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(54) **PLATED STEEL SHEET AND METHOD FOR MANUFACTURING SAME**

(57) Provided is a plated steel sheet having low lightness from immediately after being produced and suppressed detachment of a plating layer. The plated steel sheet has a plating layer comprising 1.0-22.0 mass% of Al and 1.5-10.0 mass% of Mg, the remaining portion being Zn and an optionally added trace additive. The plated steel sheet has a surface lightness (L^*) of 50 or less, and has an X-ray diffraction spectrum satis-

fying all of (1)-(3). (1): A/B is 0.001-0.015. (2): A/C is 1.2 or more. (3): The half width d of a peak indicated by A is 0.30-1.00 deg. A, B and C each represents the peak intensity of a peak indicating the 100 plane of ZnO at which 2θ appears in 31.27-32.27 deg, the peak intensity of a peak indicating the 101 plane of Zn at which 2θ appears in 42.73-43.73 deg, and the intensity when 2θ is 30.00 deg.

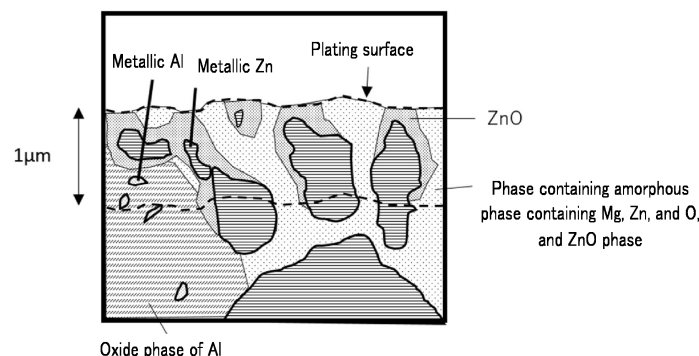


FIG. 1B

Description

Technical Field

5 **[0001]** The present invention relates to a plated steel sheet and a method for manufacturing the same.

Background Art

10 **[0002]** Steel sheets used for building roofing materials and exterior materials, home appliances, automobiles, and the like are required to have a low surface lightness (for example, blackened steel sheet) in order to enhance aesthetic appearance. For example, PTL 1 and PTL 2 describe a black-plated steel sheet in which a molten Al- and Mg-containing Zn plating layer formed on a surface of a steel sheet is subjected to steam treatment to form a black oxide, thereby exhibiting a black appearance.

15 **[0003]** PTL 3 describes that a hot-dip galvanized steel sheet subjected to a skin pass after plating undergoes a blackening phenomenon during storage or transportation.

Citation List

Patent Literature

20

[0004]

PTL 1

Japanese Patent Application Laid-Open No. 2013-241665

25

PTL 2

WO2016/157665

PTL 3

Japanese Patent Application Laid-Open No. H11-335866 A

30 Summary of Invention

Technical Problem

35 **[0005]** Plated steel sheets having low surface lightness as described in PTL 1 and PTL 2 have been considered to be applied to various uses because of their high aesthetic appearance. However, PTL 3 describes that a hot-dip galvanized steel sheet subjected to a skin pass undergoes blackening over time, and this document regards such blackening as undesirable and investigates suppression of blackening. In contrast, for applications requiring aesthetic appearance, it is preferable that the plated steel sheet have low lightness immediately after production.

40 **[0006]** It is considered that the plated steel sheets described in PTL 1 and PTL 2 have reduced lightness due to the formation of an oxide such as zinc oxide (ZnO) by steam treatment (see PTL 2). In addition, the plated steel sheet described in PTL 1 is said to be able to maintain a black appearance even in processed portions by forming black oxide also inside the plating. On the other hand, in recent years, plated steel sheets have been required to withstand more severe processing conditions, and even when subjected to such severe processing conditions, it is required that oxides formed on the surface be less likely to detach.

45 **[0007]** The present invention has been made in view of the above circumstances, and an object thereof is to provide a plated steel sheet that has low lightness immediately after production and in which detachment of the plating layer is suppressed more effectively than in the conventional art, as well as a method for manufacturing such a plated steel sheet.

50 Solution to Problem

[0008] One aspect of the present invention for achieving the above object relates to the following plated steel sheets [1] to [4].

55 [1] A plated steel sheet including:

a steel sheet; and

a plating layer having an Al content of 1.0 mass% or more and 22.0 mass% or less and an Mg content of 1.5

mass% or more and 10.0 mass% or less with a balance composed of Zn and an optionally added trace additive, in which
a lightness (L*) of a surface of the plated steel sheet is 50 or less, and
an X-ray diffraction spectrum of the plating layer satisfies all of conditions (1) to (3) below, the X-ray diffraction spectrum being obtained by X-ray diffraction using a Cu X-ray tube at a voltage of 50 kV and a current of 300 mA:

- (1) A/B is 0.001 or more and 0.015 or less;
- (2) A/C is 1.2 or more; and
- (3) a half width d of a peak indicating A is 0.30 deg or more and 1.00 deg or less,

in which

A is a peak intensity of a peak indicating a (100) plane of ZnO appearing when 2θ is in a range of 31.27 deg to 32.27 deg,
B is a peak intensity of a peak indicating a (101) plane of Zn appearing when 2θ is in a range of 42.73 deg to 43.73 deg, and
C is an intensity when 2θ is 30.00 deg.

[2] The plated steel sheet according to [1] in which
the plating layer includes a phase, the phase containing a ZnO phase and an amorphous phase containing Mg, Zn, and oxygen.

[3] The plated steel sheet according to [1] or [2] in which
when cross sections each having a length of 15 μm in a direction parallel to the surface of the plated steel sheet are observed at arbitrarily selected ten locations, respectively, the plating layer includes, in each cross section, a metallic Zn phase or a metallic Al phase within a depth of 1 μm from a surface opposite the steel sheet.

[4] A plated steel sheet according to any one of [1] to [3], further including:
a chemical conversion coating on a side of the plating layer opposite the steel sheet.

[0009] One aspect of the present invention for achieving the above object relates to a method for manufacturing a plated steel sheet according to the following [5].

A method for manufacturing a plated steel sheet, the method including:

preparing a material plated steel sheet including a steel sheet and a plating layer, the plating layer having an Al content of 1.0 mass% or more and 22.0 mass% or less and an Mg content of 1.5 mass% or more and 10.0 mass% or less with a balance composed of Zn and an optionally added trace additive;
applying strain to the plating layer by performing a skin pass using a skin pass roll having a surface arithmetic average roughness Ra of 2.1 μm or more and 2.8 μm or less under conditions such that an elongation ratio of the material plated steel sheet is 0.8% or more and 1.3% or less and a rolling load (ton) is 4.0 times or more and 7.0 times or less a product of a sheet thickness (mm) and a sheet width (m); and
steam-treating the material plated steel sheet including the plating layer to which the strain has been applied.

Advantageous Effects of Invention

[0010] According to the present invention, there are provided a plated steel sheet that has low lightness immediately after production and in which detachment of the plating layer is suppressed, and a method for manufacturing such a plated steel sheet.

Brief Description of Drawings

[0011] [FIG. 1] FIG. 1A is a cross-sectional STEM bright-field image of a cross section of a plated steel sheet according to an embodiment of the present invention, captured by a scanning transmission electron microscope (STEM); and FIG. 1B is a schematic diagram illustrating the metallic Zn phases and the metallic Al phases in FIG. 1A.

Description of Embodiments

1. Plated steel sheet

[0012] An embodiment of the present invention relates to a plated steel sheet including a steel sheet and a plating layer.

1-1. Steel sheet

[0013] The type of the steel sheet is not particularly limited. Any steel sheet can be used, such as hot-rolled mild steel sheet and steel strip described in JIS G 3131 (2018), hot-rolled steel sheet and steel strip for automobiles described in JIS G 3113 (2018), cold-rolled steel sheet and steel strip described in JIS G 3141 (2017), and various stainless steel sheets (including austenitic, martensitic, ferritic, and ferrite-martensite dual-phase types).

1-2. Plating layer

[0014] The plating layer is a plating layer referred to as an Al- and Mg-containing zinc-based plating layer in which the aluminum (Al) content is 1.0 mass% or more and 22.0 mass% or less, the magnesium (Mg) content is 1.5 mass% or more and 10.0 mass% or less, and the balance is composed of Zn and optionally added trace additives. The contents are proportions of the respective elements based on the total mass of the plating layer.

[0015] The plating layer may contain an optionally added trace additive and unavoidable impurities. The trace additive is, for example, an element added to enhance the corrosion resistance of the plating layer. Examples of the trace additive include elements such as Sn, Bi, In, Ca, Y, La, Ce, Si, Cr, Ti, Ni, Co, V, Nb, Cu, Mn, Fe, Sr, Sb, Pb, B, Li, Zr, Mo, W, Ag, and P. The content of these trace additives can be set to a level from the detection limit up to 1 mass%.

