular Al concentration distribution that satisfies the conditions (1) to (3), the average cooling rate from the start of cooling to a point at which the material temperature reaches 100°C or less is preferably 0.8°C/min or more. After the final hot rolling, a material can be rapidly cooled to effectively prevent the growth of precipitates during cooling and an increase in the area of an ultra-high concentration region or a low-concentration region or the area percentage of an intermetallic compound. In particular, since a coiled material tends to be heated for a long period of time as described above, rapid cooling after the final hot rolling is effective in suppressing the formation or an increase in the area of an ultra-high concentration region or a low-concentration region. When final solution heat treatment is performed after rolling, it is not necessarily to satisfy the cooling rate. It is, however, expected that a decrease in the area of an ultra-high concentration region or a low-concentration region or the area percentage of an intermetallic compound before the final solution heat treatment allows the area of the ultra-high concentration region or the low-concentration region or the area percentage of the intermetallic compound to be easily reduced also in a finally obtained solution-heat-treated material. The average cooling rate may be determined by measuring the material temperature at the beginning of cooling after the final hot rolling and calculating the average cooling rate using $(T_{mp} - 100)/t$ (°C/min), wherein T_{mp} (°C) denotes the measured temperature and t (min) denotes the time to reach 100°C. The cooling may be controlled to satisfy $(T_{mp} - 100)/t$ (°C/min) ≥ 0.8 (°C/min). The material temperature may be measured with a contact-type sensor, such as a thermocouple, or a non-contact sensor, such as in thermography. An ultrathin thermocouple may be attached to a material surface.

[0071] The cooling rate is preferably as high as 1°C/sec or more, more preferably 5°C/sec or more. In the cooling process, any cooling means that can achieve the cooling rate may be used. In particular, the cooling rate may be increased utilizing forced cooling. The forced cooling means may be means that utilizes a gas medium, such as a fan (air cooling) or an air blast (jet air cooling), means that utilizes a liquid medium, such as water cooling, or means that utilizes a solid medium, such as a chill roll. In particular, use of air cooling, such as an air blast, can obviate the necessity of a process of removing a liquid refrigerant deposited on a material or prevent deterioration in surface texture caused by the deposition of a liquid refrigerant. A liquid refrigerant can be used to easily increase the cooling rate. A liquid refrigerant containing a detergent (for example, a surfactant) that can remove a lubricant used in rolling is preferred because cooling and washing can be performed simultaneously. Although forced cooling means may be installed off line, in-line installation can ensure a large contact area between a material surface and a coolant, thereby improving cooling efficiency. In the case of a coiled material, after the final hot rolling, a material may be wound before the cooling. The coiled material may be directly cooled or may be unwound to easily increase the cooling rate. Natural cooling instead

of the forced cooling means may be performed, provided that the cooling rate can be achieved.

[0072] Rolling at a low rolling reduction, such as finish rolling, may be cold working. Variations in Al concentration rarely occur in cold working, and the Al concentration distribution before the cold working is substantially maintained.

[0073] In multi-pass rolling, an intermediate heat treatment between passes may be performed provided that the holding time at a temperature in the range of 150°C to 300°C is included in the total time described above. Strain, residual stress, and texture introduced into a material in plastic working up to the heat treatment (principally rolling) can be removed or reduced by intermediate heat treatment. This can prevent accidental cracking, strain, or deformation in rolling after the heat treatment, thereby allowing rolling to be performed without any interruption. The holding temperature of a material in this intermediate heat treatment is also preferably 300°C or less. The holding temperature is preferably 150°C or more, particularly preferably 250°C or more and 280°C or less. The holding time may be approximately 0.5 to 3 hours. Also in a cooling process after the intermediate heat treatment, the cooling rate is preferably increased (preferably 1°C/min or more, more preferably 50°C/min or more) to suppress the growth of precipitates.

[0074] The rolled sheet may have any thickness, width, and length. Use of a lubricant in the rolling can decrease frictional resistance during the rolling and prevent seizure of a material, thereby facilitating the rolling. A reduction roll having a recessed portion on its outer periphery (a profile roller) may be used to manufacture a rolled sheet having a rib. A reduction roll having a raised portion on its outer periphery (a profile roller) may be used to manufacture a rolled sheet having a recessed portion. A rolled sheet thus manufactured may be cut or ground in a desired recessed or raised form or a stepped form or may be provided with a boss or a through-hole.

«Final Solution Heat Treatment»

[0075] Final solution heat treatment after the rolling allows precipitates to be redissolved, thereby sufficiently reducing the area of an ultra-high concentration region or the amount of intermetallic compound and substantially eliminating a low-concentration region. A holding temperature lower than the minimum holding temperature or a holding time of less than one hour results in insufficient supersaturated solid solution and an insufficient reduction in the area of the ultra-high concentration region or the amount of intermetallic compound. An excessively high holding temperature (typically more than 450°C) or a holding time of more than 40 hours may result in seizure of a main phase or a decrease in productivity because heating after solid solution is sufficiently formed causes energy loss. Thus, the holding temperature is preferably reduced. For example, the holding temperature is 390°C or more and 420°C or less, and the holding time is 10 hours or more and 25 hours or less.

[0076] In the final solution heat treatment, the cooling rate at a temperature in the range of 330°C to 380°C in a cooling process started from the holding temperature is adjusted to 1°C/min or more. In a magnesium alloy having a high Al content of 7.3% by mass or more, it is believed that a precipitate, for example, an Al-rich intermetallic compound, such as $\text{Al}_{12}\text{Mg}_{17}$, is easily formed at a temperature in the range of 330°C to 380°C. Thus, it is desirable to pass through this temperature range as fast as possible. In the manufacture of a magnesium alloy material according to the present invention having an Al content of 7.3% by mass or more, the cooling rate at a temperature in the range of 330°C to 380°C is increased to reduce the time to pass through the temperature range in which precipitates are easily formed, thereby suppressing the precipitation of the intermetallic compound and suppressing an increase in the area of an ultra-high concentration region or a low-concentration region associated with the formation of the precipitate. The cooling rate is preferably as high as 1°C/min or more, more preferably 50°C/min or more.

[0077] At least a surface layer region of a rolled sheet to be treated satisfies the cooling rate. As described above, corrosion occurs and advances from a surface of a magnesium alloy material. Thus, at least the surface layer region to be treated in the magnesium alloy material is cooled at the cooling rate such that the surface layer region may have a high corrosion resistance state, that is, have a particular Al concentration distribution that satisfies the conditions (1) to (3). More specifically, forced cooling as described above can be suitably utilized. In particular, use of air cooling, for example, a fan or an air blast using air blast means, such as a cool air jet mechanism, has advantages, including resistance to oxidation and small variations in cooling, as well as removal of a liquid refrigerant and prevention of deterioration in surface texture caused by the deposition of a liquid refrigerant. When a liquid refrigerant is used, a cooling method, for example, mist spray for spraying a liquid refrigerant, such as water or a reducing liquid, water sprinkling, or immersion in a liquid refrigerant may be utilized. When the final solution heat treatment is followed by straightening or plastic working, such as press forming, a lubricant may be used as a liquid refrigerant, and a solution-heat-treated material may be cooled by coating with the lubricant or immersion in the lubricant. When it is desirable to remove a lubricant used in rolling, a liquid refrigerant containing a detergent may be used as forced cooling means as described above. Water cooling using a liquid refrigerant has a higher cooling rate than air cooling. A coiled material may be directly cooled or may be unwound to easily increase the cooling rate. Depending on the thickness of a sheet of a coiled material, the cooling rate of an unwound coiled material can be approximately 50°C/min for a jet mechanism and approximately 400°C/min for water cooling. After cooling to approximately room temperature, the unwound coiled material may be wound. A sheet (including a cast material) that has been subjected to the final solution heat treatment process also has

excellent plastic formability and therefore can be wound at an industrially used roll diameter even at approximately room temperature.

