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(54) **PLATED STEEL SHEET**

(57) This plated steel sheet includes a steel sheet, and a plated layer disposed on a surface of the steel sheet, in which the plated layer has a chemical composition containing, in mass%, Al: 10.0 to 30.0%, Mg: 3.0 to 15.0%, Fe: 0.01 to 2.0%, Si: more than 0 to 2.0%, and Ca: 0.05 to 2.0%, and further containing one or two selected from the group consisting of the following group A and group B, with a remainder consisting of Zn and impurities,

a number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 0 to 10 per area of 10,000 μm^2 , and a number density of Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 1 to 50 per area of 10,000 μm^2 .

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Description

TECHNICAL FIELD

[0001] The present invention relates to a plated steel sheet.

[0002] Priority is claimed on Japanese Patent Application No. 2022-100352, filed June 22, 2022, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] A Zn-Al-Mg-based hot-dip plated steel sheet having a hot-dip Zn-plated layer containing Al and Mg has excellent corrosion resistance. Therefore, Zn-Al-Mg-based hot-dip plated steel sheets are widely used, for example, as a material for structural members required to have corrosion resistance, such as building materials.

[0004] For example, Patent Document 1 discloses a plated steel material including a steel material and a plated layer including a Zn-Al-Mg alloy layer disposed on a surface of the steel material, in which the Zn-Al-Mg alloy layer has a Zn phase and contains a Mg-Sn intermetallic compound phase in the Zn phase, the plated layer includes, in mass%, Zn: more than 65.0%, Al: more than 5.0% to less than 25.0%, Mg: more than 3.0% to less than 12.5%, Sn: 0.1% to 20.0%, and impurities, and has a chemical composition satisfying the following formulas 1 to 5.

$$\text{Formula 1: Bi} + \text{In} < \text{Sn}$$

$$\text{Formula 2: Y} + \text{La} + \text{Ce} \leq \text{Ca}$$

$$\text{Formula 3: Si} < \text{Sn}$$

$$\text{Formula 4: O} \leq \text{Cr} + \text{Ti} + \text{Ni} + \text{Co} + \text{V} + \text{Nb} + \text{Cu} + \text{Mn} < 0.25$$

$$\text{Formula 5: O} \leq \text{Sr} + \text{Sb} + \text{Pb} + \text{B} < 0.5$$

[0005] Patent Document 2 discloses a plated steel material including a steel material and a plated layer disposed on a surface of the steel material and including a Zn-Al-Mg alloy layer, in which in a cross section of the Zn-Al-Mg alloy layer, an area fraction of a MgZn_2 phase is 45 to 75%, an area fraction of a total of the MgZn_2 phase and an Al phase is 70% or more, and an area fraction of a Zn-Al-Mg Zn_2 ternary eutectic structure is 0 to 5%, the plated layer includes, in mass%, Zn: more than 44.90% to less than 79.90%, Al: more than 15% to less than 35%, Mg: more than 5% to less than 20%, Ca: 0.1% to less than 3.0%, and impurities, and in a case where an element group A is Y, La, and Ce, an element group B is Cr, Ti, Ni, Co, V, Nb, Cu, and Mn, an element group C is Sr, Sb, and Pb, and an element group D is Sn, Bi, and In, a plated steel material having a chemical composition in which a total content of elements selected from the element group A is 0% to 0.5%, a total content of Ca and the elements selected from the element group A is 0.1% to less than 3.0%, a total content of elements selected from the element group B is 0% to 0.25%, a total content of elements selected from the element group C is 0% to 0.5%, and a total content of elements selected from the element group D is 0% to 20.00%.

[0006] In recent years, hot-dip plated steel materials for building materials used for roofs, wall materials, and the like are required to have both planar corrosion resistance, which is the corrosion resistance of the plated layer itself, and adhesion (coating adhesion) of a coating film when applied to a plating surface. On the other hand, a technique for achieving both planar corrosion resistance and coating adhesion at a high level has not been studied. Citation List

Patent Document

[0007]

Patent Document 1: PCT International Publication No. WO 2018/139619

Patent Document 2: PCT International Publication No. WO 2018/139620

SUMMARY OF INVENTION

Technical Problem

[0008] The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a plated steel sheet that has both excellent planar corrosion resistance and coating adhesion.

Solution to Problem

[0009] In order to solve the above problem, the present invention employs the following configurations.

[1] A plated steel sheet, including:

a steel plate, and a plated layer disposed on a surface of the steel plate,
in which the plated layer has a chemical composition containing, in mass%,
Al: 10.0 to 30.0%,

Mg: 3.0 to 15.0%,

Fe: 0.01 to 2.0%,

Si: more than 0 to 2.0%, and

Ca: 0.05 to 2.0%, and

further containing one or two selected from the group consisting of the following group A and group B,
with a remainder consisting of Zn and impurities,

a number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 0 to 10 per area of 10,000 μm^2 , and

a number density of Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 1 to 50 per area of 10,000 μm^2 .

[Group A] Ni: 0 to 1.0%

[Group B] 0 to 5% in total of one or more of Sb: 0 to 0.5%, Pb: 0 to 0.5%, Cu: 0 to 1.0%, Sn: 0 to 2.0%, Ti: 0 to 1.0%, Cr: 0 to 1.0%, Nb: 0 to 1.0%, Zr: 0 to 1.0%, Mn: 0 to 1.0%, Mo: 0 to 1.0%, Ag: 0 to 1.0%, Li: 0 to 1.0%, La: 0 to 0.5%, Ce: 0 to 0.5%, B: 0 to 0.5%, Y: 0 to 0.5%, P: 0 to 0.5%, Sr: 0 to 0.5%, Co: 0 to 0.5%, Bi: 0 to 0.5%, In: 0 to 0.5%, V: 0 to 0.5%, and W: 0 to 0.5%

[2] The plated steel sheet according to [1], in which

Mg and Si in the chemical composition of the plated layer are Mg: 4.5 to 8 mass% and Si: 0.1 to 2 mass%, and
the number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 0 to 3 per area of 10,000 μm^2 .

[3] The plated steel sheet according to [1], in which

Al, Mg, and Si in the chemical composition of the plated layer are Al: 15 to 25 mass%, Mg: 4.5 to 8 mass%, and Si: 0.1 to 2 mass%, and
the number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 0 per area of 10,000 μm^2 .

[4] The plated steel sheet according to any one of [1] to [3], in which

Al, Mg, and Si in the chemical composition of the plated layer are Al: 15 to 25 mass%, Mg: 4.5 to 8 mass%, and Si: 0.1 to 2 mass%, and
a number density of Mg-Si-Zn-Al phases having a major axis of 2 μm or more exposed on the surface of the plated layer is 5 to 150 per area of 10,000 μm^2 .

[5] The plated steel sheet according to any one of [1] to [3], in which

Sn in the chemical composition of the plated layer is Sn: 0.05 to 0.5 mass%, and
a Mg_2Sn phase is detected in the plated layer by X-ray diffraction measurement of the plated layer.

[6] The plated steel sheet according to [4], in which

Sn in the chemical composition of the plated layer is Sn: 0.05 to 0.5 mass%, and

a Mg₂Sn phase is detected in the plated layer by X-ray diffraction measurement of the plated layer.

[7] The plated steel sheet according to [1], in which the plated layer has a chemical composition containing the group A in mass%.

[8] The plated steel sheet according to [1], in which the plated layer has a chemical composition containing the group B in mass%.

[9] The plated steel sheet according to [1], in which a number density of Ca-Zn phases having an equivalent circle diameter of less than 1 μm exposed on the surface of the plated layer is 1 or more per area of 10,000 μm^2 .

Advantageous Effects of Invention

[0010] According to the above aspects of the present invention, it is possible to provide a plated steel sheet that has both excellent planar corrosion resistance and coating adhesion.

BRIEF DESCRIPTION OF DRAWINGS

[0011] [FIG. 1] A schematic cross-sectional view of the plated steel sheet according to an embodiment of the present invention.

DESCRIPTION OF EMBODIMENTS

[0012] When a Ca-Zn phase crystallizes in the plated layer and is exposed on the surface of the plated layer, corrosion of a microstructure or phase around the Ca-Zn phase (particularly, a Ca-Zn phase having an equivalent circle diameter of 1 μm or more) may be promoted. Therefore, when a coating film is formed on the plated layer where the Ca-Zn phase is exposed, coating adhesion may be reduced due to the influence of a corrosion product produced around the Ca-Zn phase. The present inventors have found that, in order to improve coating adhesion, it is necessary to minimize the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more, which promotes the corrosion of the surrounding metallographic structure or phase, on the surface of the plated layer.

[0013] In order not to crystallize the Ca-Zn phase having an equivalent circle diameter of 1 μm or more, the content of Ca in the plated layer may be reduced, but on the other hand, when Ca is contained in the plated layer, planar corrosion resistance is expected to be improved. Therefore, if the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more can be suppressed on the surface of the plated layer while containing Ca, it is expected that both planar corrosion resistance and coating adhesion can be improved.