[0016] Al in the plating layer passivates and thereby enhances the corrosion resistance of the plated steel sheet, and also suppresses dross formation during manufacturing. Further, when Al is present in an appropriate amount in the plating layer, the lightness of the plating layer is readily reduced by steam treatment. By setting the Al content to 1.0 mass% or more, the corrosion resistance of the plated steel sheet can be sufficiently enhanced, dross formation can be sufficiently suppressed, and furthermore, the lightness of the plating layer can be easily lowered. By setting the Al content to 22.0 mass% or less, adhesion of the plating layer can be sufficiently enhanced, the sacrificial corrosion protection effect of Zn can be sufficiently exhibited, and the lightness of the plating layer can be easily lowered.

[0017] Mg in the plating layer uniformly forms a dense corrosion product on the surface of the plating layer in a corrosive environment, thereby preventing penetration of corrosive factors and enhancing the corrosion resistance of the plated steel sheet. Further, when Mg is present in an appropriate amount in the plating layer, the lightness of the plating layer is readily reduced by steam treatment. By setting the Mg content to 1.5 mass% or more, the above dense and uniform corrosion product can be sufficiently formed to sufficiently enhance the corrosion resistance of the plated steel sheet, and the lightness of the plating layer can be easily lowered. By setting the Mg content to 10.0 mass% or less, the sacrificial corrosion protection effect of Zn can be sufficiently exhibited, and dross formation can be readily suppressed.

[0018] By subjecting a plated steel sheet having the above composition to steam treatment, an oxide such as zinc oxide (ZnO) can be formed on the surface layer and inside the plating layer to lower the surface lightness of the plated steel sheet. However, when an excessive amount of ZnO is formed, during processing under more severe conditions (for example, 2T bending or processing under conditions more severe than that), detachment of the plating layer may occur due to detachment of ZnO. In view of this, based on the findings described below, the present inventors have developed a plated steel sheet that is less likely to undergo detachment of the plating layer even during processing under more severe conditions while the lightness is also sufficiently lowered.

[0019] ZnO is generally a semiconductor whose band-gap energy is greater than that of visible light, and thus it transmits visible light. Accordingly, as a material ZnO is transparent, and in powder form it appears white due to diffuse reflection of light. Thus, mere formation of ZnO does not sufficiently lower the lightness of a plated steel sheet. The present inventors investigated this point and found that, in a plated steel sheet whose lightness has been lowered by steam treatment, the degree of blackening of ZnO can be evaluated by the half width of a peak (near $2\theta = 31.77^\circ$) indicating ZnO in an X-ray diffraction spectrum. A large half width in an X-ray diffraction spectrum generally indicates that there are a large number of lattice defects in the crystal and/or that the crystal size is small. From this, it was found that, in a plated steel sheet whose lightness is lowered by steam treatment, there is ZnO having features of a large number of lattice defects, small crystal size, or both. It is considered that an energy level is formed within the band gap of ZnO owing to such lattice defects or the crystal size effect, and visible light is absorbed via this energy level, so that the lightness of the steam-treated plated steel sheet is lowered.

[0020] Based on these findings, the present inventors considered that, when ZnO having more lattice defects and/or a smaller crystal size is formed in a larger proportion than in the related art, the amount of ZnO can be reduced so as to make the plating layer less likely to detach during processing, while still achieving a sufficient decrease in the

lightness of the plated steel sheet.

[0021] Specifically, in the plated steel sheet according to the present embodiment, the surface lightness (L^*) is 50 or less. By subjecting a plated steel sheet having the above composition to steam treatment, an oxide such as zinc oxide (ZnO) can be formed in the plating layer to lower the surface lightness of the plated steel sheet. The surface lightness (L^*) is preferably 45 or less, and more preferably 40 or less.

[0022] The lightness (L^* value) of the surface of the plating layer is a value measured with a color difference meter (CR-400, manufactured by Konica Minolta, Inc.) in accordance with JIS Z 8722:2009 by a diffused illumination vertical light receiving method including specular reflected light. The illumination diameter at measurement is 11 mm ϕ , and the measurement diameter is 8 mm ϕ .

[0023] In addition, in the plated steel sheet of the present embodiment, an X-ray diffraction spectrum obtained by performing X-ray diffraction on the plating layer using a Cu X-ray tube (Cu target) at a voltage of 50 kV and a current of 300 mA satisfies all of the following conditions (1) to (3):

(1) A/B is 0.001 or more and 0.015 or less,

(2) A/C is 1.2 or more, and

(3) The half width d of the peak indicating A is 0.30 deg or more and 1.00 deg or less.

[0024] Here, A is the peak intensity of a peak indicating the (100) plane of ZnO appearing when 2θ is in the range of 31.27 deg to 32.27 deg; B is the peak intensity of a peak indicating the (101) plane of Zn appearing when 2θ is in the range of 42.73 deg to 43.73 deg; and C is the intensity when 2θ is 30.00 deg.

[0025] A is the intensity (unit: cps) of the peak near 2θ of 31.77 deg indicating the (100) plane of ZnO. B is the intensity (unit: cps) of the peak near 2θ of 43.23 deg indicating the (101) plane of zinc (Zn).

[0026] Regarding condition (1), when A/B is 0.001 or more, it can be said that Zn has been oxidized and a sufficient amount of ZnO has been formed. When A/B is 0.015 or less, ZnO is not formed in excess, and therefore detachment of the plating layer due to detachment of ZnO during processing is less likely to occur. From the viewpoint of balancing these factors, A/B is preferably 0.001 or more and 0.012 or less, more preferably 0.001 or more and 0.011 or less, and even more preferably 0.001 or more and 0.008 or less.

[0027] Regarding condition (2), when A/C is 1.2 or more, it can be said that a sufficient amount of ZnO has been formed. From the viewpoint of making it less likely for the plating layer to be detached during processing due to detachment of ZnO, the upper limit of A/C is preferably 3.5 or less. From the viewpoint of balancing these factors, A/C is preferably 1.5 or more and 3.0 or less, and more preferably 1.5 or more and 2.7 or less.

[0028] Regarding condition (3), when the half width d of the peak indicating A (the (100) plane of ZnO) is 0.30 deg or more, it can be said that more lattice defects have been generated and/or finer ZnO has been formed. When the half width d is 1.00 deg or less, the peak is not excessively broadened, and it can be said that a sufficient amount of ZnO has been formed. From the viewpoint of balancing these factors, the half width d is preferably 0.40 or more and 0.90 or less, and more preferably 0.50 or more and 0.80 or less.

[0029] In this manner, in the present embodiment, while forming an appropriate amount of ZnO, the number of lattice defects of the ZnO is increased and/or the crystal size of the ZnO is reduced (that is, the half width d is increased), so that the lightness of the plating layer is sufficiently lowered even with a smaller amount of ZnO. As a result, the amount of ZnO is appropriately limited, thereby suppressing detachment of the plating layer during processing due to detachment of ZnO.

[0030] It is preferable that the plating layer includes a phase-the phase containing ZnO and an amorphous phase that contains Mg, Zn, and oxygen. The amorphous phase is a phase formed by alteration, through steam treatment, of an MgZn_2 phase present in the plating layer before the steam treatment. The MgZn_2 phase oxidizes (blackens) relatively rapidly. Therefore, when a plated steel sheet containing an MgZn_2 phase is subjected to steam treatment, a plated steel sheet having low lightness can be produced in a short time. In addition, since MgZn_2 phases are distributed relatively uniformly throughout the plating layer, a plated steel sheet having less unevenness in lightness can be obtained by steam treatment.

[0031] FIG. 1A is a cross-sectional STEM image of a cross section of the plated steel sheet of the present embodiment, and FIG. 1B is a schematic diagram illustrating the metallic Zn phases and the metallic Al phases in FIG. 1A (note that, in a STEM bright-field image, elements with larger atomic numbers appear darker; therefore, the actual color tone of the cross section is not reflected in FIG. 1A). The plated steel sheet of the present embodiment can sufficiently lower the lightness of the plating layer even when the steam treatment time is shortened. Therefore, as illustrated in FIGS. 1A and 1B, the plating layer may contain a metallic Zn phase or a metallic Al phase, which are unoxidized phases. In the present embodiment, because the efficiency of lightness reduction is enhanced by increasing the number of lattice defects in ZnO and/or reducing the crystal size of ZnO, the surface lightness (L^*) of the plating layer becomes sufficiently low even when an unoxidized metallic Zn phase or metallic Al phase is present near the plating surface layer. Further, when the plating layer contains a prescribed amount of metallic Zn phases or metallic Al

phases, these phases are softer than ZnO and therefore make the plating layer less likely to detach during processing.

