

DESCRIPTION

TITLE

HOT-DIP AL-ZN-SI-MG COATED STEEL SHEET AND PRODUCTION
5 METHOD THEREFOR, SURFACE-TREATED STEEL SHEET AND
PRODUCTION METHOD THEREFOR, AND PAINTED STEEL SHEET AND
PRODUCTION METHOD THEREFOR

TECHNICAL FIELD

10 **[0001]** The present disclosure relates to a hot-dip Al-Zn-Si-Mg coated steel
sheet stably having excellent corrosion resistance and a production method
therefor, a surface-treated steel sheet and a production method therefor, and a
painted steel sheet and a production method therefor.

15 BACKGROUND

[0002] Hot-dip Al-Zn coated steel sheets, such as 55 % Al-Zn coated steel
sheets, are known to exhibit high corrosion resistance among hot-dip
galvanized steel sheets because they have both sacrificial protection
performance of Zn and high corrosion resistance of Al. Due to their excellent
20 corrosion resistance, hot-dip Al-Zn coated steel sheets are used mainly in the
field of building materials such as roofs and walls which are exposed outdoors
for long periods and in the field of civil engineering and construction such as
guardrails, wiring and piping, and soundproof walls. In particular, given the
increasing need for materials with excellent corrosion resistance and
25 maintenance-free materials in severer use environments such as acid rain
caused by air pollution, spraying of snow melting agents for road deicing in
snow zones, and development of coastal areas, the demand for hot-dip Al-Zn
coated steel sheets is increasing in recent years.

[0003] A coating of a hot-dip Al-Zn coated steel sheet is composed of α -Al
30 phase in which Al supersaturatedly containing Zn solidifies in dendrites and a
Zn-Al eutectic structure existing in the dendrite interstices (interdendrites),
and has a structure in which a plurality of layers of the α -Al phase are stacked
in the thickness direction of the coating. Such a characteristic coating structure
makes the corrosion path from the surface complex, thus preventing corrosion
35 to progress easily. It is therefore known that a hot-dip Al-Zn coated steel sheet
achieves better corrosion resistance than a hot-dip galvanized steel sheet

having the same coating thickness.

[0004] Attempts have been made to extend the life of hot-dip Al-Zn coated steel sheets, and hot-dip Al-Zn-Si-Mg coated steel sheets having Mg added thereto have been put to practical use.

5 As such a hot-dip Al-Zn-Si-Mg coated steel sheet, for example, JP 5020228 B2 (PTL 1) discloses a hot-dip Al-Zn-Si-Mg coated steel sheet wherein the coating contains an Al-Zn-Si alloy containing Mg, the Al-Zn-Si alloy is an alloy containing 45 wt% to 60 wt% of elemental aluminum, 37 wt% to 46 wt% of elemental zinc, and 1.2 wt% to 2.3 wt% of Si, and the Mg
10 concentration is 1 wt% to 5 wt%.

 JP 5000039 B2 (PTL 2) discloses a hot-dip Al-Zn-Si-Mg coated steel sheet wherein the coating contains one or more of 2 % to 10 % of Mg and 0.01 % to 10 % of Ca in order to improve the corrosion resistance and also enhance the protective effect after the base steel sheet is exposed.

15 JP 2002-12959 A (PTL 3) discloses a hot-dip Al-Zn-Si-Mg coated steel sheet wherein a coating layer containing, in mass%, Mg: 1 % to 15 %, Si: 2 % to 15 %, and Zn: 11 % to 25 % with the balance consisting of Al and inevitable impurities is formed, and the size of intermetallic compounds such as Mg₂Si phase and MgZn₂ phase existing in the coating is limited to 10 μm or less in
20 order to improve the corrosion resistance of flat parts and end surfaces.

[0005] Hot-dip Al-Zn coated steel sheets mentioned above have aesthetic appearance with a spangle pattern of white metallic luster, and accordingly are often used in an unpainted state. There is thus high requirements for their appearance. Hence, techniques for improving the appearance of hot-dip Al-Zn
25 coated steel sheets have also been developed.

 For example, JP 3983932 B2 (PTL 4) discloses a hot-dip Al-Zn-Si-Mg coated steel sheet wherein a coating contains 0.01 % to 10 % of Sr to suppress wrinkle-like irregularity defects.

 JP 2011-514934 A (PTL 5) discloses a hot-dip Al-Zn-Si-Mg coated steel
30 sheet wherein a coating contains 500 ppm to 3000 ppm of Sr to suppress mottling defects.

[0006] Hot-dip Al-Zn coated steel sheets have a problem in that, when used in a severe corrosion environment, corrosion of the coating causes white rust. Since white rust degrades the appearance of steel sheets, the development of
35 coated steel sheets with improved white rust resistance is underway.

 For example, JP 5751093 B2 (PTL 6) discloses a hot-dip Al-Zn-Si-Mg

coated steel sheet wherein the mass ratio of Mg in Si-Mg phase to the total amount of Mg in the coating layer is adjusted for the purpose of improving the white rust resistance of the worked part.

JP 2019-155872 A (PTL 7) discloses a technique of improving the blackening resistance and the white rust resistance by forming a chemical conversion layer containing urethane resin on a coating of a hot-dip Al-Zn-Si-Mg coated steel sheet.

