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#### (54) ALUMINUM ALLOY PLATE FOR TANK AND MANUFACTURING METHOD THEREFOR

(57)Disclosed in the present invention are an aluminum alloy plate for a tank and a manufacturing method therefor. By means of optimizing the proportions of the main alloying elements of Mn, Mg, Fe and Si and accurately regulating and controlling the distribution of an intermetallic compound, the occurrence rate of perforation is effectively reduced. The utilization rate of regenerated materials of the same series of the product is ≥50%, and the product has unique hereditary structure characteristics: the proportion of a loose area of 2  $\mu m$  or more in a low-multiple section of an ingot which has not been subjected to homogenization is 0.05-0.18%, and there is no large-size second phase having a size of 70 μm or more. The conversion rate of the AIFeMnSi phase after homogenization is 80-95%. In a longitudinal section of a finished aluminum alloy plate for a tank, the total area proportion of intermetallic compound phases such as AIFeMnSi, which have a size of 5 µm or more, and inclusions is in a range of 0.08-0.80%.

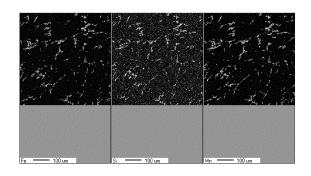


FIG. 1

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#### Description

#### **Technical Field**

**[0001]** The present disclosure relates to the technical field of metallic materials and their processing, in particular to an aluminum alloy sheet for a can body with excellent perforation resistance and low cost, and a method for preparing the same.

#### **Background Art**

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**[0002]** Compared with tin-plated steel cans, aluminum cans have become one of the most heavily used materials in the metal packaging industry due to their advantages like light weight, corrosion resistance, good thermal conductivity, good formability, easy recycling, simple post-printing processing, and environmental friendliness. An aluminum alloy sheet for a can body may be manufactured by homogenizing, hot rolling and cold rolling a large-size flat cast slab of aluminum alloy. After the resulting sheet is degreased, washed and oiled, it may be used to manufacture beer and beverage cans through processes such as cup body forming, washing, drying, coating, baking, necking and flanging.

**[0003]** Beer and beverage cans need to have a certain compressive strength. However, after baking, the strength of the cans will decrease. In order to reduce the degradation of the strength after baking, it is necessary to control and optimize the solid-dissolution amounts, relative contents and precipitation amounts of alloying elements including impurity elements. In the case of improper control, substrates with higher perforation risk will flow into downstream can-making enterprises. Since post-canning tracing is difficult for the downstream enterprises, to be on the safe side, they often isolate or return the entire batch of substrates with perforation defects. The sum of claim for compensation not only involves the can bodies themselves, but also involves the value of the entire cans and the user experience, which often exceeds the cost of the can bodies by many times, causing huge losses and waste of resources. Therefore, if recycled aluminum can be put into use, it will bring huge long-term benefits to the ecological environment and energy utilization.

[0004] At present, the waste reclamation, regeneration technology and comprehensive utilization of aluminum cans are gaining more and more attention from the product development end. However, the waste recycling will bring in additional impurity elements such as Fe, Si and the like. This brings more severe challenges to the existing use rate and quality control of a recycled material. Moreover, the level of precise control of alloying elements including impurity elements has a direct influence on the application scope of a low-cost material. Therefore, in view of the fact that the proportion of a recycled material in use is continuously increased, an unavoidable primary issue in designing a low-cost, high-performance wrought aluminum alloy packaging material is to sharpen the ability to precisely control the type and relative content, size distribution, and spatial distribution of an intermetallic compound in the aluminum alloy.

**[0005]** Among the existing aluminum alloy sheets for can bodies, there is no material that can achieve a low cost, a high use rate of recycled aluminum, and a low perforation incidence at the same time. As such, a problem in an urgent need to be solved in the industry for developing wrought aluminum alloy products is how to manufacture a new environmentally friendly aluminum alloy that has both a low cost and a low perforation incidence.

#### **Summary**

[0006] In order to solve the above problem, the inventors have conducted service simulation tests on the composition and impurity distribution of an aluminum material, and have discovered that the type and spatial size distribution feature of an intermetallic compound in the matrix are closely related with the incidence of perforation defects in the can material. [0007] On such a basis, one of the objects of the present disclosure is to provide an aluminum alloy sheet for a can body, wherein the aluminum alloy sheet for a can body is prepared using a recycled can body material of the same series, wherein the aluminum alloy sheet for a can body comprises, by mass percentage, Mn: 0.70-1.35%, Mg: 0.80-1.55%, Si: 0.30-0.50%, Fe: 0.40-0.80% (e.g., 0.40-0.75%), Cu: 0.15-0.35%, Zn: 0-0.30%, Ti: 0-0.08%, a rare earth mixture of Ce+La: 0.005-0.008%, and a balance of Al and other unavoidable impurities, wherein a mass ratio of Fe/Si is greater than 1.5; and the recycled can body material of the same series is added in an amount that accounts for at least 50% of a total weight of the aluminum alloy sheet. Preferably, by mass percentage, the aluminum alloy sheet for a can body comprises Mn: 1.00-1.15%, Mg: 0.80-1.20%, Si: 0.40-0.50%, Fe: 0.70-0.80%, Cu: 0.20-0.30%, Zn: 0.08-0.15%, Ti: 0.05-0.08%, a rare earth (RE, Rare Earth) mixture of Ce+La: 0.005-0.008%, and a balance of Al and other unavoidable impurities, wherein the mass ratio of Fe/Si is greater than 1.5 and less than or equal to 1.8.

**[0008]** As used herein, "the same series" means aluminum alloys with the same first digit in their grades according to Standard GB/T 3190-2020 (e.g., 2219 and 2195, or 7001 and 7075 belong to "aluminum alloys of the same series" respectively).

[0009] In some prior arts, in order to solve the problem that the strength of a can made from a high Si waste material is insufficient, the Fe/Si mass ratio is controlled below 1, but this solution cannot overcome perforation defects. By taking into

account the negative influences of the Si and Fe elements in a recycled aluminum alloy material on the microstructure and product performances, the present disclosure provides an aluminum alloy sheet for a can body whose chemical composition is designed to limit the mass ratio of Fe/Si to greater than 1.5, and have a relatively increased content of Mg, so as to overcome the negative influences of Si and Fe on the microstructure and product performances.