[0032] From the viewpoint of achieving satisfactory resistance to detachment of the plating at processed portions, it is preferable that the above metallic Zn phases and metallic Al phases be uniformly distributed over the surface of the plating layer. Specifically, when cross sections each having a length of 15 μm in a direction parallel to the surface of the plated steel sheet are observed at arbitrarily selected ten locations, respectively, it is preferable that the plating layer includes, in each cross section, a metallic Zn phase or a metallic Al phase within a depth of 1 μm from the surface opposite the steel sheet.

[0033] The metallic Zn phase or metallic Al phase contained in the plating layer is measured on a cross section prepared by processing, by using a focused ion beam apparatus, an average location on the surface of the plated steel sheet according to a cryo-FIB sampling method. Among the obtained cross sections, an observation range of 15 μm in width along the surface of the plated steel sheet is set, and this observation range is observed with a transmission electron microscope (TEM). Then, phases at the surface layer of the plating are identified by elemental analysis using energy-dispersive X-ray spectroscopy (EDS) and by electron diffraction analysis. Thereafter, a determination range with a depth of 1 μm and along the surface of the plating layer is set, and it is determined whether a metallic Zn phase or metallic Al phase is present within this determination range. Note that the surface of the plating layer usually does not have a straight line shape and has an irregular uneven shape. Therefore, the determination range with a depth of 1 μm is defined along this uneven shape. Ten locations representing average surface positions of the plated steel sheet are arbitrarily selected, and observation of the cross sections and determination of the presence or absence of a metallic Zn phase or a metallic Al phase are performed.

[0034] The average film thickness of the plating layer is preferably 3 μm to 100 μm . The larger the average film thickness of the plating layer, the less likely scratches generated during handling are to reach the steel sheet, improving the retention of appearance and the corrosion resistance. The smaller the average film thickness of the plating layer, the more the detachment of the plating layer during processing due to the difference in ductility between the steel sheet and the plating layer can be suppressed.

1-3. Chemical conversion coating

[0035] The plated steel sheet may have a chemical conversion coating on the outer side (the side opposite to the steel sheet). The chemical conversion coating improves adhesion between the zinc-based plating layer and a primer coating and enhances the corrosion resistance of the steel sheet. The type of the chemical conversion coating is not particularly limited, and the coating may be a layer formed by a known chemical conversion treatment such as a chromate treatment, a chromate-free treatment, or a phosphate treatment. Among these, a chromate-free chemical conversion coating formed by a chromate-free treatment is preferable.

[0036] The chromate-free chemical conversion coating may be a layer containing, for example, a binder resin, a silane coupling agent, a zirconium compound, silica, phosphoric acid or a salt thereof, a fluoride, a valve metal compound, and/or an organic acid. A chemical conversion coating containing these materials is more likely to enhance adhesion to the zinc-based plating layer and, because it has high barrier properties (denseness) against moisture and corrosive ions and other corrosive factors, it readily enhances the corrosion resistance of the plated steel sheet.

[0037] The type of the binder resin is not particularly limited, and known organic resins such as polyester resins, polyurethane resins, epoxy resins, phenolic resins, acrylic resins, and polyolefin resins can be used. From the viewpoint of enhancing adhesion to the zinc-based plating layer, it is preferable to use polyester resins, urethane resins, epoxy resins, and acrylic resins, each having a polar site or a polar functional group in the molecular chain. These resins may be used singly or in combination of two or more.

[0038] The content of the binder resin is preferably 1 mass% or more and 85 mass% or less, more preferably 1 mass% or more and 60 mass% or less, and even more preferably 1 mass% or more and 40 mass% or less, based on the total mass of the chemical conversion coating.

[0039] The valve metal compound is a compound containing at least one member selected from the group consisting of V, Nb, Ta, and W. Among them, V and Nb are particularly preferable. The valve metal compound contributes to improvement in the corrosion resistance of the chemical conversion treated steel sheet or to suppression of excessive gloss in the chemical conversion treated steel sheet. Examples of the valve metal compound include oxides, hydroxides, and fluorides of the above valve metals.

[0040] The content of the valve metal compound in the chemical conversion coating is preferably 0.005 to 2.0 mass% in terms of the valve metal atoms, from the viewpoint of improving corrosion resistance.

[0041] Examples of phosphoric acid or a salt thereof include phosphoric acids such as orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, triphosphoric acid, and tetraphosphoric acid, and salts thereof (for example, ammonium salts such as triammonium phosphate and diammonium hydrogen phosphate), phosphonic acids such as aminotri(methylene phosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra(methylene phosphonic acid), and diethylenetriamine penta(methylene phosphonic acid), and salts thereof, and organic phospho-

ric acids such as phytic acid and salts thereof. In addition to ammonium salts, metal salts with Na, Mg, Al, K, Ca, Mn, Ni, Zn, and Fe may also be used. These phosphoric acids or salts thereof may be used singly or in combination of two or more.

[0042] The content of phosphoric acid or a salt thereof is preferably 1 mass% or more and 20 mass% or less, and more preferably 1 mass% or more and 10 mass% or less, based on the total mass of the chemical conversion coating. By setting the content within the above range, adhesion between the chemical conversion coating and the zinc-based plating layer can be further enhanced, and the corrosion resistance of the plated steel sheet can be further improved.

[0043] Examples of the organic acid include tartaric acid, tannic acid, citric acid, oxalic acid, malonic acid, lactic acid, acetic acid, and ascorbic acid.

[0044] The amount of the organic acid added to a chemical conversion solution for forming the chemical conversion coating can be set to 2 g/L or more and 80 g/L or less. By setting the amount within the above range, adhesion between the chemical conversion coating and the zinc-based plating layer can be further enhanced, and the corrosion resistance of the plated steel sheet can be further improved.

[0045] The silane coupling agent and the zirconium compound form a cross-linked structure in the chemical conversion coating, thereby enhancing adhesion of the chemical conversion coating to the zinc-based plating layer and increasing barrier properties so as to further enhance the corrosion resistance of the plated steel sheet. In addition, silica, phosphoric acid or a salt thereof, a fluoride, and a vanadium compound function as inhibitors to form a precipitated coating or a passivation coating, thereby further enhancing the corrosion resistance of the plated steel sheet.

[0046] Examples of the silane coupling agent include γ -(2-aminoethyl)aminopropyltrimethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -(2-aminoethyl)aminopropyltriethoxysilane, γ -(2-aminoethyl)aminopropylmethyldiethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropyltrimethoxysilane, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropylmethyldimethoxysilane, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropyltriethoxysilane, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropylmethyldiethoxysilane, γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldimethoxysilane, γ -glycidoxypentyltriethoxysilane, γ -glycidoxypentylmethyldiethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropyltriethoxysilane, γ -mercaptopropylmethyldiethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, vinyltriethoxysilane, γ -chloropropyltrimethoxysilane, γ -chloropropylmethyldimethoxysilane, γ -chloropropyltriethoxysilane, γ -chloropropylmethyldiethoxysilane, hexamethyldisilazane, γ -anilinopropyltrimethoxysilane, γ -anilinopropylmethyldimethoxysilane, γ -anilinopropyltriethoxysilane, γ -anilinopropylmethyldiethoxysilane, vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane, octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride, octadecyldimethyl[3-(methyldimethoxysilyl)propyl]ammonium chloride, octadecyldimethyl[3-(triethoxysilyl)propyl]ammonium chloride, octadecyldimethyl[3-(methyldiethoxysilyl)propyl]ammonium chloride, γ -chloropropylmethyldimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, methyltrichlorosilane, dimethyldichlorosilane, and trimethylchlorosilane. These silane coupling agents may be used singly or in combination of two or more.

[0047] The amount of the silane coupling agent added to a chemical conversion solution for forming the chemical conversion coating can be set to 2 g/L or more and 80 g/L or less. By setting the amount within the above range, adhesion between the chemical conversion coating and the zinc-based plating layer can be further enhanced, and the corrosion resistance of the plated steel sheet can be further improved.

[0048] Examples of the zirconium compound include zirconium n-propylate, zirconium n-butylate, zirconium tetraacetylacetonate, zirconium monoacetylacetonate, zirconium bis(acetylacetonate), zirconium monoethyl acetoacetate, zirconium acetylacetonate bis(ethyl acetoacetate), zirconium acetate, zirconium monostearate, zirconium carbonate, ammonium zirconium carbonate, potassium zirconium carbonate, and sodium zirconium carbonate. These zirconium compounds may be used singly or in combination of two or more.

[0049] The amount of the zirconium compound added to a chemical conversion solution for forming the chemical conversion coating can be set to 2 g/L or more and 80 g/L or less. By setting the amount within the above range, adhesion between the chemical conversion coating and the zinc-based plating layer can be further enhanced, and the corrosion resistance of the plated steel sheet can be further improved.