[0014] Therefore, the present inventors have intensively studied to improve both planar corrosion resistance and coating adhesion of a plated layer containing Al, Mg, Ca, and Zn, and found that it is effective to form a large amount of Al-Si-Zn-Ca phase in order to suppress the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more. It is assumed that when a large amount of Al-Si-Zn-Ca phase is formed, Ca contained in the plated layer is consumed at the time of formation of this phase, and the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more is reduced.

[0015] As a result of further studies by the present inventors, a large amount of Al-Si-Zn-Ca phase was crystallized on the surface of the plated layer by adjusting the production conditions of the plated layer, and the Ca-Zn phase having an equivalent circle diameter of 1 μm or more was successfully reduced. When a number density of Ca-Zn phases on the surface of the plated layer is reduced, coating adhesion is improved, and planar corrosion resistance can also be improved by containing Ca.

[0016] Hereinafter, the plated steel sheet according to an embodiment of the present invention will be described.

[0017] A plated steel sheet of the present embodiment includes a steel sheet and a plated layer disposed on a surface of the steel sheet, in which the plated layer has a chemical composition containing, in mass%, Al: 10.0 to 30.0%, Mg: 3.0 to 15.0%, Fe: 0.01 to 2.0%, Si: more than 0 to 2.0%, and Ca: 0.05 to 2.0%, and further containing one or two selected from the group consisting of the following group A and group B, with a remainder consisting of Zn and impurities, a number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 0 to 10 per area of 10,000 μm^2 , and a number density of Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer is 1 to 50 per area of 10,000 μm^2 .

[Group A] Ni: 0 to 1.0%

[0018] [Group B] 0 to 5% in total of one or more of Sb: 0 to 0.5%, Pb: 0 to 0.5%, Cu: 0 to 1.0%, Sn: 0 to 2.0%, Ti: 0 to 1.0%, Cr: 0 to 1.0%, Nb: 0 to 1.0%, Zr: 0 to 1.0%, Mn: 0 to 1.0%, Mo: 0 to 1.0%, Ag: 0 to 1.0%, Li: 0 to 1.0%, La: 0 to 0.5%, Ce: 0 to 0.5%, B: 0 to 0.5%, Y: 0 to 0.5%, P: 0 to 0.5%, Sr: 0 to 0.5%, Co: 0 to 0.5%, Bi: 0 to 0.5%, In: 0 to 0.5%, V: 0 to 0.5%, and W: 0

to 0.5%

[0019] In the following description, the expression "%" of the content of each element in a chemical composition means "mass%". The content of an element in a chemical composition may be referred to as an element concentration (for example, Zn concentration, Mg concentration, and the like). The "planar corrosion resistance" indicates a property that the plated layer (specifically, Zn-Al-Mg alloy layer) itself is less likely to corrode. The "coating adhesion" indicates a property that when a coating film is formed on a plated layer, the coating film is hardly peeled off. The "plated layer" means a plating film produced by the so-called hot-dip plating treatment.

[0020] As illustrated in FIG. 1, a plated steel sheet 1 according to the embodiment includes a steel sheet 11. The shape of the steel sheet 11 is not particularly limited. In addition, the steel sheet 11 may be, for example, a base steel sheet formed into a steel pipe, a civil engineering and construction material (fence culvert, corrugated pipe, drain channel lid, splash preventing plate, bolt, wire mesh, guard rail, water stop wall, and the like), a home electric appliance member (a housing of an outdoor unit of an air conditioner, or the like), a vehicle component (a suspension member, or the like), or the like. The forming is, for example, various plastic working methods, such as pressing, roll forming, and bending.

[0021] The material of the steel sheet 11 is not particularly limited. The steel sheet 11 may be, for example, various steel sheets, such as general steel, Al-killed steel, ultra-low carbon steel, high carbon steel, various high tensile strength steels, and some high alloy steels (steels containing a reinforcing element such as Ni, Cr, and the like). The steel sheet 11 may be a hot-rolled steel sheet, a hot-rolled steel strip, a cold-rolled steel sheet, a cold-rolled steel strip, and the like described in JIS G 3302: 2010. The method of manufacturing the steel sheet (hot rolling method, pickling method, cold rolling method, etc.), specific manufacturing conditions thereof, and the like are also not particularly limited.

[0022] As will be described later, a steel sheet 11 whose surface roughness has been adjusted is used as a steel sheet to be a plating original sheet. The surface roughness of the steel sheet can be adjusted by, for example, a method in which the surface of a rolling roll or a skin pass roll is set to have a predetermined surface roughness, and the surface shape of the roll is transferred at the time of rolling or skin pass.

[0023] The plated steel sheet 1 according to the embodiment has a plated layer 12 disposed on a surface of the steel sheet 11. The plated layer 12 of the plated steel sheet 1 according to the present embodiment is mainly composed of a Zn-Al-Mg alloy layer due to the chemical composition described later. In addition, the plated layer 12 of the plated steel sheet 1 according to the present embodiment may include an interfacial alloy layer containing Fe and Al as main components between the steel sheet 11 and the Zn-Al-Mg alloy layer. That is, the plated layer 12 may have a single-layer structure of the Zn-Al-Mg alloy layer or a multilayer structure including the Zn-Al-Mg alloy layer and the interfacial alloy layer.

[0024] The chemical composition of the plated layer according to the present embodiment is composed of Zn and other alloying elements. The chemical composition of the plated layer will be described in detail below. Note that the elements having a lower limit concentration of 0% as described are not essential for solving the problem of the plated steel sheet according to the present embodiment, but are optional elements which are allowed to be included in the plated layer for the purpose of, for example, improving characteristics.

<Al: 10.0 to 30.0%>

[0025] Al contributes to improvement in planar corrosion resistance, coating adhesion, and workability. Therefore, the Al concentration is 10.0% or more. The Al concentration may be 11.0% or more, 12.0% or more, or 15.0% or more. On the other hand, when Al is excessive, the Mg concentration and the Zn concentration relatively decrease, and coating adhesion is deteriorated. Therefore, the Al concentration is 30.0% or less. The Al concentration may be 24.0% or less, 22.0% or less, or 20.0% or less.

<Mg: 3.0 to 15.0%>

[0026] Mg is an element essential for securing planar corrosion resistance and coating adhesion. Therefore, the Mg concentration is 3.0% or more. The Mg concentration may be 4.0% or more, 5.0% or more, or 6.0% or more. On the other hand, when the Mg concentration is excessive, workability, particularly powdering resistance, may be deteriorated, and planar corrosion resistance may be further deteriorated. Therefore, the Mg concentration is 15.0% or less. The Mg concentration may be 10.0% or less or 8.0% or less.

<Fe: 0.01% to 2.0%>

[0027] The concentration of Fe may be 0%, but Fe may be contained in the plated layer in an amount of 0.01% or more. It has been confirmed that, when the Fe concentration is 2.0% or less, the performance of the plated layer is not adversely affected. The Fe concentration may be, for example, 0.05% or more, 0.1% or more, 0.5% or more, or 1.0% or more. The Fe concentration is 2.0% or less. The Fe concentration may be 1.8% or less or 1.5% or less. Since Fe may be mixed from the base steel sheet, the Fe concentration may be 0.05% or more.

<Si: more than 0% to 2.0%>

[0028] Si contributes to improvement in planar corrosion resistance. Si is also necessary to crystallize an Al-Si-Zn-Ca phase. Therefore, the Si concentration may be more than 0%, 0.01% or more, 0.02% or more, or 0.06% or more. On the other hand, when the Si concentration is excessive, planar corrosion resistance and coating adhesion are deteriorated. Therefore, the Si concentration is 2.0% or less. The Si concentration may be 1.8% or less, 1.6% or less, 1.2% or less, or 1.0% or less.

<Ca: 0.05% to 2.0%>

[0029] Ca is an element that contributes to improvement in planar corrosion resistance, and is an element capable of adjusting the optimum Mg elution amount for imparting planar corrosion resistance. Ca is also necessary to crystallize an Al-Si-Zn-Ca phase. Therefore, the Ca concentration is 0.05% or more. Ca may be 0.10% or more or 0.20% or more. When Ca is 0.10%, the density of Ca-Zn phases having an equivalent circle diameter of less than 1 μm tends to be 1 or more. On the other hand, when the Ca concentration is excessive, coating adhesion is deteriorated. Therefore, the Ca concentration is 2.0% or less. The Ca concentration may be 1.0% or less.

[0030] Further, the plated layer of the embodiment may contain one or two selected from the following group A and group B.

[Group A] Ni: 0 to 1.0%

[0031] [Group B] 0 to 5% in total of one or more of Sb: 0 to 0.5%, Pb: 0 to 0.5%, Cu: 0 to 1.0%, Sn: 0 to 2.0%, Ti: 0 to 1.0%, Cr: 0 to 1.0%, Nb: 0 to 1.0%, Zr: 0 to 1.0%, Mn: 0 to 1.0%, Mo: 0 to 1.0%, Ag: 0 to 1.0%, Li: 0 to 1.0%, La: 0 to 0.5%, Ce: 0 to 0.5%, B: 0 to 0.5%, Y: 0 to 0.5%, P: 0 to 0.5%, Sr: 0 to 0.5%, Co: 0 to 0.5%, Bi: 0 to 0.5%, In: 0 to 0.5%, V: 0 to 0.5%, and W: 0 to 0.5%

<Ni: 0 to 1.0%>

[0032] The Ni concentration as Group A may be 0%. On the other hand, Ni contributes to improvement in coating adhesion. Therefore, the Ni concentration may be 0.05% or more, 0.08% or more, or 0.1% or more. On the other hand, when the Ni concentration is excessive, planar corrosion resistance is deteriorated. Therefore, the Ni concentration is 1.0% or less. The Ni concentration may be 0.8% or less, 0.6% or less, or 0.5% or less.