[0007] Painted steel sheets each obtained by forming, on the surface of a hot-dip Al-Zn coated steel sheet, a chemical conversion layer, a primer painting layer, a top coat painting layer, etc. are subjected to various works such as 90-degree bending and 180-degree bending by press forming, roll forming, or embossing. Such painted steel sheets are further required to have long-term painting layer durability. To meet the requirement, painted steel sheets are known that are each obtained by forming, on a hot-dip Al-Zn coated steel sheet, a chemical conversion layer containing chromate, a primer painting layer containing a chromate-based rust preventive pigment, and further a top coat painting layer excellent in atmospheric corrosion resistance such as a thermosetting polyester-based resin painting layer or a fluorine-based resin painting layer.

Recently, however, the use of chromate, which is an environmentally hazardous substance, in such painted steel sheets is considered a problem. There is thus a strong demand for the development of painted steel sheets that are chromate-free but can improve the corrosion resistance and the surface appearance.

As a technique to meet this demand, for example, JP 2005-169765 A (PTL 8) discloses a surface-treated hot-dip coated steel material obtained by forming, on the surface of a steel material, an aluminum-zinc alloy coating layer (α) containing Al, Zn, Si, and Mg in the respective adjusted amounts, forming, on the aluminum-zinc alloy coating layer (α), a coating (β) containing at least one compound (A) selected from the group consisting of a titanium compound and a zirconium compound as a film-forming component, and adjusting the mass ratio of Si-Mg phase in the aluminum-zinc alloy coating layer (α) to the total amount of Mg in the coating layer to 3 % or more.

CITATION LIST

Patent Literature

[0008] PTL 1: JP 5020228 B2
PTL 2: JP 5000039 B2
PTL 3: JP 2002-12959 A
PTL 4: JP 3983932 B2
5 PTL 5: JP 2011-514934 A
PTL 6: JP 5751093 B2
PTL 7: JP 2019-155872 A
PTL 8: JP 2005-169765 A

10 SUMMARY

(Technical Problem)

[0009] However, the techniques of including Mg in the coating as disclosed in PTL 1 to PTL 3 do not necessarily improve the corrosion resistance uniquely.

15 In the hot-dip Al-Zn-Si-Mg coated steel sheets disclosed in PTL 1 to PTL 3, Mg is simply included in the coating components to improve the corrosion resistance. However, the influence of components other than the four elements (Al, Zn, Si, Mg) and the characteristics of metallic phase and intermetallic compound phase constituting the coating are not taken into consideration, and it was not possible to uniformly decide the superiority or inferiority of corrosion resistance. Hence, even when a hot-dip Al-Zn-Si-Mg coated steel sheet is produced using a molten bath composition containing the same contents of the four element components with PTL 1 to PTL 3, the corrosion resistance varies in a corrosion acceleration test, and the corrosion resistance is not necessarily better than that of an Al-Zn coated steel sheet not containing Mg.

25 Regarding improvement in coating appearance, too, simply adding Sr to the coating does not necessarily eliminate wrinkle-like irregularity defects. Thus, in the hot-dip Al-Zn-Si-Mg coated steel sheets disclosed in PTL 4 and PTL 5, it is impossible to achieve both the corrosion resistance and the appearance in some cases. In addition, since Mg is an easily oxidizable element, Mg contained in the molten bath may cause the formation of oxides (top dross) near the bath surface, or, in the case of hot-dip coating, Fe-Al-based compounds (bottom dross) containing iron unevenly distributed inside or at the bottom of the molten bath may form with time. There is a possibility that such dross adheres to the surface of the coating and causes convex defects and the appearance of the coating surface is impaired.

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It is known that, in the case where a steel sheet is coated using a hot-dip Al-Zn-Si bath having Mg added thereto, not only α -Al phase but also Mg_2Si phase, MgZn_2 phase, and Si phase precipitate in the coating. However, it is still unclear how the precipitation amount and existence ratio of each phase influence the corrosion resistance.

[0010] Moreover, the white rust resistance cannot be sufficiently improved by any of the techniques. For the hot-dip Al-Zn-Si-Mg coated steel sheet in PTL 6, improvement in white rust resistance in the worked part and the heated flat part is mentioned, but the white rust resistance in the unheated flat part is not taken into consideration, and achieving stable white rust resistance is still an issue. For the hot-dip Al-Zn-Si-Mg coated steel sheet in PTL 7, excellent corrosion resistance and white rust resistance may not be achieved stably, and further improvement is desired.

[0011] Painted steel sheets are required to have long-term painting layer durability in a state in which they are subjected to various works such as 90-degree bending and 180-degree bending by press forming, roll forming, embossing, etc., as mentioned above. The technique in PTL 8 does not necessarily stably achieve post-working corrosion resistance and surface appearance.

The corrosion resistance of the painted steel sheet is influenced by the corrosion resistance of the underlying coated steel sheet. Regarding the surface appearance, given that the height difference of the irregularities of wrinkle-like defects is as large as several tens of micrometers, even when the surface is smoothed by the painting layer, the irregularities cannot be completely eliminated, and the appearance of the painted steel sheet is unlikely to be improved. Besides, the painting layer is thinner at the convex portions, so that the corrosion resistance may decrease locally. In order to obtain a painted steel sheet excellent in corrosion resistance and surface appearance, it is important to improve the corrosion resistance and surface appearance of the underlying coated steel sheet.