[0050] As the silica, commercially available silica gel, powdered silica, and the like can be used widely.

[0051] The amount of silica added to a chemical conversion solution for forming the chemical conversion coating can be set to 1 g/L or more and 40 g/L or less. By setting the amount within the above range, the corrosion resistance of the plated steel sheet can be further improved.

[0052] Examples of the fluoride include ammonium zirconium fluoride, ammonium silicofluoride, ammonium titanium fluoride, sodium fluoride, potassium fluoride, calcium fluoride, lithium fluoride, fluorotitanic acid, and fluoro-zirconic acid. These fluorides may be used singly or in combination of two or more.

[0053] The content of the fluoride is preferably 1 mass% or more and 20 mass% or less, and more preferably 1

mass% or more and 10 mass% or less, based on the total mass of the chemical conversion coating. By setting the content within the above range, adhesion between the chemical conversion coating and the zinc-based plating layer can be further enhanced, and the corrosion resistance of the plated steel sheet can be further improved.

[0054] Examples of the vanadium compound include vanadium compounds obtained by reducing pentavalent vanadium compounds such as vanadium pentoxide, metavanadic acid, ammonium metavanadate, sodium metavanadate, and vanadium oxytrichloride to divalent to tetravalent with a reducing agent; and divalent to tetravalent vanadium compounds such as vanadium trioxide, vanadium dioxide, vanadium oxysulfate, vanadium oxyoxalate, vanadium oxyacetylacetonate, vanadium acetylacetonate, vanadium trichloride, phosphovanadomolybdic acid, vanadium sulfate, vanadium dichloride, and vanadium oxide. These vanadium compounds may be used singly or in combination of two or more.

[0055] The content of the vanadium compound is preferably 1 mass% or more and 20 mass% or less, and more preferably 1 mass% or more and 10 mass% or less, based on the total mass of the chemical conversion coating. By setting the content within the above range, adhesion between the chemical conversion coating and the zinc-based plating layer can be further enhanced, and the corrosion resistance of the plated steel sheet can be further improved.

[0056] The coating weight of the chemical conversion coating is preferably 10 mg/m² or more and 1000 mg/m² or less, more preferably 20 mg/m² or more and 800 mg/m² or less, and still more preferably 50 mg/m² or more and 600 mg/m² or less. Further, the coating weight of an inorganic chemical conversion coating containing no binder resin is preferably 20 mg/m² or more and 100 mg/m² or less, and more preferably 40 mg/m² or more and 80 mg/m² or less, in terms of valve metal coating weight. In addition, the coating weight of an organic chemical conversion coating containing a binder resin is preferably such that the film thickness is 0.3 μm or more and 2.5 μm or less, and more preferably 0.8 μm or more and 1.5 μm or less.

[0057] The chemical conversion coating can be formed by applying, to the surface of a zinc-based plating layer, a chemical conversion solution containing the components exemplified above and then drying. The chemical conversion solution may further contain an acid or an alkali for pH adjustment.

2. Method for manufacturing plated steel sheet

[0058] Examples of a method for producing the plated steel sheet described above include a method including the following: preparing a material plated steel sheet including a steel sheet and a plating layer, the plating layer having an Al content of 1.0 mass% or more and 22.0 mass% or less and an Mg content of 1.5 mass% or more with the balance composed of Zn and an optionally added trace additive (the plated steel sheet before steam treatment thus prepared is hereinafter also simply referred to as a "material plated steel sheet"); applying strain to the plating layer of the material plated steel sheet; and performing steam treatment on the material plated steel sheet including the plating layer to which strain has been applied.

2-1. Preparation of material plated steel sheet

[0059] First, a material plated steel sheet is prepared. The material plated steel sheet may be prepared by forming, on a steel sheet, a plating layer having the above composition, or the material plated steel sheet may be prepared by purchasing a material plated steel sheet having the above plating layer on the surface of a steel sheet.

[0060] The method for forming the plating layer is not limited. For example, the plating layer can be formed by a hot-dip plating method in which a steel sheet is immersed in a plating bath with an Al content of 1.0 mass% or more and 22.0 mass% or less and an Mg content of 1.5 mass% or more and 10.0 mass% or less, with the balance composed of Zn and optionally added trace additives, and then withdrawn and cooled. At this time, the average film thickness of the plating layer can be adjusted by changing the immersion time and/or the flow rate and pressure of gas applied during cooling.

[0061] The steel sheet may be subjected, as needed, to pretreatments such as cleaning and degreasing before immersion in the plating bath.

2-2. Application of strain

[0062] Strain may be applied by rolling the material plated steel sheet.

[0063] The rolling method is not particularly limited. For example, the material plated steel sheet may be allowed to pass between opposed rotating skin pass rolls, thereby applying pressure to the material plated steel sheet.

[0064] In the present embodiment, it is preferable that the arithmetic average roughness Ra of the surface of the skin pass roll be more than 2.1 μm and 2.8 μm or less, and more preferably more than 2.3 μm and 2.6 μm or less. By setting the arithmetic average roughness Ra of the surface of the skin pass roll to 2.1 μm or more, sufficient strain can be introduced so that a larger amount of ZnO having more lattice defects and/or a smaller crystal size can be

generated. By setting the arithmetic average roughness Ra of the surface of the skin pass roll to 2.8 μm or less, it is possible to suppress degradation in aesthetic appearance of the plated steel sheet, which would be caused by excessive irregularities on the plating surface.

[0065] Further, the elongation ratio of the material plated steel sheet by skin pass is preferably 0.8% or more and 1.3% or less, and more preferably 0.8% or more and 1.1% or less. By setting the elongation ratio of the material plated steel sheet by the skin pass roll to 0.8% or more, sufficient strain can be introduced so that a larger amount of ZnO having more lattice defects and/or a smaller crystal size can be generated. By setting the elongation ratio of the material plated steel sheet by the skin pass roll to 1.3% or less, it is possible to suppress a reduction in adhesion of the plating layer which would be caused by excessive generation of ZnO.

[0066] Furthermore, the rolling load (tons) during skin pass is preferably 4 times or more and 7 times or less the product of the sheet thickness (mm) and the sheet width (m). The load during skin pass increases as the thickness of the sheet being rolled increases. By setting the pressure applied by the skin pass to 4 times or more the product of the sheet thickness (mm) and the sheet width (m), appropriate strain can be applied to the material plated steel sheet so that a larger amount of ZnO having more lattice defects and/or a smaller crystal size can be generated. By setting the rolling load (tons) during skin pass to 7 times or less the product of the sheet thickness (mm) and the sheet width (m), it becomes less likely for cracks to occur in the plating layer. By suppressing the release of strain due to cracking, it becomes easier to achieve both low brightness and suppression of detachment of the plating layer during processing.

2-3. Steam treatment

[0067] The steam treatment can be performed by placing a material plated steel sheet in an atmosphere of high temperature and high humidity to bring steam into contact with the plating layer. The steam treatment is preferably carried out in a closed vessel.

[0068] By the steam treatment, phases containing any of Zn, Al, and Mg in the plating layer can be oxidized and those phases can be caused to undergo volumetric expansion. As a result, a plurality of fine protrusions are formed on the surface of the plating layer to reduce the gloss of the plated steel sheet, and the blackened phases formed by oxidation lower the lightness of the plated steel sheet.

[0069] The temperature in the steam treatment is preferably 105°C or more and 210°C or less, and more preferably 105°C or more and 150°C or less. The higher the temperature, the faster oxidation of the plating layer proceeds to form ZnO faster, so that the lightness of the plated steel sheet can be reduced in a shorter time. On the other hand, the lower the temperature, the more cracking due to rapid oxidation can be suppressed.

[0070] The relative humidity of the atmosphere during the steam treatment is preferably 60% or more and 100% or less, and more preferably 85% or more and less than 100%. The higher the relative humidity, the more quickly the gloss and lightness of the plated steel sheet can be reduced. Meanwhile, by setting the relative humidity to less than 100%, condensation water adhering to the surface of the material plated steel sheet can be suppressed and the gloss and lightness of the plated steel sheet can be reduced more uniformly.

[0071] The oxygen concentration of the atmosphere during the steam treatment is preferably 13 vol% or less. When the oxygen concentration is high, white ZnO is more likely to be formed, and a black appearance is less likely to be obtained. The oxygen concentration can be lowered, for example, by increasing the concentration of steam (relative humidity), by introducing an inert gas into the atmosphere (e.g., replacing air in the closed vessel with an inert gas), or by evacuating the air from the closed vessel using a vacuum pump or the like. As the inert gas, Ar, N₂, or He can be used.

[0072] The treatment time (soaking time) of the steam treatment is preferably 1 hour or more and 35 hours or less, and more preferably 5 hours or more and 25 hours or less. The longer the treatment time, the more the gloss and lightness of the plated steel sheet can be reduced. The shorter the treatment time, the more cracking in the plating layer due to volumetric expansion during the steam treatment and detachment of the plating layer during subsequent processing can be suppressed.