[0078] The cooling rate may be controlled by measuring the material surface temperature after the final solution heat treatment, setting the time (min) such that the cooling rate at a temperature in the range of 330°C to 380°C is a desired rate, and controlling the cooling state to achieve a desired rate. Since a magnesium alloy has high thermal conductivity, the temperature of a region located at a depth of 10 μm or less from the surface (a surface layer region) is equivalent to the temperature of the outermost surface. Thus, the cooling rate of the surface region can be determined by measuring the temperature of the outermost surface of the material. The temperature of the outermost surface of the material may be measured with a contact-type sensor, such as a thermocouple, or a non-contact sensor, such as in thermography, as described above.

«Final Heat Treatment»

[0079] The holding temperature in the final heat treatment after rolling is preferably 300°C or less. More specific conditions include a holding temperature of 100°C or more and 300°C or less and a holding time of 5 minutes or more and 60 minutes or less. The holding time of a material (rolled sheet) at a temperature of 150°C or more and 300°C or less in the final heat treatment process is preferably included in the total time. The holding time is preferably less than 30 minutes. Under such particular conditions, a rolled sheet having the particular Al concentration distribution that satisfies the conditions (1) to (3) and having reduced or no strain resulting from rolling can be manufactured.

«Straightening»

[0080] Straightening after rolling or after final solution heat treatment can improve the flatness of a sheet. Although straightening can be performed at room temperature or lower, hot straightening can further improve the flatness. The holding temperature for hot straightening is preferably 300°C or less. More specifically, the holding temperature is 100°C or more and 300°C or less, preferably 150°C to 280°C. The holding time of a material (for example, a rolled sheet) at a temperature of 150°C or more and 300°C or less in the straightening process is preferably included in the total time. In hot straightening, for example, a roll leveler can be suitably used. The roll leveler includes a furnace for heating a material and a roll unit that includes a plurality of rolls for continuously bending (straining) the heated material. The rolls are disposed at upper and lower positions in a staggered arrangement. The roll leveler can be used to continuously straighten a long material. A hot press machine can also be used in hot straightening. Also after hot straightening, when the average cooling rate from the start of cooling to a point at which the material temperature reaches 100°C or less is 0.8°C/min or more, this can effectively suppress an increase in the area of an ultra-high concentration region or a low-concentration region caused by the growth of precipitates or an increase in the amount of precipitates, such as an intermetallic compound. This cooling rate may be achieved using forced cooling means as described above or natural cooling. In particular, when rolling is continuously followed by hot straightening, the cooling rate is preferably controlled as described above so as to realize the particular Al concentration distribution and reduce curling in a coiled material, thereby yielding a flat sheet.

«Plastic Working»

[0081] When a sheet material or a coiled material thus manufactured is subjected to plastic working, such as press forming, the sheet material or the coiled material may be heated to improve plastic formability. The material temperature is preferably 350°C or less, more preferably 300°C or less, particularly preferably 280°C or less. In particular, 150°C or more and 280°C or less and 150°C or more and 220°C or less are suitable. When a material is preheated at this temperature for a holding time of 8 hours or less as described above, this can suppress the growth of precipitates and effectively prevent an increase in the area of an ultra-high concentration region or a low-concentration region or the area percentage of an intermetallic compound. Provided that a material is heated such that desired plastic working is possible, a shorter holding time is preferred. The holding time is preferably 0.5 hours or less (30 minutes or less), more preferably 0.3 hours or less. In particular, as described above, a coiled material sometimes requires a longer time to entirely have a substantially uniform temperature than a sheet material. In order to reduce the holding time, therefore, for example, a heater for rapid heating may be used, or a fan or a baffle plate may be placed in a furnace. Although the time for plastic working, such as press forming, depends on the shape of a material, press forming takes a short time in the range of several seconds to several minutes and is substantially free from failures, such as coarsening of precipitates. Plastic working under such particular conditions can yield a plastic worked component having the particular Al concentration distribution that satisfies the conditions (1) to (3).

[0082] Heat treatment after the plastic working can remove strain or residual stress caused by the plastic working and improve the mechanical characteristics of the material. The heat treatment conditions include a holding temperature in

the range of 100°C to 300°C and a holding time in the range of approximately 5 to 60 minutes. It is desirable that the holding time at a temperature in the range of 150°C to 300°C in the heat treatment be also included in the total time described above.

5 «Total Time of Holding Material in Particular Temperature Range»

10 **[0083]** As described above, the total time for holding a material at a temperature in the range of 150°C to 300°C in the processes from the intermediate solution heat treatment to preferably the completion of an end product (such as rolling (including intermediate heat treatment), final heat treatment, straightening, and preheating before plastic working processes) is preferably as relatively short as 12 hours or less. In the case that the final solution heat treatment is performed, the total time of holding a material at a temperature in the range of 150°C to 300°C in the processes from the final solution heat treatment to the completion of an end product is preferably 12 hours or less.

15 **[0084]** In order to ensure a sufficient heating time for plastic working, such as rolling, the total time for holding a temperature in the range of 150°C to 300°C is preferably 0.01 hours or more. More preferably, manufacturing conditions, for example, the working ratio or the total working ratio in each pass of the rolling process, preheating conditions (such as preheating means and time), cooling process conditions (such as cooling means and time), and the line speed are controlled such that the temperature range is 150°C or more and 280°C or less, still more preferably 150°C or more and 220°C or less and the total time is 8 hours or less, particularly 0.3 hours or less. Since the precipitation of the Al-rich intermetallic compound increases with increasing Al content, the total time is preferably controlled also in a manner that depends on the Al content.

20 **[0085]** As described above, when the final solution heat treatment is performed in and after the intermediate solution heat treatment, it is preferable not to heat a material to more than 300°C in and after the final solution heat treatment. However, heating for a short period of time (preferably 8 hours or less, more preferably one hour or less) that causes no coarsening of precipitates may be allowable.

25 **[0086]** A specific manufacturing method as a manufacturing method that includes a rolling process as described above may include processes of casting → intermediate solution heat treatment (preferably the cooling rate is controlled in a cooling process) → rolling → intermediate heat treatment (depending on the holding temperature, the cooling rate may be controlled in the cooling process) → rolling → straightening, polishing, and washing. In accordance with this manufacturing method, intermediate solution heat treatment before rolling can decrease and minimize the size of precipitates, and the subsequent rolling can decrease the size of structure or improve mechanical characteristics.