[0012] It could therefore be helpful to provide a hot-dip Al-Zn-Si-Mg coated steel sheet stably having excellent corrosion resistance and a production method therefor.

It could also be helpful to provide a surface-treated steel sheet stably having excellent corrosion resistance and white rust resistance and a production method therefor.

It could further be helpful to provide a painted steel sheet stably having excellent corrosion resistance and worked part corrosion resistance and a production method therefor.

(Solution to Problem)

5 **[0013]** Upon careful examination, we focused on the fact that it is important to control, in the composition of a coating of a hot-dip Al-Zn-Si-Mg coated steel sheet, not only the concentrations of Al, Zn, Si, and Mg but also the concentrations of elements contained as impurities, and discovered that degradation in corrosion resistance can be suppressed effectively by
10 appropriately controlling the content of Ni among such elements, and degradation in corrosion resistance can be suppressed more effectively by appropriately controlling the size and distribution state of Ni-based compounds existing in the coating as impurities.

We also found out that Mg₂Si phase, MgZn₂ phase, and Si phase formed
15 in the coating of the hot-dip Al-Zn-Si-Mg coated steel sheet increase or decrease in their precipitation amounts and their existence ratios change depending on the balance of the components in the coating and the coating formation conditions and any of the phases may not precipitate depending on the balance of the composition, and the corrosion resistance of the hot-dip Al-
20 Zn-Si-Mg coated steel sheet changes depending on the existence ratios of these phases and, particularly in the case where MgZn₂ phase is more than Mg₂Si phase or Si phase, the corrosion resistance is improved stably. For these Mg₂Si phase, MgZn₂ phase, and Si phase, however, it is known to be very difficult to discriminate the phases from each other by a typical method such as observing
25 a secondary electron image or reflected electron image of the surface or a cross section of the coating using a scanning electron microscope. Although it is possible to obtain microscopic information by observation using a transmission electron microscope, we could not determine the existence ratios of Mg₂Si phase, MgZn₂ phase, and Si phase, which influences macroscopic information
30 such as corrosion resistance and appearance.

Upon further examination, we focused on the X-ray diffraction method, and discovered that the use of the intensity ratio of specific diffraction peaks of Mg₂Si phase, MgZn₂ phase and Si phase makes it possible to quantitatively specify the existence ratio of each phase. We also discovered that, as a result
35 of Mg₂Si phase and MgZn₂ phase in the coating satisfying a specific existence ratio, not only excellent corrosion resistance can be achieved stably but also

favorable surface appearance can be ensured without dross.

We further discovered that, by controlling the Ni content in the coating and the coating structure as mentioned above and also controlling the Sr concentration in the molten bath, a coated steel sheet excellent in surface appearance can be obtained while reliably suppressing wrinkle-like irregularity defects.

[0014] We also studied the chemical conversion layer formed on the coating, and discovered that, by forming the chemical conversion layer of a specific resin and a specific metallic compound, the affinity of the chemical conversion layer for the coating, the rust prevention effect, etc. can be enhanced to thus stably improve the white rust resistance.

We further studied the chemical conversion layer and the primer painting layer formed on the coating, and discovered that, by forming the chemical conversion layer of a specific resin and a specific inorganic compound and also forming the primer painting layer of a specific polyester resin and an inorganic compound, the barrier property and adhesion of the painting layer can be enhanced, and excellent post-working corrosion resistance can be achieved in a chromate-free manner.

[0015] The present disclosure is based on these discoveries. We thus provide:

1. A hot-dip Al-Zn-Si-Mg coated steel sheet comprising a coating having a composition containing (consisting of) Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass% with a balance consisting of Zn and inevitable impurities, wherein Ni content in the inevitable impurities is 0.010 mass% or less with respect to a total mass of the coating.

[0016] 2. The hot-dip Al-Zn-Si-Mg coated steel sheet according to 1., wherein a Ni-based compound is contained in the coating, and a major axis length of the Ni-based compound is 4.0 μm or less.

3. The hot-dip Al-Zn-Si-Mg coated steel sheet according to 1. or 2., wherein a Ni-based compound is contained in the coating, and the number of the Ni-based compound present in a direction parallel to a surface of a base steel sheet is 5 per mm or less.

4. The hot-dip Al-Zn-Si-Mg coated steel sheet according to 1., wherein a Ni-based compound is not contained in the coating.

[0017] 5. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 4., wherein respective diffraction intensities of Mg_2Si and MgZn_2 in the coating by an X-ray diffraction method satisfy the following relationship (1):

$$\text{Mg}_2\text{Si (111)}/\text{MgZn}_2 \text{ (100)} \leq 2.0 \quad \dots (1)$$

where $\text{Mg}_2\text{Si (111)}$ is a diffraction intensity of (111) plane of Mg_2Si with interplanar spacing $d = 0.3668 \text{ nm}$, and $\text{MgZn}_2 \text{ (100)}$ is a diffraction intensity of (100) plane of MgZn_2 with interplanar spacing $d = 0.4510 \text{ nm}$.

- 5 **[0018]** 6. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 5., wherein a diffraction intensity of Si in the coating by an X-ray diffraction method satisfies the following relationship (2):

$$\text{Si (111)} = 0 \quad \dots (2)$$

10 where Si (111) is a diffraction intensity of (111) plane of Si with interplanar spacing $d = 0.3135 \text{ nm}$.