[0073] At this time, the gloss and lightness of the plated steel sheet to be produced can be adjusted to the desired levels by adjusting conditions such as the temperature and treatment time of the steam treatment in accordance with the composition (phase proportions) of the material plated steel sheet.

[0074] A chemical conversion coating or the like may be formed by a known method on the plated steel sheet thus produced.

[0075] The plated steel sheet described above has low surface lightness and excellent aesthetic appearance, and is less likely to suffer detachment of the plating layer during processing. Therefore, the plated steel sheet is useful as a plated steel sheet used for roofing and exterior materials of buildings, home appliances, automobile components, and the like.

Examples

[0076] The present invention will be described in more detail below with reference to Examples, but the present invention is not limited to these Examples.

[Test 1]

1. Production of plated steel sheets

[0077] Using cold-rolled steel sheets described in JIS G 3141:2021 each having a sheet thickness of 0.6 to 1.2 mm and a sheet width of 1.05 m as a base material, a plurality of hot-dip Al- and Mg-containing Zn-plated steel sheets (material plated steel sheets) having different compositions and thicknesses of the plating layers were produced. Further, a skin pass treatment was performed by a skin pass rolling mill disposed at a subsequent stage of the plating apparatus (downstream side in the sheet passing direction). At this time, the surface roughness of the skin pass rolls of the skin pass rolling mill, the elongation ratio of the material plated steel sheet, and the rolling load were varied to apply strain to the material plated steel sheets under different conditions.

[0078] Thereafter, the material plated steel sheets were each placed in a highly accelerated life test apparatus (PC-304R8, manufactured by Hirayama Manufacturing Corporation), steam was brought into contact with the plating layer, and a plated steel sheet having reduced lightness of the plating layer was obtained. At this time, the temperature, relative humidity, and soaking time of the steam treatment were varied, and the material plated steel sheets were steam-treated under different conditions.

[0079] X-ray diffraction (XRD) measurement was performed on the produced plated steel sheets. A RINT-TTR III (manufactured by Rigaku Corporation) was used as the X-ray diffraction analyzer, and the obtained X-ray diffraction patterns were analyzed using the analysis software PDXL2 (manufactured by Rigaku Corporation). The presence or absence of peaks attributable to the MgZn_2 phase was checked by analysis, and when a MgZn_2 phase was confirmed, it was determined that a MgZn_2 phase was present in the plated steel sheet.

[0080] Tables 1 and 2 show the plating compositions, film thicknesses of the plating layers, skin pass conditions, and steam treatment conditions of plated steel sheets 1 to 26 thus obtained.

Table 1

No.	Base sheet thickness (mm)	Plating layer				Skin pass conditions					Superheated steam oxidation conditions			
		Composition (mass%)			Film thickness (μm)	Presence of MgZn ₂ phase in plating layer	Roll Roughness (Ra/μm)	Elongation ratio (%)	Rolling load (T)	Rolling Load (T) / (sheet thickness (mm) × sheet width (m))	Temperature (°C)	Relative humidity (%)	Soaking time (h)	
		Zn	Al	Mg										
1	0.8	Balance	6.0	3.0	20	Present	2.5	0.8	3.9	4.6	115	95	15	
2	0.8	Balance	11.0	3.0	20	Present	2.5	0.9	4.1	4.9	115	95	15	
3	0.8	Balance	19.0	6.0	30	Present	2.4	1.2	4.7	5.6	130	90	20	
4	0.8	Balance	2.0	3.0	20	Present	2.7	0.9	4.2	5.0	115	95	15	
5	0.8	Balance	21.0	2.0	20	Present	2.3	1.3	4.8	5.7	110	95	15	
6	0.8	Balance	6.0	1.6	20	Present	2.4	1.0	4.2	5.0	120	95	10	
7	0.8	Balance	11.0	10.0	30	Present	2.3	1.0	4.1	4.9	120	95	12	
8	0.8	Balance	6.0	3.0	20	Present	2.3	1.1	4.2	5.0	180	98	2	
9	0.8	Balance	6.0	3.0	20	Present	2.4	0.9	4.2	5.0	200	86	1	
10	0.8	Balance	10.0	4.0	35	Present	2.8	1.0	4.3	5.1	115	85	20	
11	0.8	Balance	9.0	2.5	20	Present	2.5	0.9	3.8	4.5	113	95	15	
12	0.8	Balance	6.0	3.0	30	Present	2.6	1.2	4.6	5.5	113	95	1	
13	0.8	Balance	5.0	2.0	25	Present	2.4	1.0	4.3	5.1	105	95	28	
14	0.8	Balance	5.0	2.0	25	Present	2.4	1.0	4.2	5.0	125	95	25	
15	1.2	Balance	15.0	5.0	20	Present	2.1	0.9	5.3	4.2	120	100	18	
16	0.6	Balance	11.0	3.0	20	Present	2.2	1.3	4.2	6.7	185	90	34	
17	0.6	Balance	6.0	3.0	20	Present	2.3	1.2	3.8	6.0	160	98	34	
18	0.8	Balance	19.0	6.0	20	Present	2.3	1.1	4.4	5.2	115	90	10	

Table 2

No.	Base sheet thickness (mm)	Plating layer				Presence of MgZn ₂ phase in plating layer	Skin pass conditions				Superheated steam oxidation conditions		
		Composition (mass%)			Film thickness (μm)		Roll Roughness (Ra/μm)	Elongation ratio (%)	Rolling load (T)	Rolling Load (T) / (sheet thickness (mm) × sheet width (m))	Temperature (°C)	Relative humidity (%)	Soaking time (h)
		Zn	Al	Mg									
19	0.8	Balance	0.5	2.0	20	20	2.5	0.9	4.2	5.0	115	95	8
20	0.8	Balance	6.0	1.0	20	20	2.4	1.0	4.1	4.9	115	80	10
21	0.8	Balance	6.0	3.0	20	20	2.2	1.5	2.7	3.2	130	95	20
22	0.8	Balance	35.0	5.0	30	30	2.3	1.2	4.3	5.1	125	95	8
23	0.8	Balance	11.0	5.0	30	30	1.8	1.3	4.8	5.7	125	90	12
24	0.8	Balance	9.0	3.0	25	25	2.0	0.6	2.8	3.3	125	90	38
25	0.8	Balance	12.0	3.0	25	25	2.7	0.4	2.5	3.0	105	98	21
26	0.8	Balance	6.0	3.0	20	20	2.4	1.2	6.5	7.7	120	90	18

2. Measurement and evaluation

2-1. X-ray diffraction (XRD) measurement

5 **[0081]** For the plating layers of plated steel sheets Nos. 1 to 26, X-ray diffraction patterns were obtained using a RINT-TTR III (Rigaku), an X-ray diffraction analyzer. The obtained X-ray diffraction patterns were analyzed with PDXL2 (Rigaku). The measurement was performed using a Cu X-ray tube under the measurement conditions as follows: a voltage of 50 kV, a current of 300 mA, a divergence slit of $1/2^\circ$, vertical divergence limiting slit of 5 mm, a scattering slit and a receiving slit being open, and using a horizontal goniometer having a goniometer radius of 280
10 mm with a monochrome receiving slit. D/teX Ultra Full was used as a detector, and X-ray diffraction measurement was performed at a scan speed of 2 deg/min, a step width of 0.01 deg, a scan axis of $2\theta/\theta$, and a scan range of 5 to 100 deg to obtain an X-ray diffraction pattern. From the obtained X-ray diffraction pattern, the peak intensity (A) of a peak indicating the (100) plane of ZnO appearing when 2θ was in a range of 31.27 deg to 32.27 deg, the peak intensity (B) of a peak indicating the (101) plane of Zn appearing when 2θ was in a range of 42.73 deg and 43.73 deg, and the
15 intensity (C) when 2θ was 30.00 deg were determined. Then, the values of A/B and A/C were determined. Further, for the obtained X-ray diffraction pattern, background treatment was performed by a fitting method, and after smoothing by B-spline, $K\alpha_2$ removal (intensity ratio of $K\alpha_1$ and $K\alpha_2$: 0.4970) by the Rachinger method was performed. After this treatment, the peak shape was fitted with a split pseudo-Voigt function, and then the half width d of the peak indicating A was determined on the analysis software. For ZnO, data of PDF card number 00-036-1451 was used, and for Zn,
20 data of PDF card number 00-004-0831 was used.