[0010] In this technical solution, a trace amount of rare earth element(s) (Ce and/or La) is added to capture oxygen from high-melting-point and high-hardness metal oxide inclusions SiO<sub>2</sub>, MnO<sub>2</sub>, FeO, Al<sub>2</sub>O<sub>3</sub> remaining in the melt to plastically modify the oxides, thereby increasing the solid-dissolution amounts of the main alloying elements. If the AlTi<sub>3</sub> phase formed from the Ti and Al elements is not well controlled, it is easy to form a coarse second phase. After a recycled material (aluminum cans or other waste materials) is added, the excess Ti element in the original waste material still exists. Therefore, after melt casting, the excess Ti element tends to combine with the Al element and precipitate to form a coarse second phase of AlTi<sub>3</sub>. At this point, if an AlTiB modifier is still added to refine the grains, it is easy to result in a Ti content in the matrix that is too high. Considering that rare earth elements are prone to combining with the B element to form RE-B compounds which become nucleation points and inhibit grain growth, thus having a grain refining effect, the relative content of the refiner Al-Ti-B can be reduced appropriately.

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**[0011]** In addition, since the amount of the recycled can body material of the same series added accounts for at least 50% of the total metal mass, the input of fresh aluminum is reduced greatly, which is conducive to low-carbon production of a cost-effective aluminum alloy material for a can body.

**[0012]** Further, in the aluminum alloy sheet for a can body, the total area fraction of an intermetallic compound phase (such as AIFeMnSi) and an inclusion of 5  $\mu$ m or more is in the range of 0.08% to 0.80%, preferably not more than 0.5%, such as 0.2 to 0.5%; and/or the total area fraction of an intermetallic compound phase and an inclusion of 0.5 to 5  $\mu$ m is 0.3%-1.5%, preferably 1.10%-1.35%.

[0013] Since the intermetallic compound has a sharp angle at the edge, and it's quite different from the matrix in plasticity, it's extremely prone to inducing dislocation accumulation during the can body forming process, resulting in a potential cracking point. At the same time, opposing forces exist between intermetallic compounds, leading to voids which also form cracking points inside the sheet. Therefore, the perforation incidence of the can body cannot be reduced by simply controlling the proportion of a small-sized intermetallic compound phase. In the prior art, the cracking problem of a high Si can body is solved by limiting the area fraction of a small-sized intermetallic compound phase. In contrast, in the present disclosure, the occurrence of stress concentration is reduced by controlling the area fractions of an intermetallic compound phase and an inclusion of different sizes, thereby solving the cracking problem of a low-cost thin aluminum alloy sheet. [0014] Further, 75-95% of the Fe, Si and Mn elements in the aluminum alloy sheet for a can body are converted into AlFeMnSi. Preferably, the conversion ratio (based on area fraction) of the AlFeMnSi phase in the aluminum alloy sheet for a can body is 80-95%, preferably 85-95%. The conversion ratio of an element may be obtained by scanning a metallographic sample of the aluminum alloy sheet using EPMA (Electron Probe X-ray Micro-Analyzer) and counting the total area of the pixel points corresponding to the element signal.

[0015] Since the solid solubility of Fe in Al at room temperature is only 0.002%, and the solid solubility at 500°C is also only 0.005%, the excess Fe combines with Al to form a cathodic phase FeAl<sub>3</sub>, resulting in a decrease in local corrosion resistance. Moreover, Fe is prone to combining with Mn, a solid solution strengthening alloying element, to form a coarse lamellar (FeMn)Al<sub>6</sub> compound. As a result, on the one hand, the solid-dissolution amount of the solid solution strengthening element Mn is reduced, leading to baking softening; on the other hand, improper control of the size distribution of the intermetallic compound increases the risk of perforation and cracking of the thin can wall under the pressure inside the can. The excess Si combines with Mn to form a complex ternary phase Al<sub>12</sub>Mn<sub>3</sub>Si<sub>2</sub>, with Mg to form a Mg<sub>2</sub>Si precipitation phase, and with Fe to form an Al(FeMn)Si quaternary phase. Thus, the conversion of the primary crystal compound into an  $\alpha$ AlFeMnSi phase is promoted. The corrosion potential follows the following relationship: Mg<sub>2</sub>Si>Al<sub>6</sub>Mn> $\alpha$ AlFeMnSi> $\alpha$ -Al. Therefore, increasing the relative proportion of  $\alpha$ AlFeMnSi is beneficial to improving the corrosion resistance of the can material. Moreover, the proportion of the  $\alpha$ AlFeMnSi phase also has a non-negligible positive influence on the control of the cubic texture in the subsequent rolling process.

[0016] Further, the size of the second phase (including the non-Al matrix phase such as an intermetallic compound, an elemental phase, an impurity phase or an inclusion) in the aluminum alloy sheet for a can body does not exceed 70  $\mu$ m. Controlling the size of the second phase can effectively reduce the incidence of failure caused by perforation defects in the thin aluminum alloy sheet for a can body.

[0017] Preferably, the porosity of the aluminum alloy sheet for a can body does not exceed 0.15%.

[0018] Further, the thickness of the aluminum alloy sheet for a can body is 0.23-0.50 mm.

**[0019]** Further, the aluminum alloy sheet for a can body has a tensile strength of ≥290MPa, for example, 290-310MPa; a yield strength of ≥270MPa, for example, 270-290MPa, and an elongation of ≥6.0%, for example, 6.0-7.0%.

<sup>5</sup> [0020] Further, the pre-service yield strength of the aluminum alloy sheet for a can body is ≥250MPa, for example, 250-260MPa.

[0021] Further, the perforation incidence of the aluminum alloy sheet for a can body is  $\leq$ 10ppm, for example,  $\leq$ 5ppm. [0022] Further, the perforation fracture surface of the aluminum alloy sheet for a can body is devoid of impurities.

**[0023]** The primary alloy composition of the aluminum alloy sheet for a can body provided by the present disclosure is limited, and the conversion ratio of the  $\alpha$ AlFeMnSi phase is quantitatively controlled, so that the distribution of the second phase is more dispersive and more uniform, and the size distribution at a hazardous level is further narrowed. The incidence of perforation defects after canning is reduced by at least 10ppm in comparison with those products manufactured by conventional processes, indicating excellent perforation resistance.