[0019] 7. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 6., wherein the coating further contains Sr: 0.01 mass% to 1.0 mass%.

[0020] 8. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 7., wherein Al content in the coating is 50 mass% to 60 mass%.

- 15 **[0021]** 9. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 8., wherein Si content in the coating is 1.0 mass% to 3.0 mass%.

[0022] 10. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 9., wherein Mg content in the coating is 1.0 mass% to 5.0 mass%.

- 20 **[0023]** 11. A production method for a hot-dip Al-Zn-Si-Mg coated steel sheet that includes a coating, the production method comprising a hot-dip coating treatment process of immersing a base steel sheet in a molten bath having a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass% with a balance consisting of Zn and inevitable impurities, to form the coating, wherein Ni content in the inevitable
25 impurities in the molten bath is controlled to be 0.010 mass% or less with respect to a total mass of the molten bath.

[0024] 12. The production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to 11., wherein the molten bath further contains Sr: 0.01 mass% to 1.0 mass%.

- 30 **[0025]** 13. A surface-treated steel sheet comprising: the coating according to any one of 1. to 10.; and a chemical conversion layer formed on the coating, wherein the chemical conversion layer contains: at least one resin selected from the group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin,
35 an amino resin, and a fluoro resin; and at least one metallic compound selected from the group consisting of a P compound, a Si compound, a Co compound, a

Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

5 **[0026]** 14. A production method for a surface-treated steel sheet that includes:
a coating formed by the production method for a hot-dip Al-Zn-Si-Mg coated
steel sheet according to 11. or 12.; and a chemical conversion layer formed on
the coating, wherein the chemical conversion layer contains: at least one resin
selected from the group consisting of an epoxy resin, a urethane resin, an
acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a
10 polyalkylene resin, an amino resin, and a fluororesin; and at least one metallic
compound selected from the group consisting of a P compound, a Si compound,
a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg
compound, a V compound, a Mo compound, a Zr compound, a Ti compound,
and a Ca compound.

15 **[0027]** 15. A painted steel sheet comprising: the coating according to any one
of 1. to 10.; and a painting layer formed on the coating directly or with a
chemical conversion layer therebetween, wherein the chemical conversion
layer contains: a resin component that contains (a): an anionic polyurethane
resin having an ester bond and (b): an epoxy resin having a bisphenol skeleton
20 in a total amount of 30 mass% to 50 mass% and in which a content ratio (a):(b)
between (a) and (b) is in a range of 3:97 to 60:40 in mass ratio; and an inorganic
compound that contains 2 mass% to 10 mass% of a vanadium compound, 40
mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of
a fluorine compound, and the painting layer includes at least a primer painting
25 layer that contains: a polyester resin having a urethane bond; and an inorganic
compound including a vanadium compound, a phosphate compound, and
magnesium oxide.

30 **[0028]** 16. A production method for a painted steel sheet that includes: a
coating formed by the production method for a hot-dip Al-Zn-Si-Mg coated
steel sheet according to 11. or 12.; and a painting layer formed on the coating
directly or with a chemical conversion layer therebetween, wherein the
chemical conversion layer contains: a resin component that contains (a): an
anionic polyurethane resin having an ester bond and (b): an epoxy resin having
a bisphenol skeleton in a total amount of 30 mass% to 50 mass% and in which
35 a content ratio (a):(b) between (a) and (b) is in a range of 3:97 to 60:40 in mass
ratio; and an inorganic compound that contains 2 mass% to 10 mass% of a

vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound, and the painting layer includes at least a primer painting layer that contains: a polyester resin having a urethane bond; and an inorganic compound including a vanadium compound, a phosphate compound, and magnesium oxide.

(Advantageous Effect)

[0029] It is thus possible to provide a hot-dip Al-Zn-Si-Mg coated steel sheet stably having excellent corrosion resistance.

It is also possible to provide a surface-treated steel sheet stably having excellent corrosion resistance and white rust resistance and a production method therefor.

It is further possible to provide a painted steel sheet stably having excellent corrosion resistance and worked part corrosion resistance and a production method therefor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] In the accompanying drawings:

FIG. 1 is a diagram for explaining the flow of the Japanese Automotive Standards Organization combined cyclic corrosion test (JASO-CCT).

DETAILED DESCRIPTION

[0031] (Hot-dip Al-Zn-Si-Mg coated steel sheet)

A hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure comprises a coating on the surface of a steel sheet. The coating has a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass%, with the balance consisting of Zn and inevitable impurities.

[0032] The Al content in the coating is 45 mass% to 65 mass%, and preferably 50 mass% to 60 mass%, from the viewpoint of the balance between the corrosion resistance and the operativity. If the Al content in the coating is at least 45 mass%, dendritic solidification of Al occurs, and a coating structure mainly composed of dendritic solidification structure of α -Al phase can be obtained. As a result of the dendritic solidification structure having a structure of being stacked in the thickness direction of the coating, the corrosion path is made complex, and the corrosion resistance of the coating itself is improved. When more dendrite parts of α -Al phase are stacked, the corrosion path is more

complex, making it more difficult for corrosion to reach the base steel sheet. Hence, the Al content is preferably 50 mass% or more, in order to improve the corrosion resistance. If the Al content in the coating is more than 65 mass%, the structure changes to a structure in which most of Zn dissolves in α -Al, and the dissolution reaction of α -Al phase cannot be suppressed, so that the corrosion resistance of the Al-Zn-Si-Mg coating degrades. The Al content in the coating therefore needs to be 65 mass% or less, and is preferably 60 mass% or less.