[0033] Furthermore, the plated layer according to the present embodiment may contain, as Group B, one or two or more elements selected from Sb: 0 to 0.5%, Pb: 0 to 0.5%, Cu: 0 to 1.0%, Sn: 0 to 2.0%, Ti: 0 to 1.0%, Cr: 0 to 1.0%, Nb: 0 to 1.0%, Zr: 0 to 1.0%, Mn: 0 to 1.0%, Mo: 0 to 1.0%, Ag: 0 to 1.0%, Li: 0 to 1.0%, La: 0 to 0.5%, Ce: 0 to 0.5%, B: 0 to 0.5%, Y: 0 to 0.5%, P: 0 to 0.5%, Sr: 0 to 0.5%, Co: 0 to 0.5%, Bi: 0 to 0.5%, In: 0 to 0.5%, V: 0 to 0.5%, and W: 0 to 0.5%. The total of these elements is 0 to 5%. If the total exceeds 5%, planar corrosion resistance or coating adhesion may be reduced.

<Sb, Pb: 0 to 0.5% each>

[0034] The concentration of Sb and Pb may be 0%. On the other hand, Sb and Pb contribute to improvement in coating adhesion. Therefore, the concentration of each of Sb and Pb may be 0.05% or more, 0.10% or more, or 0.15% or more. On the other hand, when the concentration of Sb and Pb are excessive, planar corrosion resistance is deteriorated. Therefore, the concentration of each of Sb and Pb is 0.5% or less. The concentration of each of Sb and Pb may be 0.4% or less, 0.3% or less, or 0.25% or less.

[0035] <Cu, Ti, Cr, Nb, Zr, Mn, Mo, Ag, and Li: 0 to 1.0% each>

[0036] The concentration of each of Cu, Ti, Cr, Nb, Zr, Mn, Mo, Ag, and Li may be 0%. On the other hand, they contribute to improvement in coating adhesion. Therefore, the concentration of each of Cu, Ti, Cr, Nb, Zr, Mn, Mo, Ag, and Li may be 0.05% or more, 0.08% or more, or 0.10% or more. On the other hand, when the concentration of Cu, Ti, Cr, Nb, Zr, Mn, Mo, Ag, and Li are excessive, planar corrosion resistance is deteriorated. Therefore, the concentration of each of Cu, Ti, Cr, Nb, Zr, Mn, Mo, Ag, and Li is 1.0% or less. The concentration of each of Cu, Ti, Cr, Nb, Zr, Mn, Mo, Ag, and Li may be 0.8% or less, 0.7% or less, or 0.6% or less.

<Sn: 0 to 2.0%>

[0037] The Sn concentration may be 0%. On the other hand, Sn is an element that forms an intermetallic compound with Mg and improves the coating adhesion of the plated layer. Therefore, the Sn concentration may be 0.05% or more, 0.1% or more, or 0.2% or more. However, when the Sn concentration is excessive, planar corrosion resistance is deteriorated.

Therefore, the Sn concentration is 2.0% or less. The Sn concentration may be 1.0% or less, 0.8% or less, or 0.5% or less.

<La, Ce, B, Y, P, and Sr: 0 to 0.5% each>

[0038] The concentration of each of La, Ce, B, Y, P, and Sr may be 0%. On the other hand, La, Ce, B, Y, P, and Sr contribute to improvement in coating adhesion. Therefore, the concentration of each of La, Ce, B, Y, P, and Sr may be 0.10% or more, 0.15% or more, or 0.20% or more. On the other hand, when the concentration of La, Ce, B, Y, P, and Sr are excessive, planar corrosion resistance is deteriorated. Therefore, the concentration of each of La, Ce, B, Y, P, and Sr is 0.5% or less. The concentration of each of La, Ce, B, Y, P, and Sr may be 0.4% or less or 0.3% or less.

<Co, Bi, In, V, and W: 0 to 0.5% each>

[0039] The concentration of each of Co, Bi, In, V, and W may be 0%. On the other hand, Co, Bi, In, V, and W contribute to improvement in coating adhesion. Therefore, the concentration of each of Co, Bi, In, V, and W may be 0.10% or more, 0.15% or more, or 0.20% or more, respectively. On the other hand, when the concentration of Co, Bi, In, V, and W is excessive, planar corrosion resistance are deteriorated. Therefore, the concentration of each of Co, Bi, In, V, and W is 0.5% or less. The concentration of each of Co, Bi, In, V, and W may be 0.4% or less or 0.3% or less.

<Remainder: Zn and impurities>

[0040] The remainder in the components of the plated layer according to the embodiment includes Zn and impurities. Zn is an element that brings planar corrosion resistance and coating adhesion to the plated layer. The impurity refers to a component that is contained in a raw material or mixed in a manufacturing step and not intentionally contained. For example, in the plated layer, a small amount of components other than Fe may be mixed as the impurity due to mutual atomic diffusion between a base steel sheet and a plating bath.

[0041] The chemical compositions of the plated layer are measured by the following method. First, an acid solution in which the plated layer is peeled off and dissolved is obtained using an acid containing an inhibitor that suppresses steel sheet corrosion. Next, the obtained acid solution is subjected to inductively coupled plasma (ICP) emission spectroscopic analysis. Thereby, the chemical composition of the plated layer can be determined. The type of the acid is not particularly limited as long as the acid can dissolve the plated layer. The chemical composition measured by the above-described means is an average chemical composition of the entire plated layer.

[0042] Next, the metallographic structure of the plated layer will be described.

[0043] On the surface of the plated layer according to the present embodiment, the Ca-Zn phase having an equivalent circle diameter of 1 μm or more should not be crystallized as much as possible. The number density of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more allowed on the surface is 0 to 10 per 10,000 μm^2 . When the Ca-Zn phase having an equivalent circle diameter of 1 μm or more is exposed on the surface of the plated layer, a corrosion product is formed around the Ca-Zn phase having an equivalent circle diameter of 1 μm or more at the initial stage of corrosion of the plated layer, and coating adhesion is reduced by the corrosion product. Therefore, the number density of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more is preferably low, and the number density is most preferably 0 (phase/10,000 μm^2). If the number density exceeds 10 per 10,000 μm^2 , coating adhesion is reduced, which is not preferable. The number density of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more may be 5 or less or 3 or less when the unit is (phases/10,000 μm^2).

[0044] An electron probe microanalyzer (EPMA) is used to identify the Ca-Zn phase on the surface of the plated layer. The surface of the plated layer is observed with a scanning electron microscope attached to EPMA, and the intermetallic compound to be analyzed is identified. Then, the identified intermetallic compound is subjected to elemental analysis to determine whether or not the intermetallic compound is a Ca-Zn phase. In the identification of the Ca-Zn phase, an intermetallic compound containing 35 to 65 atom% of Ca and 35 atom% or more of Zn is defined as the Ca-Zn phase. The Ca-Zn phase may contain Mg, Al, Si, and Fe in the range of 10 atom% or less respectively.

[0045] Since the Ca-Zn phase having an equivalent circle diameter of 1 μm or more adversely affects coating adhesion, crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more is restricted. On the other hand, the Ca-Zn phase having an equivalent circle diameter of less than 1 μm hardly affects coating adhesion, and thus does not cause a problem in the present embodiment. The Ca-Zn phase having an equivalent circle diameter of less than 1 μm is less likely to cause corrosion of the surrounding metallographic structure and phase. Thus, a Ca-Zn phase having an equivalent circle diameter of less than 1 μm is preferably formed on the surface of the plated layer. Therefore, on the surface of the plated layer according to the present embodiment, the number density of the Ca-Zn phases having an equivalent circle diameter of less than 1 μm is preferably 1 or more per 10,000 μm^2 . The number density of the Ca-Zn phases having an equivalent circle diameter of less than 1 μm may be 100 or less or 50 or less when the unit is (phases/10,000 μm^2). A more preferable number density of the Ca-Zn phases having an equivalent circle diameter of less

than 1 μm is 10 phases/10,000 μm^2 or less.

[0046] For the equivalent circle diameter of the Ca-Zn phase, the area of individual Ca-Zn phases when the Ca-Zn phase is observed with a scanning electron microscope is determined, and the diameter of the circle having the area is defined as the equivalent circle diameter of the Ca-Zn phase.

[0047] The number density of the Ca-Zn phases on the surface of the plated layer may be affected by the average chemical composition of the plated layer. When Mg and Si in the chemical composition of the plated layer are Mg: 4.5 to 8 mass% and Si: 0.1 to 2 mass%, the number density of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer may be 0 to 3 per area of 10,000 μm^2 .

[0048] Also, when Al, Mg, and Si in the chemical composition of the plated layer are Al: 15 to 25 mass%, Mg: 4.5 to 8 mass%, and Si: 0.1 to 2 mass%, the number density of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of the plated layer may be 0 per area of 10,000 μm^2 .