**[0024]** Another object of the present disclosure is to provide a method for preparing an aluminum alloy sheet for a can body, comprising the following steps:

Batching: Adding a recycled can body material of the same series, an aluminum ingot, rare earth metals and metal additives to prepare a batch material, wherein the recycled can body material of the same series is added in a mass amount that accounts for at least 50% of a total mass of the batch material, e.g., 50-70% or 50-60%; by mass percentage, the batch material is controlled to comprise Mn: 0.70-1.35%, Mg: 0.80-1.55%, Si: 0.30-0.50%, Fe: 0.40-0.80% (e.g., 0.40-0.75%), Cu: 0.15-0.35%, Zn: 0-0.30%, Ti: 0-0.08%, a rare earth mixture of Ce+La: 0.005-0.008%, and a balance of Al and unavoidable impurities; wherein a mass ratio of Fe/Si is greater than 1.5; preferably, the batch material is controlled to comprise Mn: 1.00-1.15%, Mg: 0.80-1.20%, Si: 0.40-0.50%, Fe: 0.70-0.80%, Cu: 0.20-0.30%, Zn: 0.08-0.15%, Ti: 0.05-0.08%, a rare earth (RE, Rare Earth) mixture of Ce+La: 0.005-0.008%, and a balance of Al and other unavoidable impurities, wherein the mass ratio of Fe/Si is greater than 1.5 and less than or equal to 1.8;

Smelting;

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Casting to obtain a flat cast slab; Homogenization; and

Rolling.

**[0025]** This technical solution allows the matrix structure, impurity elements and inclusions of the aluminum alloy sheet made using a recycled can body material to be more evenly distributed, reducing the incidence of perforation defects in the thin aluminum alloy sheet. At the same time, this solution also reduces the input of fresh aluminum, which is conducive to low-carbon production of a cost-effective aluminum alloy material for a can body.

[0026] Further, in the batching step, an aluminum ingot with Al≥99.70% by mass percentage is selected.

[0027] Further, the recycled can body material is a Series 3 recycled aluminum alloy material. A recycled material is also named a recovered material, or a secondary material. It is an aluminum alloy or aluminum metal obtained by smelting an aluminum waste material, an aluminum alloy waste material, or an aluminum-containing waste material. A recycled material must undergo strict internal control testing before it is put into use. The Series 3 recycled aluminum alloy material used in the present disclosure has a well-known meaning in the art, and refers to an aluminum alloy with AlMn as the main component, originating from waste materials from the AlMn aluminum alloy process, recycled can materials, etc.

**[0028]** Further, in the batching step, according to the melting points and burn-off ratios of the alloying elements, the metal additives are added in the order of Mn, Si, Fe, Cu, Mg, and the rare earth mixture to further save energy.

**[0029]** Further, in the smelting step, smelting is performed in a smelting furnace, and refining is performed in a holding furnace, followed by standing still. In some embodiments, AL-5Ti-0.2B is used as a refiner for online grain refinement in an amount of 1.0-1.3 kg per ton aluminum; a SNIF (Spinning Nozzel Inert Floatation) degassing device is used for online degassing, with the H content in the melt being controlled to be  $\le$ 0.12 ml/100 g Al; and the melt is purified by 50 PPI plate filtration and RC grade or higher tubular filtration.

**[0030]** Further, the flat cast slab obtained in the casting step has a fraction of loosening area of 2  $\mu$ m or more in a low-magnification cross section in the range of 0.05-0.18%.

**[0031]** In some embodiments, the flat cast slab is obtained by semi-continuous casting at a casting speed of 50-60 mm/min and a casting temperature of 660-710°C. Subsequently, the sprue portion and the starter head portion are saw-cut from the flat cast slab and milled, with the saw-cutting length of the sprue portion from the cast slab being  $\geq$ 150mm, and the saw-cutting length of the starter head portion from the cast slab being  $\geq$ 400mm. The cast slab obtained has a fraction of loosening area of 2  $\mu$ m or more in a low-magnification cross section in the range of 0.05-0.18%. In some embodiments, prior to homogenization, the large surface of the flat cast slab is milled with a milling amount of 10-15 mm, and the side surface of the cast slab is milled with a milling amount of 8-12 mm.

**[0032]** Further, in the homogenization step, the flat cast slab obtained in the casting step is milled and then subjected to homogenization treatment at 570-610°C for 8-15 hours, for example, 10-15 hours or 8-12 hours. Since the use of the recycled material brings in a higher content of Si and Fe, stress concentration points are formed when the coarse second phase is formed. The stress concentration points, besides inclusions, are one of the main causes of perforation defects. In addition to all the advantages brought by the composition of the elements, this technical solution also allows for optimization of the degree of elemental segregation inside the cast slab, which not only avoids overburning, but also ensures that the a phase conversion ratio is greater than 80%, and the matrix structure, impurity elements and inclusions are more evenly distributed, thereby reducing the incidence of perforation defects after canning by at least 10ppm in

comparison with those products manufactured by conventional processes. Subsequently, the flat cast slab is cooled rapidly by lowering the temperature of the flat cast slab to 510-540°C at full power, and held for 2-12 hours before being discharged from the furnace and rolled. The cooling rate is controlled within 20-80°C/h.

[0033] Further, the rolling step comprises:

Hot rough rolling: After the flat cast slab is milled, the flat cast slab is cooled rapidly, wherein the start temperature of the hot rough rolling is controlled to be  $510-540^{\circ}$ C, and the final temperature of the hot rough rolling is  $\geq 450^{\circ}$ C, so as to obtain a hot-rough-rolled sheet with a thickness of 30-45mm;

Hot finish rolling: The hot-rough-rolled sheet is subjected to hot finish rolling, wherein the final temperature of the hot finish rolling is controlled to be 320-360°C, so as to obtain a hot-finish-rolled sheet with a thickness of 1.6-3.0 mm, preferably 1.6-2.5 mm;

Cold rolling: The final temperature of the cold rolling is controlled to be  $145-160^{\circ}$ C, and the reduction rate of the final pass is controlled to be  $\geq 87\%$ , so as to obtain a cold-rolled sheet with a thickness of 0.23-0.50 mm.

5 **[0034]** In some embodiments, in the above-mentioned hot rough rolling step, a hot-rough-rolled sheet with a thickness of 30-45 mm is obtained through 19-27 passes.

[0035] In some embodiments, in the cold rolling step, the total reduction rate obtained after 3-5 passes is  $\geq$  87%.