(Manufacturing Method 2)

35 **[0087]** In the case that a magnesium alloy material according to the present invention is formed by a manufacturing method including no rolling process, typically a formed product (including a special-shaped material) formed by die casting, the magnesium alloy material can be manufactured by a method that includes the following preparation process and final solution heat treatment process.

Preparation process: a process of preparing one material selected from die-cast components, thixomold components, and extruded materials each made of a magnesium alloy containing 7.3% by mass or more and 16% by mass or less Al.

40 Final solution heat treatment process: a process of performing final solution heat treatment of the material at a holding temperature not less than a temperature (minimum holding temperature) that is 10°C lower than a temperature at which Al is dissolved in Mg in a Mg-Al binary phase diagram (% by mass) for a holding time of one hour or more and 40 hours or less.

In particular, the cooling rate at a temperature in the range of 330°C to 380°C satisfies the following.

45 A surface layer region, which is located at a depth of 10 μm or less from a surface of the material, is cooled at 1°C/min or more.

50 **[0088]** In accordance with the manufacturing method 2, a material prepared in the preparation process can be subjected to final solution heat treatment in the same manner as in the manufacturing method 1-2 to manufacture a solution-heat-treated material having a particular Al concentration distribution that satisfies the conditions (1) to (3). In particular, the manufacturing method 2 can be suitably used to manufacture a complicated three-dimensionally shaped magnesium alloy material as described above.

[0089] The die-casting conditions and the thixomold conditions may be known conditions. An extruded material can be manufactured by preparing an ingot made of a magnesium alloy containing the particular amount of Al and extruding the ingot under known conditions.

«Other Processes»

[0090] A polishing process of polishing (preferably wet polishing) a rolled sheet, a heat-treated material, a straightened

material, or a solution-heat-treated material manufactured by the manufacturing method 1 or 2 can yield a polished component having the particular Al concentration distribution that satisfies the conditions (1) to (3) (a magnesium alloy material according to one embodiment of the present invention). The manufacturing method 1 or 2 further including a process of performing corrosion protection, such as chemical conversion treatment or anodic oxidation treatment, or a process of forming a coating layer can yield a magnesium alloy material according to the present invention that includes a substrate having the particular Al concentration distribution that satisfies the conditions (1) to (3) and an anticorrosive layer or a coating layer disposed on the substrate. The materials and forming conditions for the anticorrosive layer or the coating layer may be known materials and conditions. The corrosion protection preferably includes pretreatment, such as degreasing, acid etching, desmutting, and/or surface conditioning. When plastic working is performed, the anticorrosive layer or the coating layer can be formed after the plastic working to avoid damage caused by the plastic working.

EXAMPLES

[0091] More specific embodiments of the present invention will be described below.

[Test Example 1]

[0092] Al-containing magnesium alloy materials were manufactured under various conditions. Their Al concentration distributions and corrosion resistance were examined.

[0093] In this test, magnesium alloy material samples No. 1 to No. 5 manufactured as described below and a commercially available die-cast component (an AZ91 alloy sheet having a thickness of 3 mm, a width of 75 mm, and a length of 150 mm) for a comparison purpose were prepared. The die-cast component was subjected to wet belt polishing described below under the same conditions as polishing for the samples No. 1 to No. 5 to manufacture a polished sheet, which was referred to as a sample No. 100.

[0094] The following are processes of manufacturing the samples No. 1 to No. 5.

Sample No. 1: coiled material (without final solution heat treatment after rolling)

Casting → intermediate solution heat treatment → rolling → straightening → polishing

Sample No. 2: coiled solution-heat-treated material (with final solution heat treatment after rolling)

Casting → intermediate solution heat treatment → rolling → final solution heat treatment → straightening → polishing

Sample No. 3: sheet material (rapid heated and quenched material) x without intermediate winding

Casting (cutting after casting) → intermediate solution heat treatment → rolling → straightening → polishing

Sample No. 4: solution-heat-treated material (die casting)

Preparation of die-cast component → final solution heat treatment

Sample No. 5: solution-heat-treated material (extrusion)

Preparation of extruded material → final solution heat treatment

«Samples No. 1 and No. 2»

[0095] A long cast sheet (having a thickness of 4 mm and a width of 300 mm) made of a magnesium alloy having a composition corresponding to an AZ91 alloy (Mg-8.75%Al-0.65%Zn (on a mass basis)) and manufactured by a twin-roll continuous casting process was temporarily wound to manufacture a coiled cast material. The coiled cast material was subjected to solution heat treatment (intermediate solution heat treatment) in a batch furnace at 400°C ($\geq 20 \times 8.75 + 172 = 347^\circ\text{C}$) for 24 hours. The resulting coiled intermediate-solution-heat-treated material was unwound, was subjected to a plurality of passes of rolling under the following conditions, and was wound to manufacture a coiled rolled sheet having a thickness of 0.6 mm, a width of 250 mm, and a length of 800 m.

(Rolling Conditions)

[0096]

Rolling reduction: 5% to 40%/pass

Material temperature: 200°C to 280°C

Roll temperature: 100°C to 250°C

[0097] An unwound material was fed between a feed drum in a furnace and a winding drum in another furnace and was transferred by the rotation of the drums. The material was rolled with a reduction roll disposed between the drums.

The rotation of the feed drum and the winding drum was reversed for every pass to continuously perform a plurality of passes of rolling. A material wound around a furnace was heated to the temperature described above for every pass, and the heated material was fed between the drums.

[0098] After a final pass of hot rolling was applied to the material, the material was wound, and the material temperature was controlled with the furnace. The material was unwound and was blown by a flow of air maintained at constant temperature to control the cooling rate. The temperature of the air was controlled such that the average cooling rate up to a point at which the material temperature (200°C to 280°C) reached 100°C was 2.0°C/min for the sample No. 1 or 1.7°C/min for the sample No. 2, and the average cooling rate from 100°C to room temperature (approximately 20°C) was 1.0°C/min for the sample No. 1 or 0.9°C/min for the sample No. 2. The rolled sheet cooled to room temperature was wound to manufacture a coiled rolled sheet.

[0099] The coiled rolled sheet was unwound and was subjected to hot straightening with a roll leveler to manufacture a straightened coiled material (material temperature: 250°C). The straightened coiled material was unwound and was subjected to wet belt polishing with a #600 polishing belt. The resulting polished sheet was wound to manufacture a coiled polished sheet. This coiled polished sheet is hereinafter referred to as a sample No. 1. In the manufacturing processes from the intermediate solution heat treatment to the completion of the final coiled polished sheet, the sample No. 1 was held at a temperature in the range of 150°C to 300°C for a total time of 12 hours or less and was not heated to a temperature of more than 300°C.