[0049] Next, the Al-Si-Zn-Ca phase having an equivalent circle diameter of 1 μm or more is exposed on the surface of the plated layer according to the present embodiment. The number density of the Al-Si-Zn-Ca phases on the surface is 1 to 50 per 10,000 μm^2 . When the Al-Si-Zn-Ca phase is exposed on the surface of the plated layer, Ca contained in the plated layer is consumed for the production of this phase, and the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more is suppressed. This improves coating adhesion. In this way, planar corrosion resistance and coating adhesion of the plated layer can be improved.

[0050] An electron probe microanalyzer (EPMA) is used to identify the Al-Si-Zn-Ca phase in the plated layer. The surface of the plated layer is observed with a scanning electron microscope attached to EPMA, and the intermetallic compound to be analyzed is identified. Then, the identified intermetallic compound is subjected to elemental analysis to determine whether or not the intermetallic compound is an Al-Si-Zn-Ca phase. In the identification of the Al-Si-Zn-Ca phase, an intermetallic compound containing 20 to 80 atom% of Zn, 1 to 10 atom% of Si, 5 to 25 atom% of Ca, and the remainder Al (Al: 10 atom% or more) and 0 to 5 atom% of other elements is defined as the Al-Si-Zn-Ca phase. The other elements other than Al, Si, Zn, and Ca may be any of the elements contained in the plated layer.

[0051] When the size of the Al-Si-Zn-Ca phase is small, the crystallization of the Ca-Zn phase cannot be effectively suppressed, so that the size of the Al-Si-Zn-Ca phase that limits the number density needs to be 1 μm or more in terms of an equivalent circle diameter. When the number density of the Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm is 1 (phase/10,000 μm^2) or more, the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more can be sufficiently suppressed. For the equivalent circle diameter of the Al-Si-Zn-Ca phase, the area of individual Al-Si-Zn-Ca phases when the Al-Si-Zn-Ca phase is observed with a scanning electron microscope is determined, and the diameter of the circle having the area is defined as the equivalent circle diameter of the Al-Si-Zn-Ca phase.

[0052] The number density of the Al-Si-Zn-Ca phases on the surface of the plated layer is set to 1 to 50 per 10,000 μm^2 . When the number density is less than 1 (phase/10,000 μm^2) the crystallization of Ca-Zn phase cannot be suppressed, and coating adhesion is insufficient. On the other hand, even when the number density of the Al-Si-Zn-Ca phases exceeds 50 (phases/10,000 μm^2), the effect of improving coating adhesion is saturated, and therefore the upper limit is 50 (phases/10,000 μm^2) or less. The number density of the Al-Si-Zn-Ca phases may be 3 or more or 5 or more when the unit is (phases/10,000 μm^2). Also, the number density of the Al-Si-Zn-Ca phases may be 40 or less, 30 or less, or 20 or less.

[0053] Next, the Mg-Si-Zn-Al phase having a major axis of 2 μm or more may be exposed on the surface of the plated layer according to the present embodiment. The number density of the Mg-Si-Zn-Al phases on the surface is 5 to 150 per 10,000 μm^2 . When the Mg-Si-Zn-Al phase is exposed on the surface of the plated layer, the Mg-Si-Zn-Al phase is corroded at the initial stage of corrosion of the plated layer, thereby forming a dense corrosion product of Mg, Si, Zn, and Al. By forming this corrosion product, planar corrosion resistance of the plated layer is further improved.

[0054] An electron probe microanalyzer (EPMA) is used to identify the Mg-Si-Zn-Al phase of the plated layer. The surface of the plated layer is observed with a scanning electron microscope attached to EPMA, and the intermetallic compound to be analyzed is identified. Then, the identified intermetallic compound is subjected to elemental analysis to determine whether or not the intermetallic compound is a Mg-Si-Zn-Al phase. In the identification of the Mg-Si-Zn-Al phase, an intermetallic compound containing Mg: 20 to 45 atom%, Si: 15 to 40 atom%, Zn: 15 to 40 atom%, and Al: 5 to 20 atom% is defined as the Mg-Si-Zn-Al phase.

[0055] The number density of the Mg-Si-Zn-Al phases on the surface of the plated layer is affected by the average chemical composition of the plated layer. In order to set the number density of the Mg-Si-Zn-Al phases to 5 to 150 per 10,000 μm^2 , Al, Mg, and Si in the chemical composition of the plated layer are preferably Al: 15 to 25 mass%, Mg: 4.5 to 8 mass%, and Si: 0.1 to 2%.

[0056] The Mg-Si-Zn-Al phase preferably has a shape having a major axis of 2 μm or more, and more preferably has a needle shape having a major axis of 2 μm or more. Furthermore, the Mg-Si-Zn-Al phase preferably has an aspect ratio of 2 or more. When the Mg-Si-Zn-Al phase has a shape having a major axis of 2 μm or more, the Mg-Si-Zn-Al phase is easily dissolved at the initial stage of corrosion, and more dense corrosion products can be formed, so that planar corrosion resistance can be enhanced.

[0057] The major axis of the Mg-Si-Zn-Al phase is defined as the maximum length of the Mg-Si-Zn-Al phase when the Mg-Si-Zn-Al phase is observed with an electron microscope. The aspect ratio is a ratio of a major axis to a minor axis (major axis/minor axis). The minor axis is defined as a length in a direction orthogonal to the direction of the major axis, and more specifically, a maximum length within a range of $\pm 5^\circ$ with respect to the direction orthogonal to the major axis direction.

[0058] The number density of the Mg-Si-Zn-Al phases on the surface of the plated layer is preferably 5 to 150 per 10,000 μm^2 . By setting the number density to 5 (phases/10,000 μm^2) or more, planar corrosion resistance can be further improved. On the other hand, even when the number density of the Mg-Si-Zn-Al phases exceeds 150 (phases/10,000 μm^2), the effect of improving planar corrosion resistance is saturated, and therefore the upper limit is 150 (phases/10,000 μm^2) or less. The number density of the Mg-Si-Zn-Al phases may be 10 or more or 15 or more when the unit is (phases/10,000 μm^2). Also, the number density of the Mg-Si-Zn-Al phases may be 120 or less, 100 or less, 80 or less, 70 or less, 50 or less, or 30 or less.

[0059] The Mg-Si-Zn-Al phase may be present at a number density of more than 0 to less than 5 per area of 10,000 μm^2 on the surface of the plated layer.

[0060] A method for measuring the number density of the Ca-Zn phases, the Al-Si-Zn-Ca phases, and the Mg-Si-Zn-Al phases will be described. A 50 μm square measurement region is provided on the surface of the plated layer. The number of measurement regions is eight, and the eight measurement regions are randomly arranged on the surface of the plated layer. The measurement regions are separated so as not to overlap each other. The intermetallic compound is confirmed by observing the set measurement regions with a scanning electron microscope. Then, the composition of the intermetallic compound is analyzed by EPMA to distinguish between the Ca-Zn phase, the Al-Si-Zn-Ca phase, and the Mg-Si-Zn-Al phase. Further, the number of each of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more, the number of the Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more, and the number of the Mg-Si-Zn-Al phases having a major axis of 2 μm or more in each measurement region is measured. Measurement conditions of EPMA are, for example, an acceleration voltage of 15 kV, a current of 0.05 μA , and an irradiation time of 50 ms. As the EPMA, for example, JXA-8230 manufactured by JEOL Ltd. is used.

[0061] In each of the Ca-Zn phase, the Al-Si-Zn-Ca phase, and the Mg-Si-Zn-Al phase, a part of each phase may be within the measurement region, and the remainder of each phase may be outside the measurement region, but such a phase is also included in the number to be measured.

[0062] In addition, when the Mg-Si-Zn-Al phase has a needle shape, a plurality of Mg-Si-Zn-Al phases may overlap each other. In such a case, when the major axis directions of the respective phases face different directions and overlap with each other, the respective overlapping phases are targeted for the measurement of the number. For example, when two Mg-Si-Zn-Al phases overlap each other and the major axis directions thereof are different directions, the number of Mg-Si-Zn-Al phases is counted as two.

[0063] Then, based on the number of each of the Ca-Zn phases having an equivalent circle diameter of 1 μm or more, the Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more, and the Mg-Si-Zn-Al phases having a major axis of 2 μm or more measured in the eight measurement regions and the total area of the measurement regions, the number per 10,000 μm^2 is defined as the number density.

[0064] In addition, when 0.05 to 0.5 mass% of Sn is contained in the plated layer, a Mg_2Sn phase is preferably contained in the plated layer. Since the amount of the Mg_2Sn phase is small, the presence thereof is detected and confirmed by X-ray diffraction measurement. When the plated layer contains the Mg_2Sn phase therein, the plated layer has further improved corrosion resistance. Whether or not the Mg_2Sn phase is contained in the plated layer is determined by whether or not a diffraction peak specific to Mg_2Sn appears. Here, the diffraction peak specific to Mg_2Sn refers to, for example, a peak at which a diffraction angle 2θ appears at 23.4 ± 0.3 degrees.