[0036] In the prior art, if the reduction rate of the rolling in the passes is not set to match the material, an intermetallic compound tends to aggregate and grow into a coarse and hazardous phase, instead of being broken sufficiently, which consumes the alloying element Mn around the coarse phase and fails to reduce the risk of cracking. By adopting the above technical solution, on the one hand, the size of the second phase in the aluminum alloy sheet for a can body is kept at 70  $\mu$ m or less, thereby reducing the incidence of failure caused by perforation defects in the thin aluminum alloy sheet for a can body, and on the other hand, the manufacture of a thinner sheet is enabled.

#### Description of the Drawings

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FIG. 1 shows the EPMA elemental map of the  $\alpha$ AIFeMnSi phase in Example 2, indicating a phase conversion ratio up to 91%:

FIG. 2 shows the EPMA elemental map of the  $\alpha$ AlFeMnSi phase in Comparative Example 3, indicating a phase conversion ratio of only 65%;

FIG. 3a shows the scanning electron microscope (SEM) metallograph of the matrix structure in Comparative Example 1:

FIG. 3b shows the scanning electron microscope fractograph at the perforation defect in Comparative Example 1; FIG. 3c shows the energy dispersive spectroscopy (EDS) result of the particles at the fracture surface in FIG. 3b, wherein the coarse second phase is Mg<sub>2</sub>Si;

FIG. 4a shows the scanning electron microscope fractograph at the pre-service crack in Comparative Example 2;

FIG. 4b shows the energy dispersive spectroscopy result of the particles at the fracture surface in FIG. 4a;

 $FIG.\ 5a\ shows\ the\ scanning\ electron\ microscope\ fractograph\ at\ the\ pre-service\ crack\ in\ Comparative\ Example\ 2;$ 

FIG. 5b shows the energy dispersive spectroscopy result of the particles at the fracture surface in FIG. 5a, wherein the particles are spinel-like inclusions, and cracks exist;

FIG. 6 shows the scanning electron microscope image of the matrix structure in Comparative Example 3, indicating the cracking morphology of the coarse second phase of a single particle with a size of more than 10 microns, and the surrounding pores.

#### **Detailed Description**

**[0038]** The embodiments of the present disclosure will be illustrated with reference to specific examples. Those skilled in the art can readily get knowledge of other advantages and effects of the present disclosure from the contents disclosed in this specification. Although the description of the present disclosure will be made with reference to preferred examples, it does not mean that the features of the present disclosure are limited to these embodiments. On the contrary, the purpose of introducing the present disclosure with reference to the examples is to cover other options or modifications that may be derived from the claims of the present disclosure. In order to provide an in-depth understanding of the present disclosure, the following description will include a good number of specific details. The present disclosure may also be practiced without these details. In addition, in order to avoid confusing or obscuring the main points of the present disclosure, some specific details will be omitted from the description. It should be noted that, in the absence of conflict, the examples of the present disclosure and the features in the examples may be combined with each other.

**[0039]** It should be noted that, in the present specification, like reference numerals and letters designate like items in the following drawings, and therefore, once an item is defined with reference to one drawing, it does not need to be further defined or explained in follow-up drawings. In addition, whenever a numerical range is mentioned herein, unless otherwise specified, the range shall include its endpoints and all integers and fractions within the range.

**[0040]** To make the objects, technical solutions and advantages of the present disclosure clearer, the embodiments of the present disclosure will be further described in detail with reference to the accompanying drawings.

**[0041]** The aluminum alloy sheet for a can body provided in the present disclosure may be prepared by the following method:

#### 10 (1) Batching

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**[0042]** A recycled can body material of the same series, an aluminum ingot, rare earth metals and metal additives are added to prepare a batch material, wherein the recycled can body material of the same series is added in a mass amount that accounts for at least 50% of a total mass of the batch material; wherein, by mass percentage, the batch material is controlled to comprise Mn: 0.70-1.35%, Mg: 0.80-1.55%, Si: 0.30-0.50%, Fe: 0.40-0.80%, Cu: 0.15-0.35%, Zn: 0-0.30%, Ti: 0-0.08%, a rare earth mixture of Ce+La: 0.005-0.008%, and a balance of Al and unavoidable impurities; wherein the mass ratio of Fe/Si is greater than 1.5.

[0043] In some embodiments, the recycled can body material is a Series 3 aluminum alloy recycled material; an aluminum ingot with Al ≥ 99.70% by mass percentage is selected; according to the melting points and burn-off ratios of the alloying elements, the metal additives are added in the order of Mn, Si, Fe, Cu, Mg, and the rare earth mixture to further save energy.

(2) Melting: Smelting is performed in a smelting furnace, and refining is performed in a holding furnace, followed by standing still.

**[0044]** Subsequently, in some embodiments, AL-5Ti-0.2B is used as a refiner for online grain refinement in an amount of 1.0-1.3 kg per ton aluminum; a SNIF (Spinning Nozzel Inert Floatation) degassing device is used for online degassing, with the H content in the melt being controlled to be  $\leq$ 0.12 ml/100 g Al; and the melt is purified by 50 PPI plate filtration and RC grade or higher tubular filtration.

#### (3) Casting

[0045] In some embodiments, the flat cast slab is obtained by semi-continuous casting at a casting speed of 50-60 mm/min and a casting temperature of 660-710°C. Subsequently, the sprue portion and the starter head portion are saw-cut from the cast slab and milled, with the saw-cutting length of the sprue portion from the cast slab being  $\geq$ 150mm, and the saw-cutting length of the starter head portion from the cast slab being  $\geq$ 400mm. The cast slab obtained has a fraction of loosening area of 2  $\mu$ m or more in a low-magnification cross section in the range of 0.05-0.18%.

**[0046]** Prior to homogenization, the large surface of the flat cast slab is milled with a milling amount of 10-15 mm, and the side surface of the cast slab is milled with a milling amount of 8-12 mm.

#### (4) Homogenization

[0047] The homogenization treatment is carried out at 570-610°C for 8-15 hours, for example, 10-15 hours.

**[0048]** Subsequently, the flat cast slab is cooled rapidly by lowering the temperature of the flat cast slab to 510-540°C at full power, and held for 2-12 hours before being discharged from the furnace and rolled. The cooling rate is controlled within 20-80°C/h.