[0100] The coiled rolled sheet was subjected to final solution heat treatment in a batch furnace at 350°C ($\geq (20 \times 8.75 + 172) = 347$) for one hour and was cooled to room temperature (approximately 20°C) by forced cooling. The cooling was performed by blowing cool air with a jet mechanism against the cylindrical surface of the coiled material removed from the batch furnace. In particular, the temperature, the volume, and the velocity of the cool air were controlled such that the average cooling rate in a surface layer region (a region located at a depth of 10 μm or less from the surface) of the sheet of the coiled material was 3°C/min ($\geq 1^\circ\text{C}/\text{min}$) at a temperature in the range of 380°C to 330°C. A thermocouple was attached to an appropriate position of the coiled material, and the cool air was controlled such that the cooling rate at a portion having the lowest cooling rate was 3°C/min. Although the coiled material was cooled herein, an unwound coiled material may be cooled.

[0101] The coiled solution-heat-treated material was unwound and was subjected to hot straightening and wet belt polishing under the same conditions as in the sample No. 1. The resulting coiled polished sheet is hereinafter referred to as a sample No. 2. In the manufacturing processes from the final solution heat treatment to the completion of the final coiled polished sheet, the sample No. 2 was held at a temperature in the range of 150°C to 300°C for a total time of 12 hours or less and was not heated to a temperature of more than 300°C. In and after the final solution heat treatment, a process in which the sample No. 2 was held at a temperature in the range of 150°C to 300°C was substantially only hot straightening. Since the material having a reduced thickness owing to rolling was subjected to hot straightening, the holding time at the temperature range could be several minutes.

«Sample No. 3»

[0102] A plurality of cast sheets (casted sheet materials each having a thickness of 5 mm, a width of 300 mm, and a length of 500 mm) made of a magnesium alloy having the same composition as the sample No. 1 or 2 and manufactured by a twin-roll continuous casting process were prepared. The cast sheets were subjected to solution heat treatment (intermediate solution heat treatment) at 400°C for 24 hours. While being cut to adjust the length, the cast sheets were subjected to a plurality of passes of rolling in the same manner as in the samples No. 1 and No. 2 to manufacture a rolled material (sheet) having a thickness of 0.6 mm, a width of 300 mm, and a length of 2000 mm. Before each pass of rolling, the material was preheated to a predetermined temperature with heating means for rapid heating. The total holding time for preheating was 3 hours. After a final pass of hot rolling was applied to the material, the material was placed on a steel sheet for cooling (which can control temperature by circulating a heating medium) to control the cooling rate. The temperature of the steel sheet for cooling and the residence time on the steel sheet were controlled such that the average cooling rate up to a point at which the material temperature (200°C to 280°C) reached 100°C was 60°C/min, and the average cooling rate to room temperature (approximately 20°C) was 40°C/min. The rolled sheet thus manufactured was subjected to hot straightening and wet belt polishing under the same conditions as in the samples No. 1 and No. 2. The resulting polished sheet (sheet material; hereinafter also referred to as a rapid heated and quenched material) is referred to as a sample No. 3. In the same manner as in the sample No. 1, in the manufacturing processes from the intermediate solution heat treatment to the completion of the final polished sheet, the sample No. 3 was held at a temperature in the range of 150°C to 300°C for a total time of 12 hours or less and was not heated to a temperature of more than 300°C.

«Sample No. 4»

[0103] A commercially available die-cast component like the sample No. 100 (an AZ91 alloy sheet (Al: 8.75% by mass) having a thickness of 3 mm, a width of 75 mm, and a length of 150 mm) was prepared. The die-cast component was subjected to final solution heat treatment at 380°C ($\geq (20 \times 8.75 + 172) = 347$) for 20 hours and was cooled to room temperature (approximately 20°C) by forced cooling. The cooling was performed by blowing cool air with a jet mechanism against the surface of the sheet in the same manner as in the sample No. 2. The temperature, the volume, and the velocity of the cool air were controlled such that the cooling rate in a surface layer region was 50°C/min ($\geq 1^\circ\text{C}/\text{min}$) at a temperature in the range of 380°C to 330°C. After the forced cooling, planarization (straightening) was performed by hot press forming at 250°C or less. Wet polishing was then performed in the same manner as in samples No. 1 and No. 2. The resulting polished sheet is referred to as a sample No. 4.

«Sample No. 5»

[0104] A commercially available die-cast component like the sample No. 100 was redissolved, casted, and extruded to prepare a material (an AZ91 alloy sheet having a thickness of 3 mm, a width of 50 mm, and a length of 150 mm). The extruded material was subjected to final solution heat treatment at 380°C for 20 hours and was cooled to room temperature (approximately 20°C) by forced cooling with a jet mechanism in the same manner as in the sample No. 4. After the forced cooling, the material was subjected to straightening by hot press forming and wet polishing under the same conditions as in the sample No. 4. The resulting polished sheet is referred to as a sample No. 5. Also in the case of the sample No. 5, the temperature, the volume, and the velocity of the cool air were controlled such that the cooling rate in a surface layer region was 50°C/min ($\geq 1^\circ\text{C}/\text{min}$) at a temperature in the range of 380°C to 330°C.

[0105] The cooling rate in the cooling process after the final hot rolling and the cooling rate in the final solution heat treatment process can be easily controlled by preparing correlation data as described below in advance and referring to the correlation data. Correlation data between the cooling rate and parameters of forced cooling means, such as the temperature, the volume, and the velocity of cool air, are prepared by making it possible to measure the temperature of the outermost surface of a target to be cooled, such as a plurality of coiled materials or sheet materials having different thicknesses, lengths, and numbers of turns, or a point at a depth of 10 μm from the surface of the target to be cooled with a temperature sensor (for example, a groove is formed at the point, and a temperature sensor is buried in the groove) and measuring the time required for the material temperature at the beginning of cooling in the cooling process to reach 100°C and the time for the material temperature to change from 380°C to 330°C to determine the cooling rate while the parameters are changed. When the target to be cooled is a coiled material, a temperature sensor is placed at an appropriate position on the coiled material, and correlation data with respect to the cooling rate of a portion having the lowest cooling rate may be prepared in advance.

[0106] In order to measure the Al content x% by mass of the entire sample (Al overall average), a test specimen for the total amount was cut from the samples No. 1 to No. 5 and the comparative sample No. 100. The Al overall average was determined by ICP spectroscopy using the test specimen. All the samples had $x = 8.75\%$ by mass.

[0107] A test specimen for mapping was cut from the samples No. 1 to No. 5 and the comparative sample No. 100. A surface element Al of the test specimen was analyzed with a field emission (FE)-EPMA apparatus (JXA-8530F manufactured by JEOL Ltd.). The measurement conditions are described below.

(Measurement Conditions)

[0108]

Accelerating voltage: 15 kV
Irradiation current: 100 nA
Sampling time: 50 ms

[0109] The Al content (% by mass) in the elementary analysis was determined by preparing the following calibration curve and converting the X-ray intensity of EPMA into the Al content (% by mass) using the calibration curve.

[Preparation of Calibration Curve]

[0110] A commercially available AZ31 alloy material, AZ61 alloy material, and material equivalent to an AZ91 alloy having different Al contents were subjected to solution heat treatment (400°C x 120 hours) and were homogenized to make samples. The material equivalent to an AZ91 alloy was utilized by cutting the coiled solution-heat-treated material of the sample No. 2. The Al content was measured on a surface of the sample by ICP spectroscopy. The X-ray intensity

of Al (cps/ μ A) was measured by elementary analysis with FE-EPMA under the measurement conditions described above.