[0065] The adhesion amount per one surface of the plated layer may be, for example, within a range of 20 to 150 g/m². When the adhesion amount per one surface is 20 g/m² or more, planar corrosion resistance and coating adhesion of the plated steel sheet can be further enhanced. On the other hand, when the adhesion amount per one surface is 150 g/m² or less, the workability of the plated steel sheet can be further improved.

[0066] Next, a method for manufacturing a plated steel sheet of the present embodiment will be described, but the method for manufacturing a plated steel sheet according to the present embodiment is not particularly limited. For example, according to the manufacturing conditions described below, the plated steel sheet according to the present embodiment can be obtained.

[0067] As for the method for manufacturing a plated steel sheet of the present embodiment, a steel sheet whose surface roughness has been adjusted is annealed in a reducing atmosphere, and the steel sheet immediately after the annealing is immersed in a hot-dip plating bath and then pulled up to form a plated layer on the surface of the steel sheet. Subsequently, cooling is performed by spraying a cooling gas until the temperature of the plated layer reaches 300°C or lower from the bath temperature. The gas flux when spraying a cooling gas is set such that the gas flux from the bath temperature to the controlled cooling temperature (the gas flow rate in the temperature range higher than or equal to the controlled cooling temperature and equal to or lower than the bath temperature) is set in the range of 100 to 5,000 L/min/m², and the gas flux from the controlled cooling temperature to the cooling stop temperature (in the present embodiment, 300°C or lower) (the

gas flow rate in the temperature range higher than or equal to the cooling stop temperature and equal to or lower than the controlled cooling temperature) is set in the range of 10,000 to 80,000 L/min/m².

[0068] The controlled cooling temperature is a temperature within the range of -10°C to -80°C with respect to the crystallization temperature of Al-Si-Zn-Ca phase.

[0069] For the roughness of the sheet surface to be the plating original sheet, the ratio of curve length L_p of a roughness curve per reference length L_0 (L_p/L_0) is set to 1.0 or more, and the arithmetic mean roughness R_a is set to 0.1 μm or more. When the roughness is out of this range, a large amount of the Al-Si-Zn-Ca phase crystallizes near the interface between the plated layer and the steel sheet, and the number density of the Al-Si-Zn-Ca phases on the surface of the plated layer may decrease. The upper limit of (L_p/L_0) is preferably 3.0 or less, and may be 2.5 or less or 2.0 or less. The upper limit of the arithmetic mean roughness R_a is preferably 4.0 μm or less, and may be 3.5 μm or less. The roughness of the sheet surface is not particularly limited, but may be adjusted by, for example, rolling the plating original sheet with a rolling roll or a roll for temper rolling in which the surface of the roll has been adjusted to a desired roughness to transfer the surface shape of the roll. Alternatively, the roughness may be adjusted by pickling.

[0070] (L_p/L_0) and the arithmetic mean roughness are measured using, for example, a shape measurement laser microscope (model number: VK-8700) manufactured by KEYENCE CORPORATION. As measurement conditions, for example, measurement is performed under the following conditions: measurement mode: laser confocal, measurement quality: high accuracy, pitch: 0.75 μm, double scan: ON, optical zoom: 1 time, objective lens name: Plan, γ coefficient: 0.45, and offset: 0%. The measuring device used for measuring (L_p/L_0) and the arithmetic mean roughness is not limited to the above example. According to JIS B 0601:2013, a roughness curve was obtained by sequentially applying contour curve filters of cut-off values λ_c and λ_s to the cross section curve obtained by measurement. Specifically, from the obtained measurement results, a roughness curve was obtained by removing a component with a wavelength λ_c of 0.001 mm or less and a component with a wavelength λ_s of 0.2 mm or more. (L_p/L_0) and the arithmetic mean roughness were calculated based on the obtained roughness curve.

[0071] Annealing of the steel sheet to be a plating original sheet is performed in a reducing atmosphere. The reducing atmosphere and the annealing conditions are not particularly limited. By this annealing, the oxide present on the sheet surface is removed as much as possible.

[0072] Subsequently, the steel sheet immediately after annealing is immersed in a hot-dip plating bath. The chemical composition of the hot-dip plating bath may be appropriately adjusted so as to obtain the chemical composition of the plated layer described above. The temperature of the hot-dip plating bath is also not particularly limited. It is possible to appropriately select a temperature at which hot-dip plating can be performed. For example, the plating bath temperature may be higher than the melting point of the plating bath by about 20°C or more.

[0073] Next, the steel sheet is pulled up from the hot-dip plating bath. The adhesion amount of the plated layer can be controlled by controlling the pulling speed of the steel sheet. If necessary, wiping may be performed on the steel sheet to which the plated layer is adhered to control the adhesion amount of the plated layer. The adhesion amount of the plated layer is not particularly limited, and can be, for example, within the above-described range.

[0074] Next, the plated layer is cooled. The cooling is performed by spraying a cooling gas on the steel sheet immediately after being pulled up from the hot-dip plating bath. The cooling by spraying a cooling gas is continuously performed until the temperature of the steel sheet reaches 300°C from the bath temperature. The cooling condition at less than 300°C is not particularly limited. The cooling of spraying a cooling gas may be subsequently performed, or natural cooling may be performed.

[0075] The cooling by spraying a cooling gas is performed by disposing a cooling zone along the conveyance path for the steel sheet. The cooling zone includes a plurality of spraying nozzles for cooling gas. The shape of the gas nozzle from which the cooling gas is blown out is, for example, in the range of a diameter of 1 to 50 mm. The angle formed by the tip of the gas nozzle and the steel sheet is, for example, in the range of 70 to 110°, more preferably 90° (perpendicular). The distance between the tip of the gas nozzle and the steel sheet is in the range of 30 to 1000 mm. The shape, angle, and distance of the gas nozzle are merely examples, and are not limited to the above ranges.

[0076] The cooling gas to be sprayed is not particularly limited, and may be a non-oxidizing gas such as nitrogen, an inert gas such as argon, or air, or a mixed gas thereof.

[0077] In the present embodiment, a gas flux when spraying a cooling gas is controlled in two stages. That is, on the basis of the temperature of the steel sheet, the gas flux from the plating bath temperature to the controlled cooling temperature (the temperature in the range of -10 to -80°C with respect to the crystallization temperature of Al-Si-Zn-Ca phase) is set in the range of 100 to 5,000 L/min/m², preferably in the range of 500 to 5,000 L/min/m², and the gas flux from the controlled cooling temperature to 300°C or lower is set in the range of 10,000 to 80,000 L/min/m². The controlled cooling temperature is a temperature assumed to be the crystallization start temperature of Al-Si-Zn-Ca phase.

[0078] When the gas flux is set in the range of 5,000 L/min/m² or less, it is possible to suppress vibration from being applied to the steel sheet being cooled. On the other hand, when the gas flux is set in the range of 10,000 L/min/m² or more, vibration can be applied to the steel sheet being cooled.

[0079] Then, by setting the gas flux from the plating bath temperature to the controlled cooling temperature in the range

of 100 to 5,000 L/min/m², preferably the range of 500 to 5,000 L/min/m², nucleation of a Ca-containing phase other than the Al-Si-Zn-Ca phase is promoted without applying vibration to the steel sheet, and Ca and Si are concentrated in the liquid phase in the unsolidified state. Next, by setting the gas flux from the controlled cooling temperature to 300°C or lower in the range of 10,000 to 80,000 L/min/m², vibration is applied to the surface of the liquid phase in the unsolidified state, and a large amount of Al-Si-Zn-Ca phase can be crystallized on the surface of the plated layer. When the range of the gas flux is out of the above range, it is difficult to crystallize a large amount of the Al-Si-Zn-Ca phase on the surface of the plated layer.

[0080] Since the crystallization temperature of Al-Si-Zn-Ca phase varies depending on the chemical composition of the plated layer, the crystallization temperature is calculated using a calculation phase diagram. Specifically, the crystallization temperature of Al-Si-Zn-Ca phase is determined for each chemical composition of the plated layer by constructing a calculation phase diagram database in which thermodynamic data such as an intermetallic compound phase and a metal phase that can be contained in the Al-Mg-Zn based alloy are integrated, and performing calculation by the CALPHAD method (CALculation of PHaseDiagram). More specifically, the crystallization temperature of the Al-Si-Zn-Ca phase can be estimated by using "Thermo-Calc" (Thermo-Calc is a registered trademark) manufactured by Thermo-Calc Software), which is a thermodynamic equilibrium calculation software. The thermodynamic equilibrium calculation software used for the calculation is not limited to "Thermo-Calc" (registered trademark), and other software may be used. The temperature within the range of -10 to -80°C with respect to the obtained crystallization temperature of the Al-Si-Zn-Ca phase is defined as the controlled cooling temperature.

[0081] In the above manufacturing method, nucleation of the Al-Si-Zn-Ca phase is suppressed by adjusting the surface roughness of the sheet surface in advance, whereby the crystallization of the Al-Si-Zn-Ca phase inside the plated layer is suppressed. By performing hot-dip plating on such a steel sheet and further controlling the cooling conditions after plating as described above, a large amount of the Al-Si-Zn-Ca phase is crystallized on the surface of the plated layer. As a result, it is assumed that a large number of Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more can be formed on the surface of the plated layer, and the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm or more can be suppressed.