#### (5) Rolling

[0049] Hot rough rolling: The start temperature of the hot rough rolling is controlled to be 510-540°C, for example, 530-540°C; the final temperature of the hot rough rolling is ≥ 450°C; and a hot-rough-rolled sheet with a thickness of 30-45 mm is obtained after 19-27 passes.

**[0050]** Hot finish rolling: The hot finish rolling is performed on the hot-rough-rolled sheet, and the final temperature of the hot finish rolling is controlled to be  $320-360^{\circ}$ C, so as to obtain a hot-finish-rolled sheet with a sheet thickness of 1.6-3.0 mm.

**[0051]** Cold rolling: The final temperature of the cold rolling is controlled to be 145-160°C, and the total reduction rate obtained after 3-5 passes is ≥87%, so as to obtain a cold-rolled sheet with a thickness of 0.23-0.50 mm.

[0052] Finally, the aluminum alloy sheet is trimmed, oiled, and cut up to be used for can bodies.

#### **Examples**

[0053] Following the above method, the Examples and Comparative Examples of the present disclosure are as follows:

Table 1 shows the compositions and process parameters for Examples 1 to 3 and Comparative Examples 1 to 3. The control of the alloy compositions was carried out at the melting and casting stage according to GB/T 3190-2008 "Wrought aluminium and aluminium alloys - Chemical composition", GB/T20975.1-31 "Method for chemical analysis of aluminum and aluminium alloys", and YST805-2012 "Method for analysis of rare earth in aluminium and aluminium alloys". As it can be seen by comparison, the use ratios of the recycled aluminum materials in Examples 1 to 3 were all no less than 50%, whereas the use rates of the recycled aluminum materials in Comparative Examples 1 to 3 were all no more than 35%. Compared with the Examples, the Fe/Si mass ratios in Comparative Examples 1 to 3 were lower than 1.5, and no rare earth elements (Ce+La) were added. In addition, the Cu content in Comparative Example 2 was also lower

Table 2 shows the purity indicators of Examples 1 to 3 and Comparative Examples 1 to 3. Industrial CT was used to perform nondestructive measurement of a low-density loosening matter, and the total area fraction of the intermetallic compound and inclusion of different sizes was obtained by pixel value statistics. Similarly, the area fraction of the intermetallic compound and inclusion could also be determined by examining multiple aluminum alloy sheet samples (e.g., 3) with an optical microscope or a scanning electron microscope at a magnification of 50-1000 times. EPMA was used to perform mapping measurement on the aluminum alloy sheet samples, and the conversion ratios of the Fe, Si, and Mn elements into  $\alpha$ AlFeMnSi were obtained based on the measured areas in the images. EPMA mapping was performed on the samples of Example 2 and Comparative Example 3, respectively, to detect the distribution of the Fe, Si, and Mn elements therein. The mapping results are shown by Figures 1 and 2. As found by pixel statistics, 91% of the Fe, Si, and Mn elements in Example 2 were distributed in the  $\alpha$ AlFEMnSi particles, whereas only about 73% was observed in Comparative Example 3. This means that in Example 2, the Fe, Si, and Mn elements were mostly present in the form of  $\alpha$ AlFEMnSi phase which is beneficial to the alloy performances, whereas a considerable portion of Fe and Si in Comparative Example 3 would form a corrosion-inducing phase such as FeAl<sub>3</sub>, or combine with the Mn element to form the (FeMn)Al<sub>6</sub> compound which is prone to causing baking softening, resulting in an increased risk of perforation.

Table 3 shows a comparison of the mechanical and pre-service performance indicators between Examples 1 to 3 and Comparative Examples 1 to 3. The methods for testing the mechanical performances of the alloys including tensile strength, yield strength and elongation meet the testing requirements of GB/T 228.1. Perforation incidence = (perforated cans from the same batch/finished cans from the same batch)  $\times$  100%, wherein the perforated cans are identified using a pinhole detector on a can production line. In this technical field, a reduction of 10 ppm in the incidence of perforation defects indicates that the perforation incidence of the product has been improved significantly.

Table 1: Compositions and process parameters of the Examples and Comparative Examples

)	wt%	Mn	Mg	Si	Fe	Cu	Zn	Ti	RE	Homogenization process	Use ratio of recycled material
	Ex. 1	1.13	0.85	0.43	0.77	0.30	0.11	0.06	0.005	580°C/12h	50%
5	Ex. 2	1.08	0.93	0.46	0.71	0.20	0.12	80.0	0.005	600°C/10h	55%
	Ex. 3	1.08	1.13	0.48	0.73	0.25	0.12	0.08	0.007	610°C/8h	60%
	Comp. Ex. 1	1.12	0.87	0.23	0.38	0.19	0.10	0.04	<u>0</u>	590°C/12h	30%
)	Comp. Ex. 2	1.18	1.02	0.21	0.40	<u>0.12</u>	0.19	0.03	<u>0</u>	590°C/12h	30%
	Comp. Ex. 3	1.01	1.17	0.28	0.48	0.25	0.22	0.04	<u>0</u>	590°C/12h	35%

Table 2: Purity indicators of Examples and Comparative Examples

5		Total area fraction % of intermetallic compound and inclusion of 0.5-5µm	Porosity (area fraction %)	Conversion ratio of αAIFeMnSi phase (area fraction %)	Size of second phase of cast ingot: ≥70µm within every 200mm² (number)	Total area fraction of intermetallic compound and inclusion of more than 5µm (area fraction %)
10	Ex. 1	1.31	0.11	87	0	0.28
	Ex. 2	1.29	0.10	91	0	0.33
	Ex. 3	1.15	0.14	90	0	0.49
	Comp. Ex. 1	0.47	0.24	67	2	1.61
	Comp. Ex. 2	0.33	0.26	70	5	1.83
15	Comp. Ex. 3	0.31	0.30	73	8	2.07

Table 3: Comparison of mechanical and pre-service performance indicators of Examples

20	No.	Traditional	mechanical p	erformances	Pre- service	Caus	Gauge	
		Tensile strength MPa	Yield strength MPa	Elongation %	Yield strength MPa	Perforation incidence ppm	Perforation fracture surface analysis	Sheet thickness (mm)
	Ex. 1	301	279	6.5	256	3	Fracture surface devoid of impurities	0.23
30	Ex. 2	296	274	6.3	253	2	Fracture surface devoid of impurities	0.23
	Ex. 3	299	276	6.4	255	4	Fracture surface devoid of impurities	0.25
35	Comp. Ex. 1 303		280	5.9	252	18	Coarse second phase	0.25
	Comp. Ex. 2	299	279	6.0	250	15	Inclusion, second phase	0.25
40	Comp. Ex. 3	305	282	5.8	253	21	Coarse second phase	0.30