2-2. STEM measurement

25 **[0082]** Cross sections were prepared from average locations on the surface of the plated steel sheets using a focused ion beam apparatus by a cryo-FIB- μ sampling method, and STEM measurements were performed on the cross sections. Samples were produced using NB5000 manufactured by Hitachi High-Technologies Corporation as the focused ion beam apparatus. Specifically, in the obtained cross section, an observation range having a width of 15 μm along the surface of the plated steel sheet was set, and this observation range was observed with a transmission electron microscope (TEM). Phases in the plating surface layer were identified by elemental analysis by energy-dispersive X-ray spectroscopy (EDS) and electron diffraction analysis. A 200 kV field emission transmission electron microscope JEM-2100F (manufactured by JEOL Ltd.) was used as the electron microscope, and JED-2300T (manu-
30 factured by JEOL Ltd.) was used as the EDS analyzer. Then, a determination range having a depth of 1 μm was set along the surface of the plating layer, and it was determined whether or not a metallic Zn phase or a metallic Al phase was contained within this determination range. Note that the determination range having a depth of 1 μm was a range
35 of 1 μm from each surface along the uneven shape of the surface of the plating layer. Ten average locations on the surface of the plated steel sheet were arbitrarily set, and observation and identification were performed to confirm whether either a metallic Zn phase or a metallic Al phase was present in all the cross sections. When there is one or more cross sections in which either a metallic Zn phase or a metallic Al phase was present among the ten set locations, the evaluation was determined as "Present", and when there was less than one location, the evaluation
40 was determined as "Absent".

2-3. Evaluation of lightness

45 **[0083]** Using a color difference meter (CR-400, manufactured by Konica Minolta, Inc.), the surface lightness (L^* value) of the plating layer was measured by a diffused illumination vertical light receiving method including specular reflection light in accordance with JIS Z8722:2009. The illumination diameter during measurement was 11 mm Φ , and the measurement diameter was 8 mm Φ . Based on the obtained lightness (L^* value), detachment of the plating layer was evaluated according to the following criteria.

- 50 ⊙: L^* value is 40 or less
 ◦: L^* value is more than 40 and 50 or less
 ×: L^* value is more than 50

2-4. Evaluation of detachment of plating layer

55 **[0084]** A test specimen of 50 mm $\times$ 50 mm having a sheet thickness of 0.8 mm obtained from each plated steel sheet was subjected to 2T bending. Thereafter, an adhesive tape (cellophane tape manufactured by Nichiban Co., Ltd.) was attached to the apex of the bent portion and peeled off, and the peeled adhesive tape was observed with a

magnifying glass. Based on the maximum size of the plating detached fragment (maximum distance between apexes of the detached fragment) adhering to the adhesive tape, detachment of the plating layer was evaluated according to the following criteria.

- 5 ⊙: The maximum size of the detached plating fragment is less than 0.2 mm
 ∘: The maximum size of the detached plating fragment is 0.2 mm or more and less than 0.5 mm
 △: The maximum size of the detached plating fragment is 0.5 mm or more and less than 1 mm
 ×: The maximum size of the detached plating fragment is 1 mm or more

10 **[0085]** The measurement and evaluation results are shown in Table 3.

Table 3

Classification	No.	XRD measurement			STEM measurement	Performance evaluation	
		A/B	A/C	Half width of A	Presence of metallic Zn and Al phases within 1 μm from surface	Lightness (L* value)	Detachment of plating layer
Example	1	0.006	2.4	0.63	Present	38(⊙)	⊙
Example	2	0.009	2.6	0.71	Present	39(⊙)	⊙
Example	3	0.009	1.9	0.82	Present	42(○)	⊙
Example	4	0.008	2.1	0.56	Present	43(○)	⊙
Example	5	0.010	1.3	0.61	Present	41(○)	⊙
Example	6	0.007	1.6	0.77	Present	39(⊙)	⊙
Example	7	0.011	2.5	0.65	Present	37(⊙)	⊙
Example	8	0.009	2.2	0.40	Present	43(○)	⊙
Example	9	0.012	2.1	0.64	Present	40(⊙)	○
Example	10	0.002	1.3	0.80	Present	47(○)	⊙
Example	11	0.012	2.5	0.65	Present	40(⊙)	⊙
Example	12	0.005	1.9	0.35	Present	44(⊙)	⊙
Example	13	0.014	2.5	0.85	Present	39(⊙)	○
Example	14	0.008	1.8	0.95	Present	41(○)	⊙
Example	15	0.011	2.0	0.75	Present	41(○)	⊙
Example	16	0.014	2.5	0.51	Absent	29(⊙)	○
Example	17	0.015	3.0	0.39	Absent	41(○)	○
Example	18	0.005	2.6	0.75	Present	41(○)	⊙
Comparative example	19	0.006	1.7	0.68	Present	51(×)	⊙
Comparative example	20	0.010	1.5	0.55	Present	55(×)	⊙
Comparative example	21	0.018	2.4	0.58	Absent	39(⊙)	△
Comparative example	22	0.002	1.2	0.45	Present	61(×)	○
Comparative example	23	0.015	2.5	0.28	Absent	41(○)	△
Comparative example	24	0.019	2.9	0.24	Absent	42(○)	△
Comparative example	25	0.016	2.4	0.25	Present	52(×)	○
Comparative example	26	0.008	2.5	0.19	Present	58(×)	○

[0086] As shown in Tables 1 to 3, by steam-treating a material plated steel sheet including a plating layer in which the Al content is 1.0 mass% or more and 22.0 mass% or less, the Mg content is 1.5 mass% or more and 10.0 mass%

or less, and the balance consists of Zn and an optionally added trace additive, plated steel sheets having low lightness could be obtained (plated steel sheets 1 to 18).

[0087] At this time, by applying an appropriate strain to the material plated steel sheet before the steam treatment, it was possible to obtain a plated steel sheet in which the lightness of the plating layer was sufficiently reduced and from which the plating layer was less likely to detach even in a 2T bending test, which is more severe than in the related art (plated steel sheets 1 to 18).

[0088] On the other hand, in plated steel sheet 19 in which the amount of Al in the plating layer was small, plated steel sheet 20 in which the amount of Mg in the plating layer was small, and plated steel sheet 22 in which the amount of Al was excessive, the plating layer was not sufficiently blackened even after the steam treatment.

[0089] Further, in plated steel sheet 21 in which the elongation ratio during the skin pass treatment was excessive, a large amount of ZnO was generated during the steam treatment, and a large amount of the plating layer detached in the 2T bending test. In addition, in plated steel sheets 23 and 24 in which the amount of applied strain was small because the roll roughness, elongation ratio, or load during the skin pass test was small, ZnO having more lattice defects and/or a smaller crystal size was not sufficiently generated, and it was necessary to generate a large amount of ZnO to achieve sufficient blackening; therefore, a large amount of the plating layer detached in the 2T bending test. Similarly, when plated steel sheet 25, in which the amount of applied strain was small because the elongation ratio or load during the skin pass test was small, was subjected to steam treatment to the extent that the plating layer did not detach significantly in a 2T bending test, the plating layer did not blacken sufficiently. Furthermore, in plated steel sheet 26, in which the load during the skin pass test was excessive, cracks occurred and strain was released, so that ZnO having more lattice defects or a smaller crystal size was not sufficiently generated. Therefore, when the plated steel sheet was subjected to steam treatment to the extent that the plating layer did not detach significantly in a 2T bending test, the plating layer did not blacken sufficiently.

[0090] Further, STEM measurement was performed on cross sections of plated steel sheets 1 to 18 obtained by processing average locations on the surface by a cryo-FIB- μ sampling method using a focused ion beam apparatus. This observation range was observed with a transmission electron microscope (TEM), and phases in the plating surface layer were identified by elemental analysis by energy-dispersive X-ray spectroscopy (EDS) and electron diffraction analysis. As a result, it was confirmed that in all plated steel sheets, the MgZn_2 phase had changed to a phase containing an amorphous phase containing Mg, Zn, and O, and a ZnO phase.

[0091] Further, in plated steel sheet 26 in which the rolling load during the skin pass was increased, observation of the plating surface with a scanning electron microscope revealed that cracks had occurred in the plating layer. Then, it is probable that the strain was released due to the cracks, so that the plating layer could not be sufficiently blackened.

[Experiment 2]

1. Production of plated steel sheets

[0092] In the same manner as in Experiment 1, formation of a plating layer, skin pass treatment, and steam treatment were performed to obtain plated steel sheet A and plated steel sheet B. Table 4 shows the plating compositions, film thicknesses of the plating layers, skin pass conditions, and steam treatment conditions of plated steel sheet A and plated steel sheet B.