[0033] Si in the coating is mainly added for the purpose of suppressing the growth of a Fe-Al and/or Fe-Al-Si interfacial alloy layer formed at the interface with the base steel sheet and preventing degradation in the adhesion between the coating and the steel sheet. When a steel sheet is actually immersed in an Al-Zn molten bath containing Si, Fe at the steel sheet surface and Al and Si in the bath undergo an alloying reaction, resulting in the formation of a Fe-Al and/or Fe-Al-Si intermetallic compound layer at the interface between the base steel sheet and the coating. Here, since a Fe-Al-Si alloy has a lower growth rate than a Fe-Al alloy, the growth of the whole interfacial alloy layer is suppressed more when the ratio of the Fe-Al-Si alloy is higher. The Si content in the coating therefore needs to be 1.0 mass% or more. If the Si content in the coating is more than 4.0 mass%, not only the effect of suppressing the growth of the interfacial alloy layer is saturated, but also the presence of excessive Si phase in the coating accelerates corrosion. The Si content is therefore 4.0 % or less. The Si content in the coating is preferably 3.0 % or less, from the viewpoint of suppressing the presence of excessive Si phase. From the viewpoint of satisfying the below-described relational formula (1) in relation to the below-described Mg content, too, the Si content is preferably 1.0 mass% to 3.0 mass%.

[0034] The Mg content in the coating is 1.0 % to 10.0 %. As a result of Mg being contained in the coating, Si can exist in the form of an intermetallic compound of Mg_2Si phase, and corrosion acceleration can be suppressed.

Moreover, as a result of Mg being contained in the coating, $MgZn_2$ phase which is an intermetallic compound is formed in the coating. This has the effect of further improving the corrosion resistance. If the Mg content in the coating is less than 1.0 mass%, Mg is used for the solute formation into α -Al phase which is a main phase rather than for the formation of the intermetallic compound (Mg_2Si , $MgZn_2$), and accordingly sufficient corrosion

resistance cannot be ensured. If the Mg content in the coating is high, not only the corrosion resistance improving effect is saturated but also the workability decreases with the weakening of α -Al phase. The content is therefore 10.0 % or less. The Mg content in the coating is preferably 5.0 mass% or less, from the viewpoint of suppressing dross generation during coating formation and easing molten bath management. From the viewpoint of satisfying the below-described relational formula (1) in relation to the Si content, the Mg content is preferably 3.0 mass%. Considering the compatibility with dross suppression, the Mg content is more preferably 3.0 mass% to 5.0 mass%.

[0035] The coating contains Zn and inevitable impurities. The inevitable impurities contain Fe. Fe is inevitably contained in the coating as a result of elution from the steel sheet or in-bath equipment into the molten bath and/or as a result of diffusion from the base steel sheet during the formation of the interfacial alloy layer. The Fe content in the coating is typically about 0.3 mass% to 2.0 mass%.

The other inevitable impurities include, for example, Cr, Ni, and Cu. These components are inevitably contained in the coating as a result of elution from the base steel sheet or stainless-steel in-bath equipment into the molten bath, as a result of inclusion as impurities in metal lumps which are the material of the molten bath, and/or as a result of use of a pot or in-bath equipment used in the production of a coated steel sheet to which these components are intentionally added.

[0036] In the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the Ni content in the inevitable impurities is 0.010 mass% or less with respect to the total mass of the coating. Ni contained in the coating may degrade the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet. By appropriately controlling the contents of Al, Zn, Si, and Mg in the coating and further reducing the Ni content as an inevitable impurity, degradation in corrosion resistance can be suppressed. From the same viewpoint, the Ni content in the inevitable impurities is preferably 0.005 mass% or less with respect to the total mass of the coating.

[0037] In the case where Ni is contained in the inevitable impurities, there is a possibility that Ni-based compounds are contained as impurities in the coating of the hot-dip Al-Zn-Si-Mg coated steel sheet. Herein, the “Ni-based compounds” refer to Ni-based compounds including, for example, binary intermetallic compounds such as Ni-Al compounds and ternary intermetallic

compounds such as Ni-Al-Fe compounds. Non-limiting examples of the Ni-Al compounds include intermetallic compounds such as NiAl_3 . Non-limiting examples of the Ni-Al-Fe compounds include intermetallic compounds such as $(\text{Ni}, \text{Fe})\text{Al}_3$ obtained by substituting part of Ni in NiAl_3 by Fe.

5 Here, the existence of Ni-based compounds in the coating can be determined, for example, by observing a secondary electron image or reflected electron image of the surface or a cross section of the coating using a scanning electron microscope and analyzing it by energy dispersive X-ray spectroscopy (EDS). For example, the composition of Ni-based inclusions can be determined
10 by randomly selecting about five to ten 100 μm coating cross sections, performing observation and elemental mapping analysis on each cross section with an accelerating voltage of 5 kv or less, and further performing point analysis on each part where Ni is detected. This method is merely an example, and any method capable of determining the existence of Ni-based compounds
15 may be used without limitation.