[0111] As illustrated in Fig. 4, the X-ray intensity y was expressed as a linear function of the Al content x . An approximate expression of the linear function $y = 11977x + 1542.5$ is used as a calibration curve. The approximate expression has a correlation coefficient R^2 of 0.9998 and is reliable.

[0112] Figures 1(A) to 1(D) are mapping images (observation field: $24\ \mu\text{m} \times 18\ \mu\text{m}$) with respect to the Al content measured on the surface of the sample with FE-EPMA. Figure 1(A) shows the coiled material of the sample No. 1. Figure 1(B) shows the coiled solution-heat-treated material of the sample No. 2. Figure 1(C) shows the sheet material (rapid heated and quenched material) of the sample No. 3. Figure 1(D) shows the die-cast component of the sample No. 100. Although shown in a gray scale in Fig. 1, depending on the Al concentration, Fig. 1 is practically colored in black (Al concentration: 0% by mass), dark blue, blue, light blue, green, yellow, orange, red, pink, and white (Al concentration: $8.75 \times 1.4 = 12.25\%$ by mass or more) in increasing order of the Al content. White granules in Fig. 1(A), Fig. 1(B), and Fig. 1(C) and white substances of indefinite shapes in Fig. 1(D) are Al-rich intermetallic compounds.

[0113] Figure 1(D) shows that the die-cast component of the sample No. 100 has many regions having a very high Al concentration. It is also shown that there is a region having a very low Al concentration. In contrast, Figs. 1(A) to 1(C) show that the coiled material of the sample No. 1, the coiled solution-heat-treated material of the sample No. 2, and the sheet material (rapid heated and quenched material) of the sample No. 3 have no local large region having a very high Al concentration. In particular, it is shown that the coiled solution-heat-treated material of the sample No. 2 has a very few small regions having a very high Al concentration. It is also shown that the coiled material, the coiled solution-heat-treated material, and the sheet material (rapid heated and quenched material) have substantially no region having a very low Al concentration. In the same manner as in the sample No. 2, the samples No. 4 and No. 5 of the die-cast component and the extruded material that have been subjected to final solution heat treatment had a very few small region having a very high Al concentration and substantially no region having a very low Al concentration.

[0114] Using these mapping images, the area percentage of a low-concentration region having an Al concentration of 4.2% by mass or less, the area percentage of a central composition region having an Al concentration of $0.8x$ ($= 8.75 \times 0.8 = 7\%$) by mass or more and $1.2x$ ($= 8.75 \times 1.2 = 10.5\%$) by mass or less, the area percentage of a region having an Al concentration of $0.9x$ ($= 8.75 \times 0.9 = 7.875\%$) by mass or more and $1.2x\%$ by mass or less, the area percentage of an ultra-high concentration region having an Al concentration of $1.4x$ ($= 8.75 \times 1.4 = 12.25\%$) by mass or more, and the maximum value and the minimum value of the Al concentration were determined in the observation fields of the samples. Table shows the results. Figures 2(A) to 2(D) are graphs of the Al concentration distribution.

[0115] Figures 3(A) to 3(D) are scanning electron microscope (SEM) photomicrographs ($\times 5000$) of the samples No. 1 to No. 3 and No. 100. Light gray granules in Figs. 3(A) to 3(C) and light gray substances of indefinite shapes in Fig. 3(D) are precipitates. Figure 3(D) shows that the die-cast component of the sample No. 100 contains large precipitates of indefinite shapes. This agrees with the fact that ultra-high concentration regions having a very high Al concentration have large indefinite shapes in the mapping image. In contrast, it is shown that the coiled material of the sample No. 1 in Fig. 3(A), the coiled solution-heat-treated material of the sample No. 2 in Fig. 3(B), and the sheet material (rapid heated and quenched material) of the sample No. 3 in Fig. 3(C) contain small precipitates and substantially uniformly distributed circular granules. In particular, it is shown that the coiled material of the sample No. 1 contains substantially uniformly dispersed circular granules having a substantially uniform size, and the coiled solution-heat-treated material of the sample No. 2 contains a very few very small precipitates. This agrees with the fact that small ultra-high concentration regions are dispersed in the mapping image. The solution-heat-treated materials of the samples No. 4 and No. 5 contained a very few very small precipitates as in the coiled solution-heat-treated material of the sample No. 2. The compositions of the light gray granules and the substances of indefinite shapes were examined with an energy dispersive X-ray spectrometer (EDS). They were found to be intermetallic compounds containing Al and Mg, such as $\text{Mg}_{17}\text{Al}_{12}$ and Al (MnFe). The presence of the intermetallic compounds can also be detected by analyzing the composition and structure by X-ray diffraction.

[0116] The average particle size (μm) and the total area ratio (% by area) of the intermetallic compounds in the samples No. 1 to No. 5 and No. 100 were measured. Table also shows the results. The average particle size and the area ratio can be easily determined by image processing of the photomicrographs using a commercially available image-processing apparatus.

[0117] The average particle size of an intermetallic compound was measured as described below. For each sample, three fields (a $22.7\ \mu\text{m} \times 17\ \mu\text{m}$ region per field) are selected for each observed image of five cross sections in the thickness direction. These fields were selected in the surface side region located at a depth of $100\ \mu\text{m}$ or less from the sample surface. The equivalent circular diameter (the diameter of a circle having an area equivalent to the area of an intermetallic compound) of each intermetallic compound in one observation field is determined for each observation field. The average particle size in an observation field is calculated by dividing the sum total of the equivalent circular diameters by the number of intermetallic compounds in the observation field: (the total of the equivalent circular diameters) / (the total number). Table shows the average of the average particle sizes of 15 observation fields for each sample.

[0118] The total area ratio of an intermetallic compound was measured as described below. As described above,

observation fields were selected in the surface side region. For each observation field, the areas of all the intermetallic compounds in one observation field are measured to calculate the total area. The area ratio of an observation field is calculated by dividing the total area by the area of the observation field ($385.9 \mu\text{m}^2$): (the total area)/(the area of the observation field). Table shows the average of the area ratios of 15 observation fields for each sample.

[0119] The corrosion loss ($\mu\text{g}/\text{cm}^2$) and the amount of eluted Mg ($\mu\text{g}/\text{cm}^2$) of the samples No. 1 to No. 5 and No. 100 were measured in a saltwater corrosion test. Table shows the results.

[0120] The corrosion loss was measured in a salt spray test according to JIS H 8502 (1999) performed as the saltwater corrosion test. A test specimen for corrosion is prepared from the samples No. 1 to No. 5 and No. 100. The mass (initial value) of the test specimen for corrosion is measured. An unnecessary portion of the test specimen for corrosion is masked such that a test surface having a predetermined size is exposed in the test specimen for corrosion. The masked test specimen for corrosion is placed in a corrosion test apparatus. The masked test specimen for corrosion is leaned against the apparatus at a predetermined angle with respect to the bottom of the apparatus (the angle between the bottom of the apparatus and the test specimen: 70 to 80 degrees). The test specimen for corrosion is sprayed with a test solution (5% by mass aqueous NaCl solution, temperature: $35 \pm 2^\circ\text{C}$) and is left to stand for a predetermined time (96 hours). After the predetermined time, the test specimen for corrosion is removed from the corrosion test apparatus, and the mask is removed. A corrosion product on the test specimen for corrosion is removed by chromic acid dissolution in accordance with a method described in Reference Table 1 in JIS Z 2371 (2000). After the corrosion product is removed, the mass of the test specimen for corrosion is measured. A difference between the mass and the initial value is divided by the area of the test surface of the test specimen for corrosion to determine the corrosion loss ($\mu\text{g}/\text{cm}^2$).