[0082] As long as the requirements shown in the present invention are satisfied, the method for manufacturing a plated steel sheet is not limited to the above contents, and instead of the hot-dip plating method, an electro plating method, a vapor deposition plating method, a thermal spraying method, a cold spraying method, or the like may be adopted.

Examples

[0083] Hereinafter, examples of the present invention will be described. However, the conditions in Examples are merely one condition example adopted to confirm the operability and effects of the present invention. The present invention is not limited to this one condition example. The present invention can adopt various conditions as long as the object of the present invention is achieved without departing from the gist of the present invention.

[0084] A cold-rolled steel sheet (0.05 C-0.1 Si-0.2 Mn) having a sheet thickness of 1.2 mm was used as a plating original sheet. The surface roughness of a part of the plating original sheet was controlled using a skin pass mill or the like. The steel sheet whose surface roughness had been adjusted was annealed. The annealed steel sheet was immersed in various hot-dip plating baths and then pulled up to adhere a plated layer to the sheet surface. Subsequently, various plated steel sheets were manufactured by cooling the plated layer immediately after being pulled up from the plating bath until the temperature of the plated layer reached 300°C using a cooling gas.

[0085] For the surface roughness of the sheet surface to be the plating original sheet, the ratio of curve length L_p of a roughness curve per reference length L_0 (L_p/L_0) was set to 1.1 to 2.6, and the arithmetic mean roughness R_a was set in the range of 0.6 to 3.7 μm.

[0086] (L_p/L_0) and the arithmetic mean roughness were measured using a shape measurement laser microscope (model number: VK-8700) manufactured by KEYENCE CORPORATION. As measurement conditions, measurement was performed under the following conditions: measurement mode: laser confocal, measurement quality: high accuracy, pitch: 0.75 μm, double scan: ON, optical zoom: 1 time, objective lens name: Plan, γ coefficient: 0.45, and offset: 0%.

[0087] Annealing conditions when the steel sheet was annealed in a reducing atmosphere were a soaking temperature of 600°C and a soaking time of 10 seconds. The annealing atmosphere was a reducing atmosphere composed of a mixed gas of 5% hydrogen and the remainder nitrogen. Then, the annealed steel sheet was air-cooled with a nitrogen gas, and after the temperature of the immersion sheet reached the bath temperature + 20°C, the steel sheet was immersed in a hot-dip plating bath and then pulled up. The pulling speed was set to 20 to 200 mm/sec.

[0088] The chemical composition of the hot-dip plated layer was as shown in Table 1. The manufacturing conditions were as shown in Table 2. Also, the metallographic structure of the plated layer was evaluated, and the results are shown in Table 3. Furthermore, the planar corrosion resistance and coating adhesion of the plated steel sheet were evaluated, and the results are shown in Table 3.

[0089] The chemical composition of the plated layer and the metallographic structure of the plated layer were evaluated by the means described above. A Ca-Zn phase having an equivalent circle diameter of 1 μm or more and a Ca-Zn phase

having an equivalent circle diameter of less than 1 μm were targeted for measurement. An Al-Si-Zn-Ca phase having an equivalent circle diameter of 1 μm or more was targeted for measurement. In addition, a Mg-Si-Zn-Al phase having a major axis of 2 μm or more was targeted for measurement. All the measured Mg-Si-Zn-Al phases had an aspect ratio of 2 or more.

[0090] The planar corrosion resistance was evaluated as follows. The obtained plated steel sheet was cut into 100 mm $\times$ 50 mm and subjected to an evaluation test of planar corrosion resistance. The planar corrosion resistance was evaluated by the corrosion acceleration test specified in JASO-CCT-M609. After 150 cycles, the corrosion loss was compared. The evaluation criteria were as follows, and "AAA", "AA", and "A" were regarded as acceptable.

[0091]

- AAA: Corrosion loss of less than 50 g/m²
- AA: Corrosion loss of 50 g/m² or more and less than 90 g/m²
- A: Corrosion loss of 90 g/m² or more and less than 120 g/m²
- B: Corrosion loss of 120 g/m² or more

[0092] The coating adhesion was evaluated as follows. The obtained plated steel sheet was cut into 100 mm $\times$ 50 mm and subjected to a test of coating adhesion. After a coating film layer was formed on the test piece, an end surface and a rear surface were sealed with a silicon resin.

[0093] Next, a cut defect reaching a base metal was applied onto a front surface with a cutter knife. The cut defects were applied in a grid pattern with an interval of 1 mm. In this way, 100 one square millimeter regions partitioned by cut defects were formed. Next, the steel sheet was continuously immersed in a 5% NaCl aqueous solution at 50°C for 500 hours, then washed with water, and dried. Then, tape peeling was performed by attaching an adhesive tape to the cut defect part of the dried sample and then peeling the tape, and the peeling area ratio was measured.

<Coating film layer>

[0094] A primer coating material resin and a topcoat coating material resin described below were applied onto the surface of the plating layer to form a coating film layer. The thickness of the layer formed of the primer coating material resin was 5 μm , the thickness of the layer formed of the topcoat coating material resin was 15 μm , and the total thickness was 20 μm .

<Film-forming component of coating film layer>

(1) Primer coating material resin on front surface and rear surface

[0095] Combined curing type of polyester/melamine + isocyanate (FLC687 coating material resin manufactured by Nippon Fine Coatings Inc.)

(2) Topcoat coating material resin on front surface

[0096] Polymer polyester/melamine curing type (FLC7000 coating material resin manufactured by Nippon Fine Coatings Inc.)

(3) Topcoat coating material resin on rear surface

[0097] Polyester/melamine curing type (FLC100HQ coating material resin manufactured by Nippon Fine Coatings Inc.)

[0098] Evaluation criteria for coating adhesion are shown below. Determination was made according to the following scoring. "AAA", "AA", and "A" were regarded as acceptable.

[0099]

- AAA: Peeling area ratio of less than 10%
- AA: Peeling area ratio of 10 to 20% or less
- A: Peeling area ratio of 20 to 30% or less
- B: Peeling area ratio of 30% or more

[0100] As shown in Tables 1 to 3, Examples 1 to 30, and 39 according to the present invention, in which the chemical composition and the metallographic structure of the plated layer were appropriately controlled, had both excellent planar corrosion resistance and coating adhesion. In Examples, the adhesion amount per one surface of the plated layer was within a range of 20 to 150 g/m².

[0101] Comparative Example 31 had an insufficient Al amount in the plated layer. Therefore, in Comparative Example 31, the crystallization temperature of the Ca-Zn phase increased, and a large amount of the Ca-Zn phase having an equivalent circle diameter of 1 μm was crystallized. As a result, planar corrosion resistance was insufficient.

[0102] Comparative Example 32 had an excessive Al amount in the plated layer. Therefore, in Comparative Example 32, a large amount of the Ca-Zn phase having an equivalent circle diameter of 1 μm in which Al was solid-solved was crystallized. As a result, coating adhesion was reduced.

[0103] Comparative Example 33 had an insufficient Mg amount in the plated layer. Therefore, in Comparative Example 33, the crystallization temperature of the Ca-Zn phase increased, and a large amount of the Ca-Zn phase having an equivalent circle diameter of 1 μm was crystallized. As a result, planar corrosion resistance and coating adhesion were reduced.

[0104] Comparative Example 34 had an excessive Mg amount in the plated layer. Therefore, in Comparative Example 34, the external appearance of the plating layer was significantly deteriorated.

[0105] Comparative Example 35 had an excessive Si amount in the plated layer. Therefore, in Comparative Example 35, Si was crystallized not as an Al-Si-Zn-Ca phase but as a Si phase, so that the crystallization of the Ca-Zn phase having an equivalent circle diameter of 1 μm was not suppressed, and planar corrosion resistance and coating adhesion were reduced.

[0106] Comparative Example 36 had an excessive Ca amount in the hot-dip plated layer. Therefore, in Comparative Example 36, the Ca-Zn phase having an equivalent circle diameter of 1 μm was excessively crystallized on the surface of the plated layer, and planar corrosion resistance and coating adhesion were reduced.

[0107] In Comparative Example 37, the cooling gas flux from the bath temperature to the controlled cooling temperature was excessive. Therefore, in Comparative Example 37, nucleation of the Ca-Zn phase having an equivalent circle diameter of 1 μm proceeded on the surface of the plated layer due to the influence of vibration, and planar corrosion resistance and coating adhesion were reduced.

[0108] In Comparative Example 38, the cooling gas flux from the controlled cooling temperature to 300°C was insufficient. Therefore, in Comparative Example 38, vibration was not sufficiently applied, formation of the Al-Si-Zn-Ca phase was insufficient, the Ca-Zn phase having an equivalent circle diameter of 1 μm was excessively crystallized, and planar corrosion resistance and coating adhesion were reduced.