[0038] In the case where Ni-based compounds are contained in the coating, the major axis length of the Ni-based compounds is preferably 4.0 μm or less.

Ni-based compounds present in the coating function as a cathode in a corrosion environment and form a local battery with its surrounding
20 solidification structure, which may cause degradation in corrosion resistance. Particularly in the case where coarse Ni-based compounds are present in the coating, the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet is likely to decrease significantly. Thus, an effective way of obtaining a hot-dip Al-Zn-Si-Mg coated steel sheet having better corrosion resistance is to
25 control the size of the Ni-based compounds contained as impurities in the coating to be small. Specifically, the major axis length of the Ni-based compounds is preferably 4.0 μm or less, more preferably 3.0 μm or less, and further preferably 2.0 μm or less.

The major axis length of the Ni-based compounds can be measured, for
30 example, by observing a reflected electron image of a cross section of the coating using a scanning electron microscope to determine the existence of Ni-based compounds by EDS and then observing a reflected electron image with an expanded observation field including the Ni-based compounds. The major axis length of the Ni-based compounds is the maximum major axis length of
35 the Ni-based compounds observed in the observation field of the coating.

[0039] In the case where Ni-based compounds are contained in the coating, it

is also effective to reduce the existence amount of the Ni-based compounds which serve as a corrosion initiation point, from the viewpoint of achieving high corrosion resistance more stably. Specifically, the number of Ni-based compounds in the coating is preferably 5 per mm or less, more preferably 2 per mm or less, and most preferably 0 per mm (i.e. there are no Ni-based compounds) in a direction parallel to the surface of the base steel sheet.

Hence, by reducing the existence amount of compounds containing Ni in the coating, degradation in the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet can be suppressed more reliably. In order to obtain such a coating structure (a coating structure not containing Ni-based compounds), it is important to reduce the Ni content in the inevitable impurities, specifically, limit the Ni content to 0.005 mass% or less with respect to the total mass of the coating.

For the number of Ni-based compounds, for example, the number of Ni-based compounds existing within a length of 1 mm can be calculated by continuously observing a reflected electron image of a cross section of the coating parallel to the surface of the base steel sheet for a length of 1 mm or more using a scanning electron microscope and dividing the number of Ni-based compounds determined by EDS by the measurement length (mm).

[0040] The total content of the inevitable impurities in the coating is not limited. However, in the case where the total content of the inevitable impurities is excessively high, various properties of the coated steel sheet may be affected. The total content of the inevitable impurities is therefore preferably 5.0 mass% or less.

[0041] In addition to the foregoing control of the concentrations of Al, Zn, Si, and Mg, and Ni as an inevitable impurity, it is preferable that, in the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the diffraction intensities of Mg₂Si and MgZn₂ in the coating by the X-ray diffraction method satisfy the following relationship (1), from the viewpoint of improving the corrosion resistance more stably:

$$\text{Mg}_2\text{Si (111)}/\text{MgZn}_2\text{ (100)} \leq 2.0 \quad \dots (1)$$

where Mg₂Si (111) is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668$ nm) of Mg₂Si, and MgZn₂ (100) is the diffraction intensity of (100) plane (interplanar spacing $d = 0.4510$ nm) of MgZn₂.

[0042] It is important to, in the hot-dip Al-Zn-Si-Mg coated steel sheet

according to the present disclosure, control the existence ratios of intermetallic compounds such as Mg_2Si and MgZn_2 formed in the coating as a result of inclusion of Mg to specific ratios, as mentioned above. The influence of such factors on the corrosion resistance is largely unknown and is currently under investigation, but the following mechanism is presumed.

[0043] In the case where the hot-dip Al-Zn-Si-Mg coated steel sheet is exposed to a corrosion environment, the foregoing intermetallic compounds dissolve preferentially over α -Al phase, as a result of which Mg is rich in the vicinity of the corrosion products formed. In such a Mg-rich environment, the corrosion products formed are difficult to decompose, and consequently the protective effect of the coating increases. Since MgZn_2 contributes more to the improvement of the protective effect of the coating than Mg_2Si , increasing the existence ratio of MgZn_2 among the intermetallic compounds present in the coating is effective.

[0044] It is preferable that the existence ratios of Mg_2Si and MgZn_2 in the coating satisfy the relationship (1): $\text{Mg}_2\text{Si} (111)/\text{MgZn}_2 (100) \leq 2.0$, using the diffraction peak intensities obtained by the X-ray diffraction method. If the existence ratios of Mg_2Si and MgZn_2 in the coating do not satisfy the relationship (1), i.e. if $\text{Mg}_2\text{Si} (111)/\text{MgZn}_2 (100) > 2.0$, the existence of Mg_2Si is high among the intermetallic compounds present in the coating, so that the foregoing Mg-rich environment cannot be created in the vicinity of the corrosion products. This is likely to hinder the improvement of the protective effect of the coating.

[0045] In the relationship (1), $\text{Mg}_2\text{Si} (111)$ is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668$ nm) of Mg_2Si , and $\text{MgZn}_2 (100)$ is the diffraction intensity of (100) plane (interplanar spacing $d = 0.4510$ nm) of MgZn_2 .