[0121] The amount of eluted Mg was measured under the following conditions in a salt immersion test performed as the saltwater corrosion test. A test specimen for corrosion is prepared from the samples No. 1 to No. 5 and No. 100. An unnecessary portion of the test specimen for corrosion is masked such that a test surface having a predetermined size is exposed in the test specimen for corrosion. The masked test specimen for corrosion is completely immersed in a test solution (5% by mass aqueous NaCl solution, fluid volume: (A) x 20 ml, wherein (A) cm^2 denotes the area (exposed area) of the test surface of the test specimen) for a predetermined time (96 hours, at room temperature ($25 \pm 2^\circ\text{C}$) with air conditioning). After the predetermined time, the test solution is collected. The amount of Mg ions in the test solution is measured by ICP-AES. The amount of Mg ions is divided by the area of the test surface of the test specimen for corrosion to determine the amount of eluted Mg ($\mu\text{g}/\text{cm}^2$).

[0122] [Table I]

[Table]

Sample No.	1	2	3	4	5	100
Form	Coiled material (without final solution heat treatment)	Coiled solution-heat-treated material (with final solution heat treatment)	Sheet material (rapid heated and quenched material)	Solution-heat-treated material (die casting)	Solution-heat-treated material (extrusion)	Die-cast component
Region having Al content of 4.2% or less (area%)	0	0	0	0	0	0.3
Region having Al content of 0.8x%-1.2x% (area%)	56.5	95.3	91.8	95.0	94.0	41.1
Region having Al content of 0.9x%-1.2x% (area%)	30.1	39.0	70.1	45.9	44.9	28.2
Region having Al content of 1.4x% or more (area%)	13.5	0.1	4.0	0.2	2.9	17.7

(continued)

Sample No.	1	2	3	4	5	100
Maximum Al (mass%)	29.8	15.7	25.2	21.4	21.4	34.8
Minimum Al (mass%)	5.1	6.1	6.4	6.9	6.9	3.5
Average particle size of intermetallic compound (μm)	0.3	<0.1	0.2	<0.1	<0.1	1.0
Area ratio of intermetallic compound (area%)	9.1	0.3	3.5	0.2	2.9	5.5
Corrosion loss ($\mu\text{g}/\text{cm}^2$)	625	242.1	173.4	220.9	219.0	2200
Amount of eluted Mg ($\mu\text{g}/\text{cm}^2$)	625.6	401.0	330.4	445.6	443.1	818.6

[0123] As shown by the table, in the samples No. 1 to No. 5, a central composition region having an Al concentration in the range of 0.8x% to 1.2x% by mass ($x = 8.75$) in at least the surface side region occupies 50% by area or more, there is no low-concentration region having an Al concentration of 4.2% by mass or less, and an ultra-high concentration region having an Al concentration of 1.4x% by mass or more occupies 17.5% by area or less. In particular, in the samples No. 1 to No. 5, the ultra-high concentration region occupies 15% by area or less, and a region having an Al concentration in the range of 0.9x% to 1.2% by mass occupies 30% by area or more. Thus, the samples No. 1 to No. 5 have small variations in Al concentration. This is also shown by the graphs in Figs. 2(A) to 2(D). Figures 2(A) to 2(C) show that the Al concentration distributions of the samples No. 1 to No. 3 have peaks at an Al overall average of 8.75% by mass and its vicinity. It is shown that the samples No. 1 to No. 3 have no portion having a very low Al concentration. The samples No. 4 and No. 5 also had an Al concentration distribution similar to that of the sample No. 2. As shown by the table, the samples No. 1 to No. 5 having such small variations in Al concentration have small corrosion loss and a small amount of eluted Mg, thus having high corrosion resistance.

[0124] In particular, the coiled solution-heat-treated material of the sample No. 2, the sheet material of the sample No. 3, and the solution-heat-treated materials of the samples No. 4 and No. 5 have a very large central composition region having an Al concentration in the range of 0.8x% to 1.2x% by mass, which occupies 70% by area or more, and a very small ultra-high concentration region having an Al concentration of 1.4x% by mass or more, which occupies 5% by area or less. The central composition region occupies 90% by area or more in some samples, and the ultra-high concentration region occupies 3% by area or less in some samples. Thus, Al is more uniformly distributed in the samples No. 2 to No. 5. In particular, the sample No. 2 has a very small ultra-high concentration region and has a small difference between the maximum value and the minimum value of the Al concentration, indicating that Al is still more uniformly distributed. The samples No. 2 to No. 5 having such a substantially uniform composition have high corrosion resistance.

[0125] In the coiled solution-heat-treated material of the sample No. 2 and the solution-heat-treated materials of the samples No. 4 and No. 5 that have been subjected to final solution heat treatment, the intermetallic compound is as little as 3% by area or less, and the maximum value of the Al concentration is relatively low. This also indicates that the samples No. 2, No. 4, and No. 5 have high corrosion resistance. In particular, since the sample No. 2 is a long material, the sample No. 2 can contribute to the mass production of a plastic worked component having high corrosion resistance and is expected to be of industrial importance.

[0126] In contrast, the die-cast component of the sample No. 100 contains a little central composition region having an Al concentration in the range of 0.8x% to 1.2x% by mass and a low-concentration region having an Al concentration of 4.2% by mass or less. In particular, the minimum value of Al corresponds to that of an AZ31 alloy. The sample No. 100 has a high area percentage of the intermetallic compound. Thus, it is supposed that the sample No. 100 has a portion having relatively low corrosion resistance and therefore has low corrosion resistance.

[Test Example 2]

[0127] The sheets of the samples No. 1 to No. 5 manufactured in the test example 1 was subjected to press forming, and their Al concentrations were measured in the same manner. The coiled material of the sample No. 1 and the coiled solution-heat-treated material of the sample No. 2 were unwound and were cut into rectangular sheets having a predetermined length. The sheets were preheated to 250°C and were subjected to press forming during heating. The total time of the holding time for the preheating and press forming is 2 minutes (0.1 hours or less).

[0128] The press formed materials (plastic worked components) had an Al concentration distribution similar to those of the samples No. 1 to No. 5. Thus, it is supposed that the press formed materials also have high corrosion resistance.

[0129] The present invention is not limited to these embodiments and may be modified within the gist of the present invention. For example, the composition (in particular, the Al content) of a magnesium alloy and the shape, specifications (thickness, width, and length), and manufacturing conditions of a magnesium alloy material may be modified.