Table 4

No.	Base sheet thickness (mm)	Plating layer			Skin pass conditions				Superheated steam oxidation conditions		
		Composition (mass%)			Roll roughness (Ra/ μm)	Elongation ratio (%)	Rolling load (T)	Rolling Load (T) / (sheet thickness (mm) $\times$ sheet width (m))	Temperature ($^{\circ}\text{C}$)	Relative humidity (%)	Soaking time (h)
		Zn	Al	Mg							
A	0.8	Balance	6.0	3.0	2.5	1.0	4.3	5.1	115	95	15
B	0.8	Balance	11.0	3.0	2.5	0.9	4.2	5.0	125	95	10

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[0093] The materials shown in Table 5 were added to water in the amounts shown in the table and mixed to prepare treatment liquids 1 to 18 for chemical conversion treatment.

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Table 5

No.	Organic resin		Valve metal compound		Phosphate		Organic acid	
	Type	Concentration (g/L)	Type	Concentration (g/L)	Type	Concentration (g/L)	Type	Concentration (g/L)
1	-	-	(NH ₄) ₂ TiF ₆	Ti: 8	H ₃ PO ₄	P: 10	-	-
2	-	-	V ₂ O ₅	V: 5	NH ₄ H ₂ PO ₄	P: 8	-	-
3	-	-	VOSO ₄	V: 5	-	-	Tannic acid	5
4	-	-	ZrO(NO ₃) ₂	Zr: 5	(NH ₄) ₃ PO ₄ ·3H ₂ O	P: 5	-	-
5	-	-	(NH ₄) ₂ ZrO(CO ₃) ₂	Zr: 5	H ₃ PO ₄	P: 10	-	-
6	-	-	(NH ₄) ₆ Mo ₇ O ₂₄	Mo: 5	-	-	Tartaric acid	10
7	-	-	V ₂ O ₅ (NH ₄) ₂ ZrO(CO ₃) ₂	V: 3 Zr: 6	H ₃ PO ₄	P: 5	-	-
8	-	-	(NH ₄) ₂ TiF ₆ VOSO ₄	Ti: 2 V: 4	-	-	-	-
9	-	-	H ₂ SiF ₆	Si: 5	(NH ₄) ₃ PO ₄ ·3H ₂ O	P: 5	-	-
10	Urethane resin	100.0	-	-	H ₃ PO ₄	P: 5	Tannic acid	3
11	Urethane resin	100.0	ZrO(NO ₃) ₂	Zr: 2	H ₃ PO ₄	P: 3	-	-
12	Urethane resin	100.0	(NH ₄) ₂ ZrO(CO ₃) ₂	Zr: 5	-	-	-	-
13	Urethane resin	100.0	(NH ₄) ₂ TiF ₆	Ti: 5	-	-	Tannic acid	5
14	Epoxy resin	100.0	V ₂ O ₅	V: 5	NH ₄ H ₂ PO ₄	P: 5	-	-
15	Epoxy resin	100.0	(NH ₄) ₆ Mo ₇ O ₂₄	Mo: 8	-	-	Tartaric acid	5
16	Acrylic resin	100.0	(NH ₄) ₂ ZrO(CO ₃) ₂	Zr: 5	H ₃ PO ₄	P: 5	-	-
17	Polyolefin resin	100.0	V ₂ O ₅	V: 5	NH ₄ H ₂ PO ₄	P: 5	-	-

[0094] Each treatment liquid was applied to the surface of plated steel sheet A or plated steel sheet B, and heated and dried at a peak metal temperature of 120°C to form a chemical conversion coating. The amount of an applied treatment liquid was adjusted such that for treatment liquids 1 to 9, which are inorganic treatment liquids, the amount of valve metal in the chemical conversion coating was the amount shown in Table 5, and for treatment liquids 10 to 18, which are organic treatment liquids, the film thickness of the chemical conversion coating was the amount shown in Table 6.

2. Measurement and evaluation

2-1. X-ray diffraction (XRD) measurement

[0095] X-ray diffraction measurement was performed in the same manner as in Experiment 1 to obtain an X-ray diffraction pattern. From the obtained X-ray diffraction pattern, the values of A/B and A/C were determined. Further, the half width d of the peak indicating A was determined.

2-2. STEM measurement

[0096] STEM measurement was performed in the same manner as in Experiment 1. Then, it was determined whether or not a metallic Zn phase or a metallic Al phase was contained within a determination range having a depth of 1 μm along the surface of the plating layer.

2-3. Evaluation of lightness

[0097] The surface lightness (L* value) of the plating layer was measured in the same manner as in Experiment 1.

2-4. Evaluation of detachment of plating layer

[0098] Detachment of the plating layer was evaluated in the same manner as in Experiment 1.

2-5. Evaluation of corrosion resistance

[0099] A test specimen of 50 mm × 100 mm having a sheet thickness of 0.8 mm obtained from each plated steel sheet was sealed at its end faces, and then a salt spray test was performed in which a NaCl aqueous solution at 35°C was sprayed for 12 hours in accordance with JIS Z2371:2015. After spraying for 12 hours, the area ratio of white rust generated on the test specimen was measured to determine the proportion of the area where white rust was generated in the total area of the test specimen (area where white rust was generated / total area of test specimen = white rust occurrence ratio), and corrosion resistance was evaluated according to the following criteria.

◎: White rust occurrence ratio was 0%

◦: White rust occurrence ratio was more than 0% and less than 5%

△: White rust occurrence ratio was 5% or more

[0100] Table 6 and Table 7 show the measurement and evaluation results.

Table 6

Classification	No.	Plated steel sheet	Chemical conversion treatment		XRD measurement			STEM measurement	Evaluation		
			Treatment solution No.	Coating weight of valve metal (mg/m ²)	A/B	A/C	Half width of A		Lightness (L* value)	Detachment of plating layer	Corrosion resistance: White rust occurrence area ratio (%)
Example	27	A	1	Ti: 40	0.006	2.4	0.63	Presence of metallic Zn and Al phases within 1 μm from surface	38(⊙)	⊙	0(⊙)
Example	28		2	V: 30	0.007	2.4	0.65	Presence	39(⊙)	⊙	0(⊙)
Example	29		3	V: 30	0.006	2.5	0.61	Presence	38(⊙)	⊙	2(○)
Example	30		4	Zr: 25	0.006	2.5	0.63	Presence	40(⊙)	⊙	0(⊙)
Example	31		5	Zr: 30	0.007	2.4	0.60	Presence	41(○)	⊙	0(⊙)
Example	32		-	-	0.006	2.3	0.64	Presence	38(⊙)	⊙	40(Δ)
Example	33	B	6	Mo: 35	0.009	2.1	0.51	Presence	39(⊙)	⊙	0(⊙)
Example	34		7	V: 10 Zr: 20	0.009	2.0	0.53	Presence	37(⊙)	⊙	0(⊙)
Example	35		8	Ti: 10 V: 20	0.011	2.2	0.53	Presence	43(○)	⊙	0(⊙)
Example	36		9	Si: 30	0.010	2.1	0.51	Presence	40(⊙)	○	3(0)
Example	37		-	-	0.008	2.1	0.54	Presence	39(⊙)	○	35(Δ)

Table 7

Classification	No.	Plated steel sheet	Chemical conversion treatment		XRD measurement			STEM measurement	Evaluation		
			Treatment solution No.	Film thickness (μm)	A/B	A/C	Half width of A	Presence of metallic Zn and Al phases within 1 μm from surface	Lightness (L* value)	Detachment of plating layer	Corrosion resistance: White rust occurrence area ratio (%)
Example	38	A	10	1.5	0.007	2.4	0.68	Present	37(⊙)	⊙	0(⊙)
Example	39		11	1.2	0.008	2.5	0.65	Present	40(⊙)	⊙	0(⊙)
Example	40		12	2.0	0.005	2.3	0.66	Present	37(⊙)	⊙	0(⊙)
Example	41		13	1.5	0.006	2.5	0.67	Present	39(⊙)	⊙	0(⊙)
Example	42	B	14	1.5	0.006	2.4	0.64	Present	41(○)	⊙	0(⊙)
Example	43		15	1.2	0.011	2.0	0.75	Present	43(○)	⊙	0(⊙)
Example	44		16	1.4	0.014	2.2	0.51	Present	42(○)	⊙	0(⊙)
Example	45		17	1.5	0.015	2.1	0.39	Present	39(⊙)	⊙	0(⊙)
Example	46		18	1.5	0.005	2.0	0.75	Present	41(○)	⊙	0(⊙)

[0101] As shown in Tables 3 to 7, even with the plated steel sheets subjected to the chemical conversion treatment, it was possible to obtain plated steel sheets in which the lightness of the plating layer was sufficiently reduced and from which the plating layer was less likely to detach even in a 2T bending test, which is more severe than in the related art.

[0102] This application is entitled to and claims the benefit of Japanese Patent Application No. 2023-211053 filed on December 14, 2023. The entire contents described in the description, claims, and drawings of the original application are incorporated herein by reference.

Industrial Applicability

[0103] The plated steel sheet of the present invention has low surface lightness and excellent aesthetic appearance, and detachment of the plating layer due to processing is less likely to occur. Therefore, the present plated steel sheet can be suitably used in various fields requiring aesthetic appearance.