[0054] As it can be seen from the results of the comparison, the aluminum alloy sheet for a can body provided according to the present disclosure exhibits superior purity indicators. Its porosity is reduced (<0.15%); the inclusion with larger size and higher hardness is controlled and modified effectively; the conversion ratio of the second phase (the conversion ratio of the  $\alpha$ AlFeMnSi phase) is further improved; and the size distribution at a hazardous level is further narrowed. With the same sheet thickness, the incidence of perforation defects after canning is reduced by at least 10ppm in comparison with those products manufactured by conventional processes. The metallographic sample of Comparative Example 1 was subjected to scanning electron microscopy analysis. As shown by FIG. 3a, multiple particles of at least 10 µm were present in the sample structure. The fracture position of the perforated sample of Comparative Example 1 was subjected to scanning electron microscopy analysis, with the result shown by FIG. 3b. Particles with a width of about 10 µm were visible at the fracture position. The particles at the fracture surface were subjected to energy dispersive spectroscopy analysis, with the result shown by FIG. 3c, indicating that the particles at the fracture surface were Mg<sub>2</sub>Si. A fracture surface of the sample in Comparative Example 2 at the pre-service cracking site was subjected to scanning electron microscopy analysis, with the result shown by FIG. 4a. Particles of at least 10 µm were visible at the fracture surface. The particles were subjected to energy dispersive spectroscopy analysis, with the result shown by FIG. 4b, indicating that the particles at the fracture surface were SiO2. Another fracture surface of the sample in Comparative Example 2 at the pre-service cracking site was subjected to scanning electron microscopy analysis, with the result shown by FIG. 5a. Broken particles of at least

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 $10~\mu m$  were also visible at the fracture surface. The particles were subjected to energy dispersive spectroscopy analysis, with the result shown by FIG. 5b, indicating a mixture of the Mg-Si-O elements, which was inferred to be a spinel-like inclusion. This suggests that the particles of the strengthening phase in the structure in Comparative Example 2 were not fine or distributed dispersively, not conducive to the performances of the aluminum alloy sheet. The metallographic sample of Comparative Example 3 was subjected to scanning electron microscopy analysis. As shown by FIG. 6, it can be seen that multiple large particles of at least  $10~\mu m$  were present in the sample structure, and pores or cracks were present between the particles and the matrix, indicating that these particles had an adverse effect on the mechanical performances of the aluminum alloy sheet.

**[0055]** While the aluminum alloy sheets of Examples 1-3 had lower perforation risk and better structural performances, the input rate of the recycled materials of the same series in Examples 1-3 was increased to at least 50%, which could save the total cost by 350-420 yuan/ton compared with Comparative Examples 1-3.

**[0056]** Although the present disclosure has been illustrated and described with reference to certain preferred embodiments of the present disclosure, those skilled in the art shall understand that the above contents are intended to further describe the present disclosure in detail with reference to the specific embodiments, and it shall not be construed that the specific practice of the present disclosure is limited to these descriptions. Those skilled in the art can make various changes in form and details, including making several simple deductions or substitutions, without departing from the spirit and scope of the present disclosure.

#### 20 Claims

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- 1. An aluminum alloy sheet for a can body, wherein the aluminum alloy sheet for a can body comprises, by mass percentage:
- <sup>25</sup> Mn: 0.70-1.35%, Mg: 0.80-1.55%, Si: 0.30-0.50%, Fe: 0.40-0.80%, Cu: 0.15-0.35%, Zn: 0-0.30%, Ti: 0-0.08%, a rare earth mixture of Ce+La: 0.005-0.008%, and a balance of Al and other unavoidable impurities; wherein a mass ratio of Fe/Si is greater than 1.5;
  - preferably, the aluminum alloy sheet for a can body comprises, by mass percentage, Mn: 1.00-1.15%, Mg: 0.80-1.20%, Si: 0.40-0.50%, Fe: 0.70-0.80%, Cu: 0.20-0.30%, Zn: 0.08-0.15%, Ti: 0.05-0.08%, a rare earth (RE, Rare Earth) mixture of Ce+La: 0.005-0.008%, and a balance of Al and other unavoidable impurities, wherein the mass ratio of Fe/Si is greater than 1.5 and less than or equal to 1.8;
  - wherein in the aluminum alloy sheet for a can body, a content of a recycled can body material of the same series accounts for at least 50% of a total weight of the aluminum alloy sheet.
- 2. The aluminum alloy sheet for a can body according to claim 1, wherein in the aluminum alloy sheet for a can body:
  - a total area fraction of an intermetallic compound phase and an inclusion of 5  $\mu$ m or more is in the range of 0.08% to 0.80%; and/or
  - a total area fraction of an intermetallic compound phase and an inclusion of 0.5 to 5  $\mu m$  is 0.3%-1.5%.
  - 3. The aluminum alloy sheet for a can body according to claim 1, wherein in the aluminum alloy sheet for a can body:
    - a total area fraction of an intermetallic compound phase and an inclusion of 5  $\mu$ m or more is not more than 0.5%; and/or
- 45 a total area fraction of an intermetallic compound phase and an inclusion of 0.5 to 5 μm is 1.10%-1.35%.
  - **4.** The aluminum alloy sheet for a can body according to claim 1, wherein 75-95%, preferably no less than 80% of Fe, Si and Mn elements in the aluminum alloy sheet for a can body are converted into AIFeMnSi phase.
- 50 **5.** The aluminum alloy sheet for a can body according to claim 1, wherein:
  - the aluminum alloy sheet for a can body has a tensile strength of  $\geq$ 290MPa, for example, 290-310MPa; a yield strength of  $\geq$ 270MPa, for example, 270-290MPa, and an elongation of  $\geq$ 6.0%, for example, 6.0-7.0%; and/or the aluminum alloy sheet for a can body has a pre-service yield strength of  $\geq$ 250MPa, for example, 250-260MPa; and/or
  - the aluminum alloy sheet for a can body has a perforation incidence of  $\leq$ 10ppm, for example,  $\leq$ 5ppm; and/or the aluminum alloy sheet for a can body has a perforation fracture surface devoid of impurities.