For example, the measurement of $\text{Mg}_2\text{Si} (111)$ and $\text{MgZn}_2 (100)$ by X-ray diffraction can be performed by mechanically scraping off part of the coating and powdering it to perform X-ray diffraction (powder X-ray diffraction measurement method). In the diffraction intensity measurement, the diffraction peak intensity of Mg_2Si corresponding to interplanar spacing $d = 0.3668$ nm and the diffraction peak intensity of MgZn_2 corresponding to interplanar spacing $d = 0.4510$ nm are measured. Calculating the ratio between these diffraction peak intensities can yield $\text{Mg}_2\text{Si} (111)/\text{MgZn}_2 (100)$.

The amount of coating required for powder X-ray diffraction

measurement (amount of coating scraped off) is 0.1 g or more, and preferably 0.3 g or more, from the viewpoint of accurately measuring Mg₂Si (111) and MgZn₂ (100). When scraping off the coating, there is a possibility that steel sheet components other than the coating are contained in the powder. However, these intermetallic compound phases are contained only in the coating, and the foregoing peak intensities are not affected. The reason why the coating is powdered and subjected to X-ray diffraction is that, in the case of performing X-ray diffraction on the coating formed in the coated steel sheet, it is difficult to calculate the correct phase ratio due to the influence of the plane orientation of the coating solidification structure.

[0046] In addition to the foregoing control of the concentrations of Al, Zn, Si, and Mg, and Ni as an inevitable impurity, it is preferable that, in the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the diffraction intensity of Si in the coating by the X-ray diffraction method satisfies the following relationship (2), from the viewpoint of improving the corrosion resistance more stably:

$$\text{Si (111)} = 0 \quad \dots (2)$$

where Si (111) is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135 \text{ nm}$) of Si.

It is commonly known that, in the dissolution reaction of an Al alloy in an aqueous solution, the presence of Si phase as a cathodic site promotes the dissolution of its surrounding α -Al phase. Hence, reducing Si phase is effective from the viewpoint of suppressing the dissolution of α -Al phase. In particular, it is best if Si phase does not exist in the coating as in the relationship (2) (i.e. the diffraction peak intensity of Si (111) is 0), for stable corrosion resistance.

The method of measuring the diffraction peak intensity of (111) plane of Si by X-ray diffraction may be the same as the foregoing method of measuring Mg₂Si (111) and MgZn₂ (100).

[0047] The methods of satisfying the relationship (1) and the relationship (2) are not limited. For example, to satisfy the relationship (1) and the relationship (2), the balance of the Si content, the Mg content, and the Al content in the coating may be adjusted to thus control the existence ratios of Mg₂Si, MgZn₂ and Si (the diffraction intensities of Mg₂Si (111), MgZn₂ (100), and Si (111)). For the balance of the Si content, the Mg content, and the Al content in the coating, setting constant content ratios does not necessarily satisfy the relationship (1) and the relationship (2), and, for example, the content ratios

of Mg and Al need to be changed depending on the Si content (mass%).

In addition to adjusting the balance of the Si content, the Mg content, and the Al content in the coating, the coating formation conditions (for example, the conditions of cooling after coating) may be adjusted to control the
5 diffraction intensities of Mg_2Si (111), MgZn_2 (100), and Si (111) so as to satisfy the relationship (1) and the relationship (2).

[0048] In the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the coating preferably contains 0.01 mass% to 1.0 mass% of Sr. As a result of the coating containing Sr, surface defects such as wrinkle-like
10 irregularity defects can be suppressed more reliably, and favorable surface appearance can be achieved.

Herein, the “wrinkle-like defects” refer to wrinkle-like irregularities on the surface of the coating, and are observed as whitish streaks on the surface of the coating. Such wrinkle-like defects tend to occur when a large amount of
15 Mg is added to the coating. In the hot-dip coated steel sheet, the coating contains Sr, so that Sr oxidizes preferentially over Mg in the surface layer of the coating and the oxidation reaction of Mg is suppressed. This can suppress wrinkle-like defects.

[0049] In the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, it is preferable that the existence ratios of Mg_2Si and MgZn_2 in the
20 coating satisfies the relationship (1) and the coating contains 0.01 mass% to 1.0 mass% of Sr. In this way, the foregoing surface appearance improving effect by Sr can be further enhanced. The reason for this is not clear, but it is presumed that, if the content of Mg_2Si in the coating is high, it is difficult to
25 suppress the oxidation of the surface layer of the coating, which affects the appearance improving effect by the addition of Sr. If the Sr content in the coating is less than 0.01 mass%, the effect of suppressing wrinkle-like defects is insufficient. If the Sr content in the coating is more than 1.0 mass%, Sr is excessively incorporated into the interfacial alloy layer, which may affect the
30 coating adhesion and the like beyond its contribution to the appearance improving effect. The Sr content in the coating is therefore preferably 0.01 mass% to 1.0 mass%.

[0050] The coating preferably further contains one or more selected from the group consisting of Cr, Mn, V, Mo, Ti, Ca, Co, Sb, and B in a total amount of
35 0.01 mass% to 10 mass%, from the viewpoint of improving the stability of corrosion products and delaying the progress of corrosion as with Mg described

above. If the total content of these components is 0.01 mass% to 10 mass%, the corrosion delay effect is sufficient and is not saturated.