Claims

1. A plated steel sheet comprising:

a steel sheet; and
a plating layer having an Al content of 1.0 mass% or more and 22.0 mass% or less and an Mg content of 1.5 mass% or more and 10.0 mass% or less with a balance composed of Zn and an optionally added trace additive, wherein
a lightness (L^*) of a surface of the plated steel sheet is 50 or less, and
an X-ray diffraction spectrum of the plating layer satisfies all of conditions (1) to (3) below, the X-ray diffraction spectrum being obtained by X-ray diffraction using a Cu X-ray tube at a voltage of 50 kV and a current of 300 mA:

- (1) A/B is 0.001 or more and 0.015 or less;
- (2) A/C is 1.2 or more; and
- (3) a half width d of a peak indicating A is 0.30 deg or more and 1.00 deg or less,

wherein

A is a peak intensity of a peak indicating a (100) plane of ZnO appearing when 2θ is in a range of 31.27 deg to 32.27 deg,
B is a peak intensity of a peak indicating a (101) plane of Zn appearing when 2θ is in a range of 42.73 deg to 43.73 deg, and
C is an intensity when 2θ is 30.00 deg.

2. The plated steel sheet according to claim 1, wherein the plating layer includes a phase, the phase containing ZnO and an amorphous phase containing Mg, Zn, and oxygen.

3. The plated steel sheet according to claim 1 or 2, wherein when cross sections each having a length of 15 μm in a direction parallel to the surface of the plated steel sheet are observed at arbitrarily selected ten locations, respectively, the plating layer includes, in each cross section, a metallic Zn phase or a metallic Al phase within a depth of 1 μm from a surface opposite the steel sheet.

4. The plated steel sheet according to any one of claims 1 to 3, further comprising: a chemical conversion coating on a side of the plating layer opposite the steel sheet.

5. A method for manufacturing a plated steel sheet, the method comprising:

preparing a material plated steel sheet comprising a steel sheet and a plating layer, the plating layer having an Al content of 1.0 mass% or more and 22.0 mass% or less and an Mg content of 1.5 mass% or more and 10.0 mass% or less with a balance composed of Zn and an optionally added trace additive;
applying strain to the plating layer by performing a skin pass using a skin pass roll having a surface arithmetic

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average roughness Ra of 2.1 μm or more and 2.8 μm or less under conditions such that an elongation ratio of the material plated steel sheet is 0.8% or more and 1.3% or less and a rolling load (ton) is 4.0 times or more and 7.0 times or less a product of a sheet thickness (mm) and a sheet width (m); and steam-treating the material plated steel sheet including the plating layer to which the strain has been applied.

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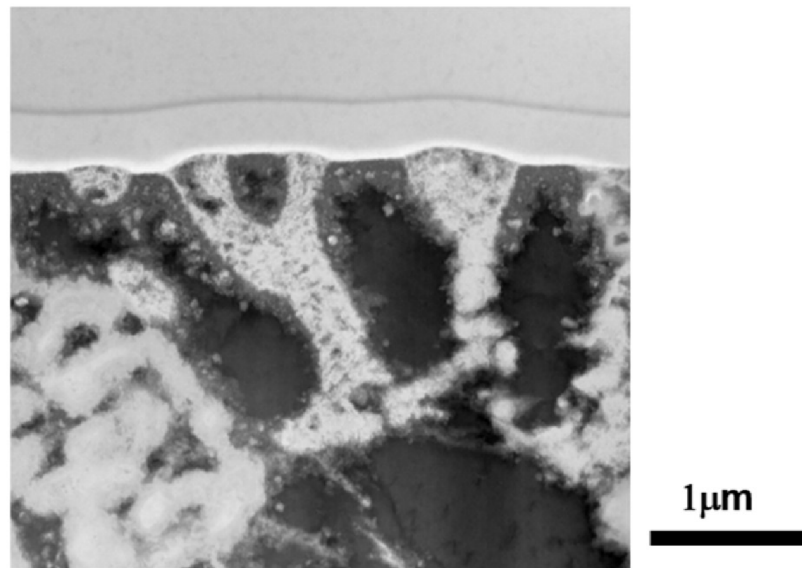
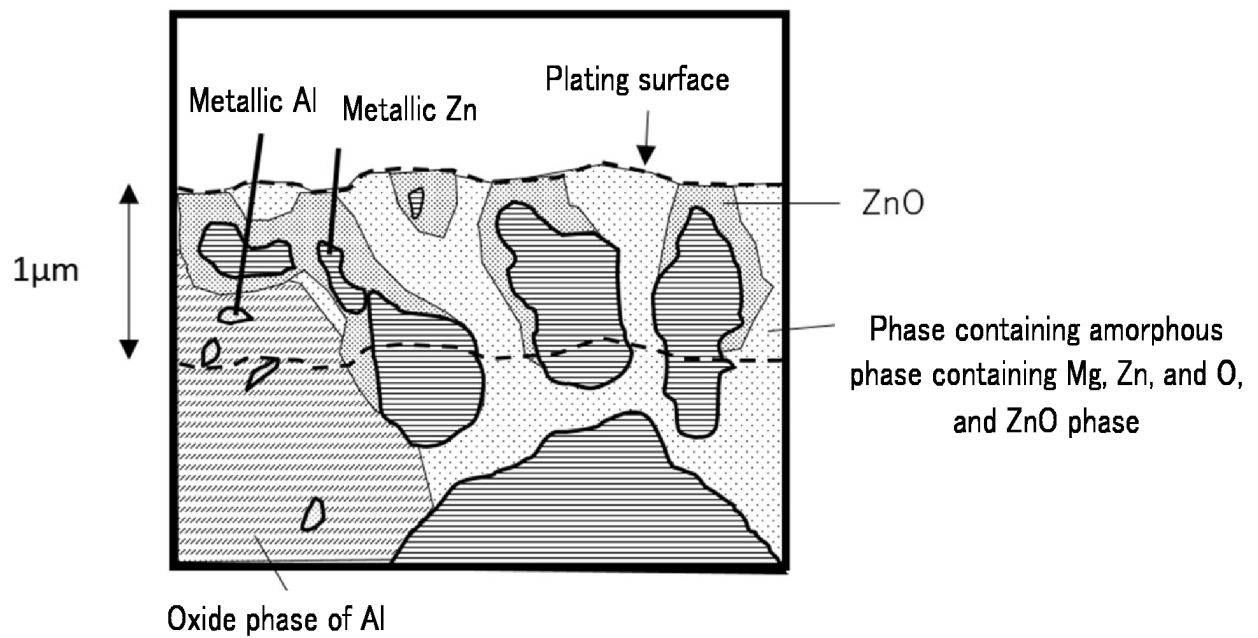


FIG. 1A



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/025818

A. CLASSIFICATION OF SUBJECT MATTER

C23C 2/06(2006.01)i; **C22C 18/00**(2006.01)i; **C22C 18/04**(2006.01)i; **C23C 2/26**(2006.01)i
 FI: C23C2/06; C23C2/26; C22C18/04; C22C18/00

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; C22C18/00; C22C18/04; C23C2/26

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 1971-2024
 Registered utility model specifications of Japan 1996-2024
 Published registered utility model applications of Japan 1994-2024

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.
A	JP 2017-218647 A (NISSHIN STEEL CO., LTD.) 14 December 2017 (2017-12-14) paragraphs [0017]-[0039], [0062]-[0079], fig. 3	1-5
A	JP 2006-061952 A (SUMITOMO METAL INDUSTRIES, LTD.) 09 March 2006 (2006-03-09) paragraphs [0053]-[0062]	1-5
A	CN 101905240 A (PANZHIHUA GROUP PANZHIHUA STEEL & VANADIUM CO., LTD.) 08 December 2010 (2010-12-08) paragraphs [0023]-[0057]	1-5
A	US 2018/0345339 A1 (POSCO) 06 December 2018 (2018-12-06) paragraphs [0055]-[0061]	1-5

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

☒ See patent family annex.

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

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“Y” 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

“&” document member of the same patent family

Date of the actual completion of the international search

26 September 2024

Date of mailing of the international search report

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Name and mailing address of the ISA/JP

**Japan Patent Office (ISA/JP)
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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2024/025818

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP	2017-218647	A	14 December 2017	(Family: none)	
JP	2006-061952	A	09 March 2006	(Family: none)	
CN	101905240	A	08 December 2010	(Family: none)	
US	2018/0345339	A1	06 December 2018	WO	2017/052306 A1
				EP	3354360 A1
				CN	108136454 A
				KR	10-1677390 B1

REFERENCES CITED IN THE DESCRIPTION

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- WO 2016157665 A [0004]
- JP H11335866 A [0004]
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