- **6.** The aluminum alloy sheet for a can body according to claim 1, wherein the aluminum alloy sheet for a can body has a porosity of no more than 0.15%.
- 7. The aluminum alloy sheet for a can body according to claim 1, wherein a second phase in the aluminum alloy sheet for a can body has a size of no more than 70 μm.
  - 8. The aluminum alloy sheet for a can body according to claim 1, wherein the aluminum alloy sheet for a can body has a thickness of 0.23-0.50 mm.
- 10 9. A preparation method for an aluminum alloy sheet for a can body, comprising the following steps:

Batching: Adding a recycled can body material of the same series, an aluminum ingot, rare earth metals and metal additives to prepare a batch material, wherein the recycled can body material of the same series is added in a mass amount that accounts for at least 50% of a total mass of the batch material; by mass percentage, the batch material is controlled to comprise Mn: 0.70-1.35%, Mg: 0.80-1.55%, Si: 0.30-0.50%, Fe: 0.40-0.80%, Cu: 0.15-0.35%, Zn: 0-0.30%, Ti: 0-0.08%, a rare earth mixture of Ce+La: 0.005-0.008%, and a balance of Al and unavoidable impurities; wherein a mass ratio of Fe/Si is greater than 1.5; preferably, by mass percentage, the batch material is controlled to comprise Mn: 1.00-1.15%, Mg: 0.80-1.20%, Si: 0.40-0.50%, Fe: 0.70-0.80%, Cu: 0.20-0.30%, Zn: 0.08-0.15%, Ti: 0.05-0.08%, a rare earth (RE, Rare Earth) mixture of Ce+La:

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0.005-0.008%, and a balance of Al and other unavoidable impurities, wherein the mass ratio of Fe/Si is greater than 1.5 and less than or equal to 1.8;

Smelting;

Casting to obtain a flat cast slab;

Homogenization; and

Rolling.

- 10. The preparation method for an aluminum alloy sheet for a can body according to claim 9, wherein: the recycled can body material is a Series 3 recycled aluminum alloy material; and/or the aluminum ingot has an Al content of ≥99.70wt%.
- 11. The preparation method for an aluminum alloy sheet for a can body according to claim 9, wherein in the batching step, the metal additives are added in the order of Mn, Si, Fe, Cu, Mg, and the rare earth mixture.
- 12. The preparation method for an aluminum alloy sheet for a can body according to claim 9, wherein the smelting is performed in a smelting furnace, and refining is performed in a holding furnace, followed by standing still; preferably, Al-5Ti-0.2B is used as a refiner for online grain refinement in an amount of 1.0-1.3 kg per ton aluminum; a SNIF degassing device is used for online degassing, with a H content in a melt being controlled to be ≤0.12 ml/100 g Al; and the melt is purified by 50 PPI plate filtration and RC grade or higher tubular filtration.

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- 13. The preparation method for an aluminum alloy sheet for a can body according to claim 9, wherein the flat cast slab obtained in the casting step has a fraction of loosening area of 2 μm or more in a low-magnification cross section in the range of 0.05-0.18%;
- preferably, the flat cast slab is obtained by semi-continuous casting at a casting speed of 50-60 mm/min and a casting temperature of 660-710°C; subsequently, a sprue portion and a starter head portion are saw-cut from the cast slab and milled, with a saw-cutting length of the sprue portion from the cast slab being ≥150mm, and a saw-cutting length of the starter head portion from the cast slab being ≥400mm.
- 14. The preparation method for an aluminum alloy sheet for a can body according to claim 9, wherein in the homogenization step, the flat cast slab obtained in the casting step is milled and then subjected to homogenization treatment at 570-610°C for 8-15 hours;

preferably, a large surface of the flat cast slab is milled with a milling amount of 10-15 mm, and a side surface of the flat cast slab is milled with a milling amount of 8-12 mm; preferably, after the homogenization treatment, the flat cast slab is cooled at a cooling rate of 20-80°C/h to lower a

temperature of the flat cast slab to 510-540°C, held for 2-12 hours, and then discharged.

15. The preparation method for an aluminum alloy sheet for a can body according to claim 9, wherein the rolling step

## comprises:

Hot rough rolling: After the flat cast slab is milled, the flat cast slab is cooled rapidly, wherein a start temperature of the hot rough rolling is controlled to be  $510-540^{\circ}$ C, and a final temperature of the hot rough rolling is  $\geq 450^{\circ}$ C, so as to obtain a hot-rough-rolled sheet with a thickness of 30-45mm; preferably, a hot-rough-rolled sheet with a thickness of 30-45mm is obtained after 19-27 passes;

Hot finish rolling: The hot finish rolling is performed on the hot-rough-rolled sheet, and a final temperature of the hot finish rolling is controlled to be 320-360°C, so as to obtain a hot-finish-rolled sheet with a sheet thickness of 1.6-3.0 mm;

Cold rolling: A final temperature of the cold rolling is controlled to be 145-160°C, and a total processing degree of the final pass is  $\ge$ 87%, so as to obtain a cold-rolled sheet with a thickness of 0.23-0.50 mm; preferably, a total reduction rate obtained after 3-5 passes is  $\ge$  87%.