Industrial Applicability

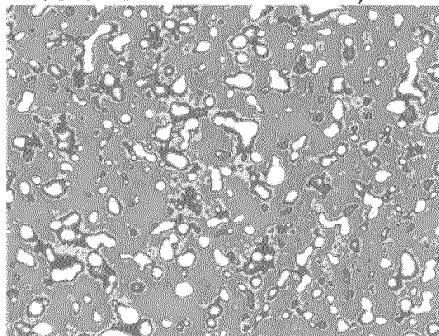
[0130] A magnesium alloy material according to the present invention can be suitably utilized in components of various electronic and electrical devices, particularly housings for mobile or small electronic and electrical devices, components for various fields requiring high strength, for example, parts of automobiles and components for transportation equipment, such as aircrafts, skeleton components, and bags. A magnesium alloy material according to the present invention can be suitably utilized as a material for these components.

Claims

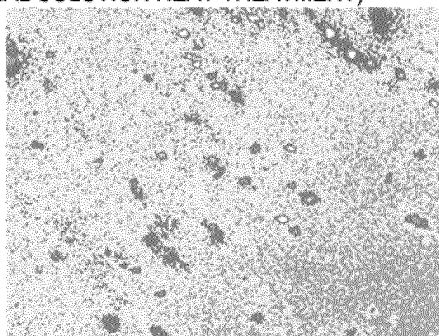
1. A magnesium alloy material, comprising a magnesium alloy that contains 7.3% by mass or more and 16% by mass or less Al, wherein
a region having an Al content of $(x \times 0.8)\%$ by mass or more and $(x \times 1.2)\%$ by mass or less occupies 50% by area or more,
a region having an Al content of $(x \times 1.4)\%$ by mass or more occupies 17.5% by area or less,
wherein $x\%$ by mass denotes the Al content of the entire magnesium alloy material, and
there is substantially no region having an Al content of 4.2% by mass or less.
2. The magnesium alloy material according to Claim 1, wherein
the region having an Al content of $(x \times 0.8)\%$ by mass or more and $(x \times 1.2)\%$ by mass or less occupies 70% by area or more, and
the region having an Al content of $(x \times 1.4)\%$ by mass or more occupies 5% by area or less.
3. The magnesium alloy material according to Claim 1 or 2, wherein a region having an Al content of $(x \times 0.9)\%$ by mass or more and $(x \times 1.2)\%$ by mass or less occupies 50% by area or more.
4. The magnesium alloy material according to any one of Claims 1 to 3, wherein the total area of an intermetallic compound containing at least one of Al and Mg is 3% by area or less in a cross section in a surface side region of the magnesium alloy material.
5. The magnesium alloy material according to any one of Claims 1 to 4, wherein the magnesium alloy material is a sheet.
6. The magnesium alloy material according to any one of Claims 1 to 5, wherein the magnesium alloy material is a coiled long sheet.
7. The magnesium alloy material according to any one of Claims 1 to 5, wherein the magnesium alloy material is a plastic worked component, which is a sheet that has been subjected to plastic working.

FIG. 1

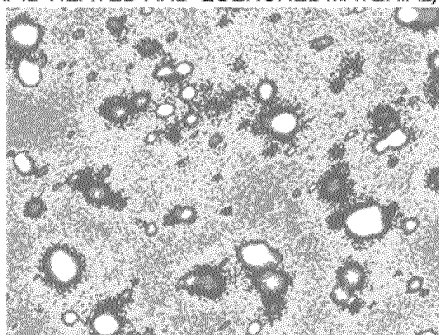
(A) SAMPLE NO. 1 COILED MATERIAL (WITHOUT FINAL SOLUTION HEAT TREATMENT)



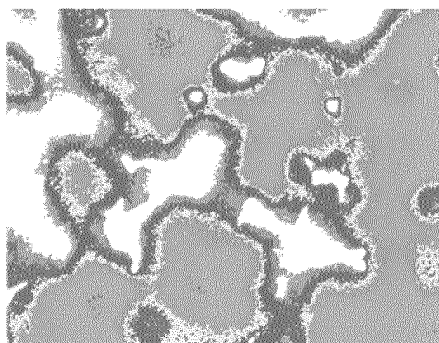
(B) SAMPLE NO. 2 COILED MATERIAL (WITH FINAL SOLUTION HEAT TREATMENT)



(C) SAMPLE NO. 3 SHEET MATERIAL (RAPID HEATED AND QUENCHED MATERIAL)



(D) SAMPLE NO. 100 DIE-CAST COMPONENT



5 μ m

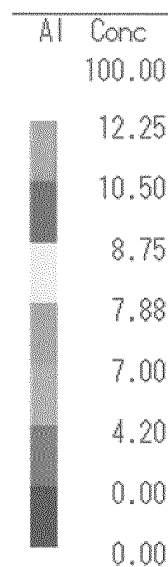


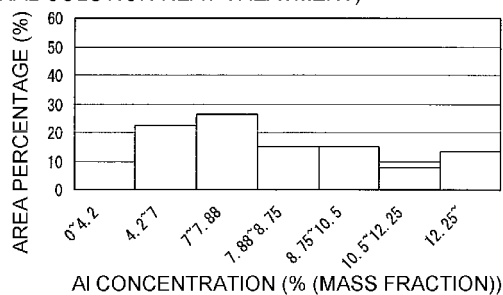
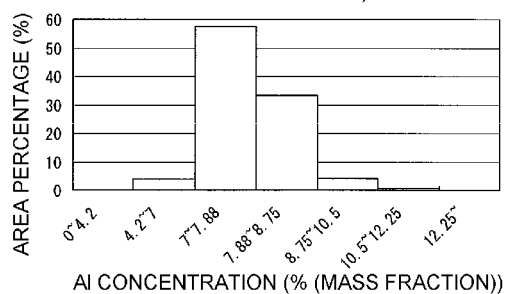
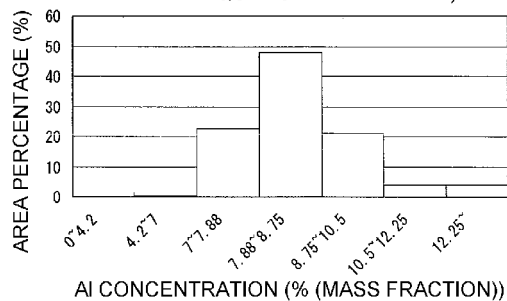
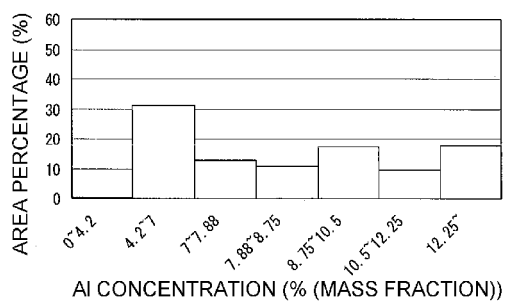
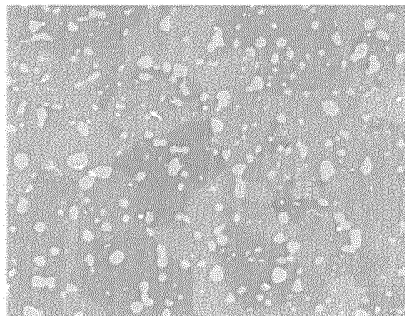
FIG. 2**(A)** SAMPLE NO. 1 COILED MATERIAL (WITHOUT FINAL SOLUTION HEAT TREATMENT)**(B)** SAMPLE NO. 2 COILED MATERIAL (WITH FINAL SOLUTION HEAT TREATMENT)**(C)** SAMPLE NO. 3 SHEET MATERIAL (RAPID HEATED AND QUENCHED MATERIAL)**(D)** SAMPLE NO. 100 DIE-CAST COMPONENT