[Table 1]

Category	No.	Plated layer components (mass%) Remainder: Zn and impurities									
		Zn	Al	Mg	Sn	Si	Ca	Ni	Fe	Other elements	
										Type	Total (%)
Example	1	Balance	10.0	3.0	0	0.01	0.05	0	0.05	-	-
Example	2	Balance	11	3.0	0.05	0.1	0.07	0	0.05	Co	0.006
Example	3	Balance	10	4.5	0	0.02	0.10	0	0.05	Bi	0.004
Example	4	Balance	10	5.0	0	0.06	0.2	0	0.08	v	0.008
Example	5	Balance	11	5.0	0	0.08	0.2	0	0.08	Pb	0.03
Example	6	Balance	11	5.0	0	0.08	0.2	0	0.08	Pb	0.02
Example	7	Balance	12	6.0	0	0.1	0.2	0	0.1	-	-
Example	8	Balance	12	6.0	0	0.15	0.2	0	0.08	Sr	0.01
Example	9	Balance	14	5.0	0	0.2	0.2	0	0.1	Li	0.01
Example	10	Balance	16	5.0	0.07	0.2	0.2	0	0.2	Ag	0.01
Example	11	Balance	16	5.0	0	0.2	0.2	0.001	0.2	P	0.001
Example	12	Balance	18	6.0	0	0.4	0.2	0	0.2	-	-
Example	13	Balance	19	6.0	0.2	0.6	0.2	0	0.1	Sb	0.01
Example	14	Balance	19	6.0	0.5	0.2	0.2	0	0.1	Mn	0.02
Example	15	Balance	19	6.0	0	0.2	0.2	0	0.1	In	0.02
Example	16	Balance	19	6.0	0	0.2	0.2	0	0.3	-	-
Example	17	Balance	20	10	0	1.4	2.0	0	0.1	W	0.02

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(continued)

Category	No.	Plated layer components (mass%) Remainder: Zn and impurities									
		Zn	Al	Mg	Sn	Si	Ca	Ni	Fe	Other elements	
										Type	Total (%)
Example	18	Balance	20	7.0	0	0.4	0.2	0	0.1	B	0.01
Example	19	Balance	20	3.0	0	0.2	0.2	0	0.3	P	0.01
Example	20	Balance	22	6.0	0	0.4	0.2	0	0.1	La	0.02
Example	21	Balance	22	8.0	0	0.7	0.8	0	0.2	Ce	0.01
Example	22	Balance	22	4.0	0	0.1	0.2	0	0.2	Zr	0.01
Example	23	Balance	24	3.0	0	0.1	0.2	0	0.3	W	0.01
Example	24	Balance	22	4.0	0	0.1	0.2	0.01	0.4	Cr	0.05
Example	25	Balance	22	4.0	0	0.1	0.2	0.01	0.4	Mo	0.01
Example	26	Balance	23	8.0	0	0.7	0.8	0	0.6	-	-
Example	27	Balance	23	8.0	0	0.7	0.8	0	0.6	Ti	0.02
Example	28	Balance	24	8.0	0	1.2	0.8	0	1.0	Cu	0.2
Example	29	Balance	28	7.0	0	1.6	1.0	0	1.4	Y	0.02
Example	30	Balance	30	15.0	0	2.0	2.0	0	1.3	Nb	0.01
Comparative Example	31	Balance	<u>6.5</u>	4	0	<u>0</u>	0.2	0	0.1	-	-
Comparative Example	32	Balance	<u>32</u>	7	0	0.1	0.2	0	0.1	-	-
Comparative Example	33	Balance	19	<u>2.6</u>	0	0.2	0.2	0	0.1	-	-
Comparative Example	34	Balance	19	<u>16</u>	0	<u>0</u>	0.2	0	0.1	-	-
Comparative Example	35	Balance	19	5	0	<u>2.2</u>	0.2	0	0.1	-	-
Comparative Example	36	Balance	20	5	0	0.2	<u>2.5</u>	0	0.1	-	-
Comparative Example	37	Balance	20	5	0	0.6	0.2	0	0.8	-	-
Comparative Example	38	Balance	20	5	0	0.6	0.2	0	0.8	-	-
Example	39	Balance	19	6.7	0	0.3	0.2	0	0.1	-	-
Underline means outside of the range of the present invention.											

[Table 2]

Category	No.	Manufacturing conditions							
		Plating original sheet roughness Ra (μm)	L _p /L ₀ (-)	Bath temperature (°C)	Controlled cooling temperature (°C)	Cooling gas flux from bath temperature to controlled cooling temperature (L/min/m ²)	Cooling rate from bath temperature to controlled cooling temperature (°C/sec)	Cooling gas flux from controlled cooling temperature to 300°C (L/min/m ²)	Cooling rate from controlled cooling temperature to 300°C (°C/sec)
Example	1	1.1	2.0	460	400	5000	15	10000	10
Example	2	1.2	1.5	480	420	5000	15	10000	10
Example	3	2.2	1.6	500	440	5000	15	10000	10
Example	4	1.5	1.6	500	440	2500	15	10000	10
Example	5	1.6	1.6	530	470	2000	15	10000	10
Example	6	3.7	2.6	530	470	2000	15	10000	10
Example	7	1.7	1.5	530	470	1000	15	10000	10
Example	8	1.2	1.2	530	470	500	15	10000	10
Example	9	1.4	1.6	530	470	4000	15	10000	12
Example	10	1.2	1.6	530	470	4000	15	10000	12
Example	11	0.9	1.6	530	470	500	15	10000	12
Example	12	0.6	1.1	530	470	4000	15	10000	12
Example	13	1.2	1.2	530	470	4000	15	10000	12
Example	14	1.6	1.6	530	470	500	15	10000	12
Example	15	1.7	1.6	530	470	500	15	10000	12
Example	16	1.7	1.2	530	490	500	15	10000	12
Example	17	1.7	1.4	590	530	1000	15	10000	12
Example	18	1.6	1.6	540	480	500	15	10000	12
Example	19	1.7	1.7	540	480	1000	20	10000	14
Example	20	1.9	1.3	540	480	500	20	10000	14
Example	21	1.9	1.9	540	480	500	20	10000	14
Example	22	1.9	1.6	540	480	5000	20	10000	14

(continued)

Category	No.	Manufacturing conditions							
		Plating original sheet roughness Ra (μm)	L _p /L ₀ (-)	Bath temperature (°C)	Controlled cooling temperature (°C)	Cooling gas flux from bath temperature to controlled cooling temperature (L/min/m ²)	Cooling rate from bath temperature to controlled cooling temperature (°C/sec)	Cooling gas flux from controlled cooling temperature to 300°C (L/min/m ²)	Cooling rate from controlled cooling temperature to 300°C (°C/sec)
Example	23	1.7	1.5	560	500	5000	20	10000	14
Example	24	1.7	1.6	540	480	5000	20	10000	14
Example	25	1.6	1.6	540	480	5000	20	10000	14
Example	26	3.6	2.1	550	490	1000	20	10000	14
Example	27	1.8	1.6	550	490	1000	20	10000	14
Example	28	1.1	1.7	550	490	900	20	10000	14
Example	29	1.9	1.8	550	490	5000	20	10000	14
Example	30	2.4	1.8	600	540	5000	20	10000	14
Comparative Example	31	1.8	1.6	450	390	5000	15	10000	10
Comparative Example	32	1.7	1.7	600	540	5000	15	10000	10
Comparative Example	33	1.8	1.8	540	480	5000	15	10000	10
Comparative Example	34	1.8	1.2	540	480	5000	15	10000	10
Comparative Example	35	1.6	1.5	510	450	5000	15	10000	10
Comparative Example	36	1.8	1.6	540	480	5000	15	10000	10
Comparative Example	37	1.8	1.7	520	460	<u>5500</u>	15	10000	10
Comparative Example	38	1.8	1.8	520	460	5000	15	<u>5000</u>	10

(continued)

Category	No.	Manufacturing conditions					
		Plating original sheet roughness Ra (μm)	L_p/L_0 (-)	Bath temperature (°C)	Controlled cooling temperature (°C)	Cooling gas flux from bath temperature to controlled cooling temperature (L/min/m ²)	Cooling rate from bath temperature to controlled cooling temperature (°C/sec)
Example	39	1.7	1.6	530	470	500	15
							80000
							12
Underline means outside of the range of the preferred manufacturing conditions.							