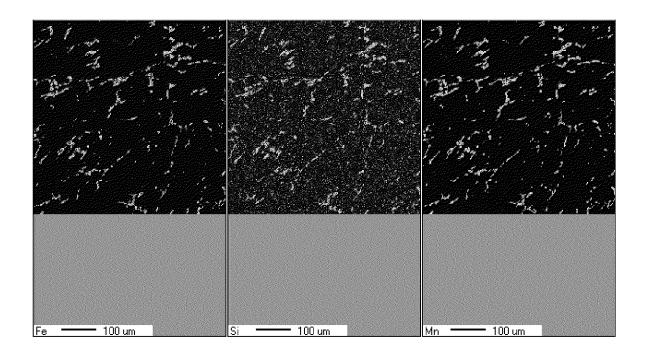


FIG. 1

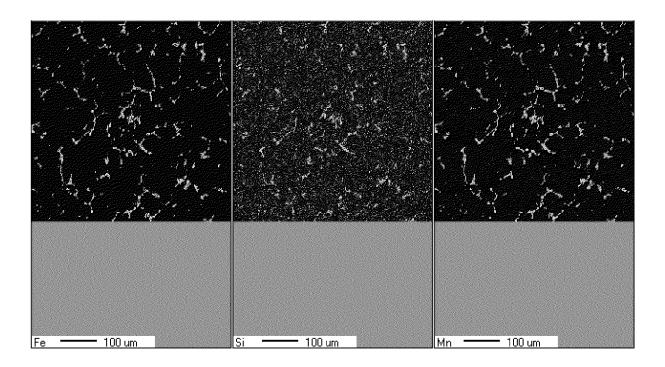


FIG. 2

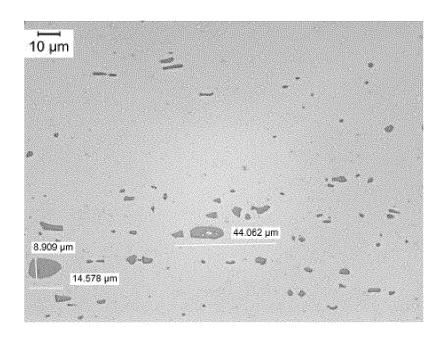


FIG. 3a

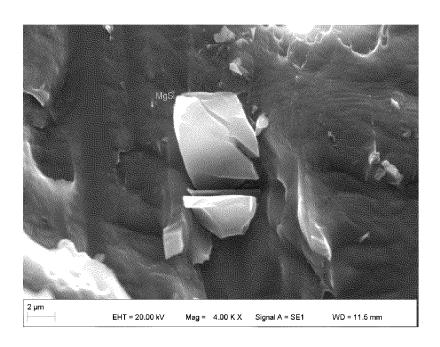


FIG. 3b

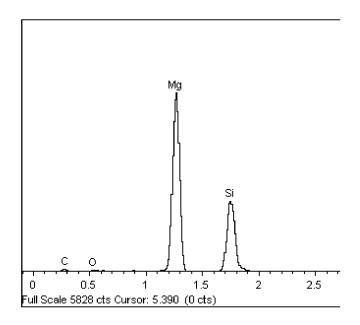


FIG. 3c



FIG. 4a

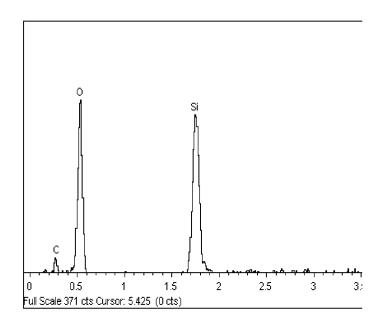


FIG. 4b

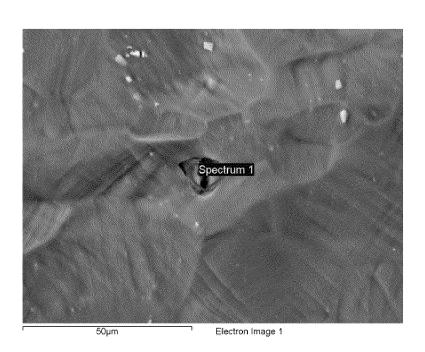


FIG. 5a

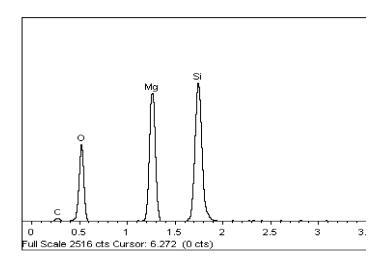


FIG. 5b

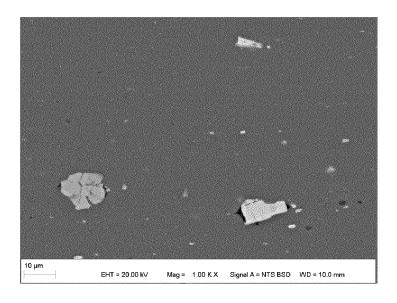


FIG. 6

International application No.

INTERNATIONAL SEARCH REPORT

PCT/CN2023/089036 5 CLASSIFICATION OF SUBJECT MATTER C22C21/08(2006.01)i;C22F1/05(2006.01)i;C22C1/06(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC 10 FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC: C22C, C22F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched 15 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CNKI, CNABS, DWPI: 铝合金, 板, 罐, 锰, 镁, 铁, 硅, 稀土, 镧, 铈, aluminum alloy, plate, can, manganese, magnesium, iron, silicon, rare earths, lanthanum, cerium C. DOCUMENTS CONSIDERED TO BE RELEVANT 20 Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. CN 113549794 A (SHANDONG HONGQIAO NEW MATERIAL CO., LTD. et al.) 26 1-15 October 2021 (2021-10-26) claims 1-10 25 Y JP H01119637 A (FURUKAWA ALUMINIUM) 11 May 1989 (1989-05-11) 1-15 description, page 2 CN 111910111 A (CHALCO RUIMIN CO., LTD. et al.) 10 November 2020 (2020-11-10) Y 1-15 claims 1-10 Y CN 105441742 A (HEFEI BIAOBING KAIJI NEW MATERIALS CO., LTD.) 30 March 2016 1-15 30 (2016-03-30) claims 1-9 CN 109518044 A (CHALCO MATERIAL APPLICATION RES INSTITUTE CO., LTD.) 26 Y 1-15 March 2019 (2019-03-26) claims 1-9 35 Y JP 2012188704 A (KOBE STEEL LTD. et al.) 04 October 2012 (2012-10-04) 1-15 Further documents are listed in the continuation of Box C. See patent family annex. later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention Special categories of cited documents: 40 document defining the general state of the art which is not considered to be of particular relevance document cited by the applicant in the international application 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 "D" earlier application or patent but published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art 45 document referring to an oral disclosure, use, exhibition or other document member of the same patent family document published prior to the international filing date but later than the priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 11 May 2023 17 May 2023 50 Name and mailing address of the ISA/CN Authorized officer China National Intellectual Property Administration (ISA/ China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088 55 Telephone No.

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# INTERNATIONAL SEARCH REPORT International application No. PCT/CN2023/089036 5 C. DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. US 2018282848 A1 (UACJ CORP. et al.) 04 October 2018 (2018-10-04) 1-15 claims 1-12 10 15 20 25 30 35 40 45 50

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