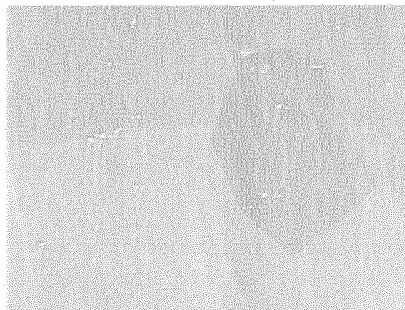
FIG. 3

(A) SAMPLE NO. 1 COILED MATERIAL(WITHOUT
FINAL SOLUTION HEAT TREATMENT)

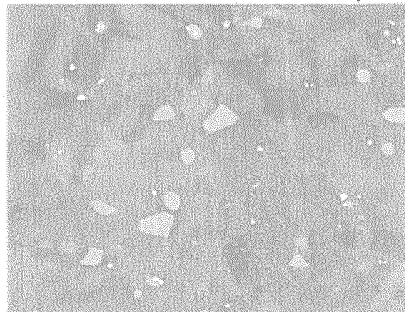
1 μ m



(B) SAMPLE NO. 2 COILED MATERIAL(WITH
FINAL SOLUTION HEAT TREATMENT)



(C) SAMPLE NO. 3 SHEET MATERIAL
(RAPID HEATED AND QUENCHED MATERIAL)



(D) SAMPLE NO. 100 DIE-CAST COMPONENT

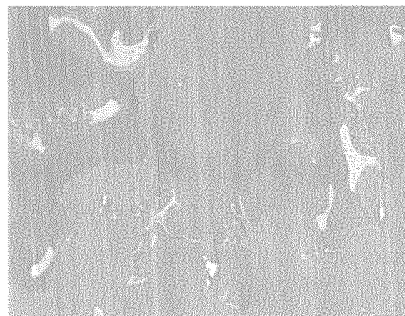
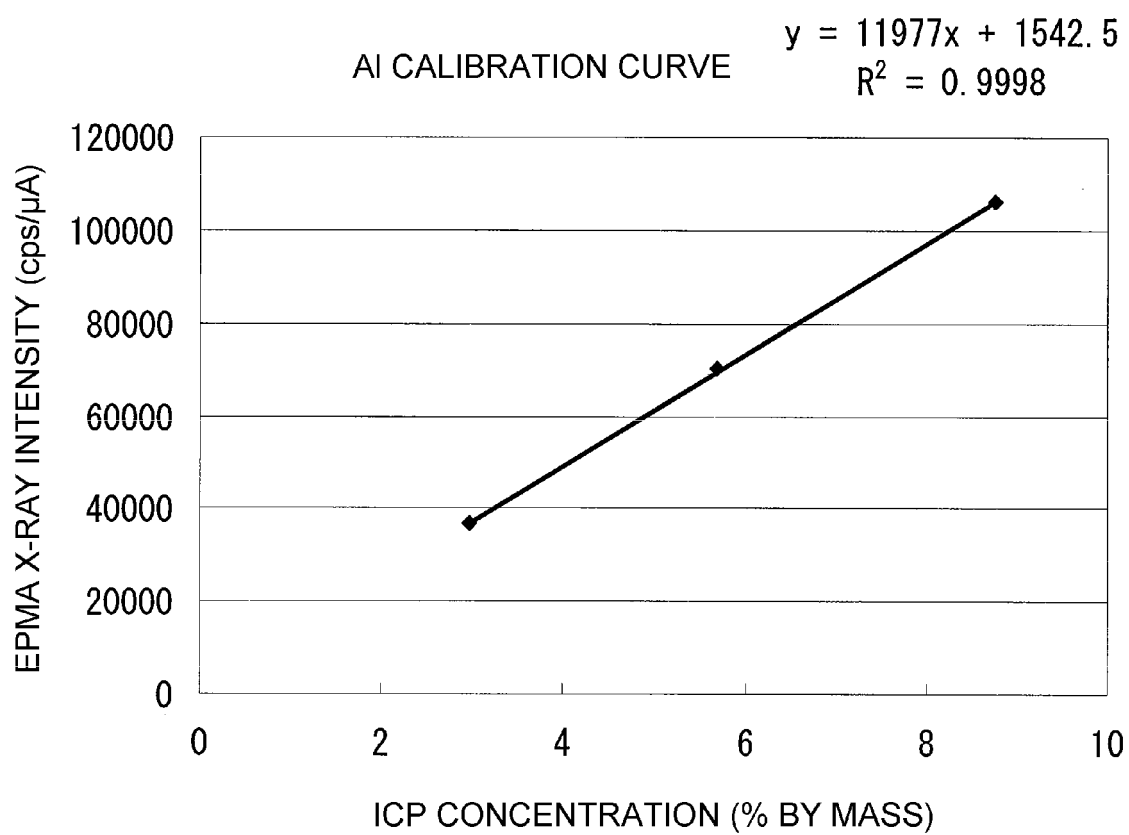


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/080455

A. CLASSIFICATION OF SUBJECT MATTER

C22C23/02(2006.01)i, C22C23/00(2006.01)n, C22C23/04(2006.01)n, C22C23/06(2006.01)n, C22F1/00(2006.01)n, C22F1/06(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, C22C23/00, C22C23/04, C22C23/06, C22F1/00, C22F1/06

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/047045 A1 (Sumitomo Electric Industries, Ltd.), 29 April 2010 (29.04.2010), paragraphs [0013] to [0017] & EP 2351863 A1	1-7
X	JP 11-36035 A (Matsushita Electric Industrial Co., Ltd.), 09 February 1999 (09.02.1999), claim 1; paragraphs [0009], [0018] & EP 892074 A1	1-7
X	JP 5-78775 A (Toyota Motor Corp.), 30 March 1993 (30.03.1993), claims; paragraphs [0020], [0021] (Family: none)	1-7

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search
02 April, 2012 (02.04.12)

Date of mailing of the international search report
10 April, 2012 (10.04.12)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/080455

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 5-171332 A (Toyota Motor Corp.), 09 July 1993 (09.07.1993), claims; paragraph [0016] (Family: none)	1-7
A	JP 2010-242146 A (Toyota Central Research and Development Laboratories, Inc.), 28 October 2010 (28.10.2010), entire text (Family: none)	1-7
A	JP 2006-348349 A (Katsuyoshi KONDO), 28 December 2006 (28.12.2006), entire text & US 2009/0263268 A1 & EP 1897638 A1 & WO 2006/134980 A1 & CN 101193715 A & KR 10-2008-0028362 A	1-7

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2007098470 A [0005]