[Table 3]

Category	No.	Surface structure of plated layer					Performance	
		Al-Si-Zn-Ca phase	Ca-Zn phase having equivalent circle diameter of 1 μm or more	Ca-Zn phase having equivalent circle diameter of less than 1 μm	Mg-Si-Zn-Al phase	Mg ₂ Sn phase	Planar corrosion resistance	Coating adhesion
		Number density (phases/ (10000 μm^2))	Number density (phases/ (10000 μm^2))	Number density (phases/ (10000 μm^2))	Number density (phases/ (10000 μm^2))	Present or absent		
Example	1	1	10	0	0	Absent	A	A
Example	2	1	9	0	0	Present	A	AA
Example	3	2	6	2	5	Absent	AA	A
Example	4	1	3	3	14	Absent	AA	AA
Example	5	2	2	4	15	Absent	AA	AA
Example	6	2	8	2	0	Absent	A	A
Example	7	3	0	4	24	Absent	AAA	AAA
Example	8	2	0	5	22	Absent	AAA	AAA
Example	9	3	3	4	31	Absent	AA	AA
Example	10	2	3	5	21	Present	AA	AAA
Example	11	3	0	5	1	Absent	AAA	AAA
Example	12	4	2	6	41	Absent	AA	AA
Example	13	5	0	3	61	Present	AA	AAA
Example	14	4	0	5	23	Present	AAA	AAA
Example	15	5	0	5	30	Absent	AAA	AAA
Example	16	6	0	4	28	Absent	AAA	AAA
Example	17	41	10	50	122	Absent	A	A
Example	18	21	0	5	32	Absent	AAA	AAA
Example	19	5	1	4	19	Absent	AA	AA
Example	20	11	0	5	21	Absent	AAA	AAA
Example	21	24	0	4	35	Absent	AAA	AAA
Example	22	2	7	2	1	Absent	A	A
Example	23	3	6	1	2	Absent	A	A
Example	24	2	6	2	1	Absent	A	A
Example	25	3	4	3	2	Absent	A	A
Example	26	19	1	3	4	Absent	AA	AA
Example	27	29	1	3	56	Absent	AAA	AAA
Example	28	34	1	4	72	Absent	AAA	AAA
Example	29	41	1	4	122	Absent	AA	AAA

(continued)

Category	No.	Surface structure of plated layer					Performance	
		Al-Si-Zn-Ca phase	Ca-Zn phase having equivalent circle diameter of 1 μm or more	Ca-Zn phase having equivalent circle diameter of less than 1 μm	Mg-Si-Zn-Al phase	Mg ₂ Sn phase	Planar corrosion resistance	Coating adhesion
		Number density (phases/ (10000 μm^2))	Number density (phases/ (10000 μm^2))	Number density (phases/ (10000 μm^2))	Number density (phases/ (10000 μm^2))	Present or absent		
Example	30	50	1	5	150	Absent	A	A
Comparative Example	31	<u>0</u>	<u>11</u>	2	0	Absent	B	A
Comparative Example	32	<u>0</u>	<u>15</u>	2	0	Absent	AA	B
Comparative Example	33	<u>0</u>	<u>13</u>	2	0	Absent	B	B
Comparative Example	34	Defect in external appearance						
Comparative Example	35	<u>0</u>	<u>15</u>	1	0	Absent	B	B
Comparative Example	36	<u>0</u>	<u>40</u>	2	0	Absent	B	B
Comparative Example	37	<u>0</u>	<u>12</u>	2	0	Absent	B	B
Comparative Example	38	<u>0</u>	<u>18</u>	1	0	Absent	B	B
Example	39	5	0	5	30	Absent	AAA	AAA
Underline means outside of the range of the present invention.								

INDUSTRIAL APPLICABILITY

[0109] The plated steel sheet of the present disclosure has both excellent planar corrosion resistance and coating adhesion and thus has high industrial applicability.

REFERENCE SIGNS LIST

[0110]

1 Plated steel sheet

11 Steel sheet

12 Plated layer

Claims

1. A plated steel sheet, comprising:

a steel plate, and a plated layer disposed on a surface of the steel plate,
 wherein the plated layer has a chemical composition containing, in mass%,
 Al: 10.0 to 30.0%,
 Mg: 3.0 to 15.0%,
 Fe: 0.01 to 2.0%,
 Si: more than 0 to 2.0%, and
 Ca: 0.05 to 2.0%, and
 further containing one or two selected from the group consisting of the following group A and group B,
 with a remainder consisting of Zn and impurities,
 a number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface of
 the plated layer is 0 to 10 per area of 10,000 μm^2 , and
 a number density of Al-Si-Zn-Ca phases having an equivalent circle diameter of 1 μm or more exposed on the
 surface of the plated layer is 1 to 50 per area of 10,000 μm^2
 [Group A] Ni: 0 to 1.0%
 [Group B] 0 to 5% in total of one or more of Sb: 0 to 0.5%, Pb: 0 to 0.5%, Cu: 0 to 1.0%, Sn: 0 to 2.0%, Ti: 0 to 1.0%,
 Cr: 0 to 1.0%, Nb: 0 to 1.0%, Zr: 0 to 1.0%, Mn: 0 to 1.0%, Mo: 0 to 1.0%, Ag: 0 to 1.0%, Li: 0 to 1.0%, La: 0 to 0.5%,
 Ce: 0 to 0.5%, B: 0 to 0.5%, Y: 0 to 0.5%, P: 0 to 0.5%, Sr: 0 to 0.5%, Co: 0 to 0.5%, Bi: 0 to 0.5%, In: 0 to 0.5%, V: 0 to
 0.5%, and W: 0 to 0.5%.

2. The plated steel sheet according to claim 1, wherein

Mg and Si in the chemical composition of the plated layer are Mg: 4.5 to 8 mass% and Si: 0.1 to 2 mass%, and
 the number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface
 of the plated layer is 0 to 3 per area of 10,000 μm^2 .

3. The plated steel sheet according to claim 1, wherein

Al, Mg, and Si in the chemical composition of the plated layer are Al: 15 to 25 mass%, Mg: 4.5 to 8 mass%, and Si:
 0.1 to 2 mass%, and
 the number density of Ca-Zn phases having an equivalent circle diameter of 1 μm or more exposed on the surface
 of the plated layer is 0 per area of 10,000 μm^2 .

4. The plated steel sheet according to any one of claims 1 to 3, wherein

Al, Mg, and Si in the chemical composition of the plated layer are Al: 15 to 25 mass%, Mg: 4.5 to 8 mass%, and Si:
 0.1 to 2 mass%, and
 a number density of Mg-Si-Zn-Al phases having a major axis of 2 μm or more exposed on the surface of the plated
 layer is 5 to 150 per area of 10,000 μm^2 .

5. The plated steel sheet according to any one of claims 1 to 3, wherein

Sn in the chemical composition of the plated layer is Sn: 0.05 to 0.5 mass%, and
 a Mg_2Sn phase is detected in the plated layer by X-ray diffraction measurement of the plated layer.

6. The plated steel sheet according to claim 4, wherein

Sn in the chemical composition of the plated layer is Sn: 0.05 to 0.5 mass%, and
 a Mg_2Sn phase is detected in the plated layer by X-ray diffraction measurement of the plated layer.

7. The plated steel sheet according to claim 1, wherein the plated layer has a chemical composition containing the group A in mass%.

8. The plated steel sheet according to claim 1, wherein the plated layer has a chemical composition containing the group B in mass%.

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9. The plated steel sheet according to claim 1, wherein a number density of Ca-Zn phases having an equivalent circle diameter of less than 1 μm exposed on the surface of the plated layer is 1 or more per area of 10,000 μm^2 .

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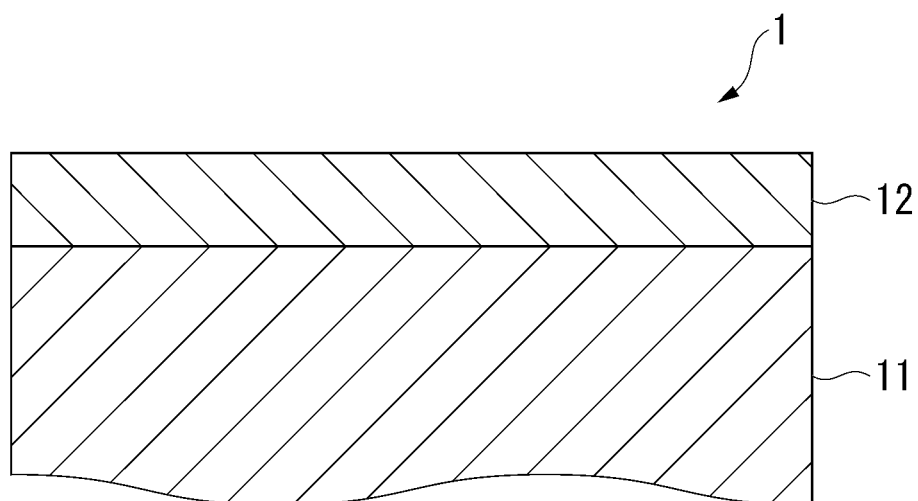
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FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/022632

A. CLASSIFICATION OF SUBJECT MATTER

C23C 2/06(2006.01)i; *C22C 18/04*(2006.01)i; *C23C 2/26*(2006.01)i; *C23C 2/40*(2006.01)i
 FI: C23C2/06; C23C2/40; C22C18/04; C23C2/26

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)

C23C2/06; C22C18/04; C23C2/26; C23C2/40

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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 2021/171514 A1 (NIPPON STEEL CORP.) 02 September 2021 (2021-09-02) examples 2-3, 5, paragraphs [0040]-[0050], fig. 2	1-2, 5, 7-8
A		3-4, 6, 9

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

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Date of the actual completion of the international search

15 August 2023

Date of mailing of the international search report

29 August 2023

Name and mailing address of the ISA/JP

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 Japan

Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT Information on patent family members				International application No. PCT/JP2023/022632		
Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)
WO	2021/171514	A1	02 September 2021	EP	4112768	A1
				examples 2-3, 5, paragraphs		
				[0040]-[0050], fig. 2		
				CN	114945698	A
				KR	10-2022-0127890	A

REFERENCES CITED IN THE DESCRIPTION

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- WO 2018139619 A [0007]
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