[0051] The coating weight of the coating is preferably 45 g/m² to 120 g/m² per side, from the viewpoint of satisfying various properties. If the coating weight
5 of the coating is 45 g/m² or more, sufficient corrosion resistance can be achieved even for applications that require long-term corrosion resistance, such as building materials. If the coating weight of the coating is 120 g/m² or less, excellent corrosion resistance can be achieved while suppressing coating cracks and the like during working. From the same viewpoint, the coating
10 weight of the coating is more preferably 45 g/m² to 100 g/m².

[0052] The coating weight of the coating can be derived, for example, by a method of dissolving and peeling a specific area of the coating with a liquid mixture of hydrochloric acid and hexamethylenetetramine as described in JIS
H 0401: 2013 and calculating the coating weight from the difference in the
15 weight of the steel sheet between before and after the peeling. With this method, the coating weight per side can be obtained by performing the foregoing dissolution after sealing, with tape, the coating surface not subjected to evaluation so as not to be exposed.

[0053] The chemical composition of the coating can be determined by
20 immersing the coating in hydrochloric acid or the like to dissolve it and examining the solution by ICP optical emission spectrometry, atomic absorption spectrometry, or the like, as with the Ni content described above. This method is merely an example, and any method that can accurately quantify the chemical composition of the coating may be used without limitation.

[0054] The coating of the hot-dip Al-Zn-Si-Mg coated steel sheet obtained
25 according to the present disclosure as a whole has substantially the same composition as the molten bath. Accordingly, the composition of the coating can be accurately controlled by controlling the composition of the molten bath.

[0055] The base steel sheet of the hot-dip Al-Zn-Si-Mg coated steel sheet
30 according to the present disclosure is not limited, and a cold-rolled steel sheet, a hot-rolled steel sheet, or the like may be used as appropriate depending on the required performance and standards.

[0056] The method of obtaining the base steel sheet is not limited. For example,
the hot-rolled steel sheet can be produced through a hot rolling process and a
35 pickling process, and the cold-rolled steel sheet can be produced further through a cold rolling process. A recrystallization annealing process and the

like may be performed before a hot-dip coating process, in order to obtain the properties of the steel sheet.

[0057] (Production method for hot-dip Al-Zn-Si-Mg coated steel sheet)

A production method for a hot-dip Al-Zn-Si-Mg coated steel sheet
5 according to the present disclosure is a production method for a hot-dip Al-Zn-Si-Mg coated steel sheet that includes a coating, comprising a hot-dip coating treatment process of immersing a base steel sheet in a molten bath having a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass% with the balance consisting of Zn
10 and inevitable impurities to form the coating.

The hot-dip coating treatment process is not limited except for the below-described molten bath conditions. For example, the base steel sheet may be subjected to cleaning, heating, and molten bath immersion in a continuous hot-dip coating line. In the steel sheet heating process, it is effective to perform
15 recrystallization annealing and the like for controlling the structure of the base steel sheet itself and also perform heating in a reducing atmosphere such as a nitrogen-hydrogen atmosphere to prevent oxidation of the steel sheet and reduce a small amount of oxide film existing on the surface.

[0058] The molten bath that can be used in the hot-dip coating treatment
20 process has a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass% with the balance consisting of Zn and inevitable impurities, given that the composition of the coating as a whole is substantially the same as the composition of the molten bath as mentioned above.

[0059] In the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet
25 according to the present disclosure, the Ni content in the inevitable impurities in the molten bath is controlled to 0.010 mass% or less with respect to the total mass of the molten bath. Ni contained in the coating may degrade the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet, as mentioned above.
30 By appropriately controlling the contents of Al, Zn, Si, and Mg in the molten bath and further reducing the Ni content as an inevitable impurity, degradation in corrosion resistance can be suppressed.

The Ni content as an inevitable impurity in the molten bath needs to be 0.010 mass% or less and is preferably 0.005 mass% or less, with respect to the
35 total mass of the molten bath. If the Ni content in the molten bath is more than 0.005 mass%, the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel

sheet produced may degrade. If the Ni content in the molten bath is more than 0.010 %, significant degradation in corrosion resistance is likely to occur. No lower limit is placed on the Ni content which adversely affects the corrosion resistance.

5 **[0060]** The means of reducing the Ni content in the molten bath is not limited.

For example, given that suppressing elution of stainless-steel in-bath equipment into the molten bath is effective, it is preferable to treat the surface of the in-bath equipment by spray coating or the like. The formation of the spray coating or the like can make the in-bath equipment have corrosion-resistant against the molten bath, and suppress elution of the in-bath equipment into the molten bath. The type of the spray coating is not limited, and a coating having heat resistance and corrosion resistance, such as a WC-based or MoB-based coating, may be selected. The use of in-bath equipment made of a heat-resistant material not containing Ni is more effective. In this case, an increase of the Ni content can be prevented even when the in-bath equipment is eluted.

10 **[0061]** As another means of reducing the Ni content in the molten bath, it is preferable to use, as the material of the molten bath, metal lumps having low Ni content in impurities.

It is also effective not to use, in the production of the hot-dip Al-Zn-Si-Mg coated steel sheet, a pot or in-bath equipment used in the production of a coated steel sheet to which Ni is intentionally added. A situation in which metal lumps containing Ni adhering to such pot or in-bath equipment dissolve and mix into the molten bath can thus be suppressed.

15 **[0062]** The bath temperature of the molten bath is not limited, but is preferably in the temperature range of (melting point + 20 °C) to 650 °C.

The reason why the lower limit of the bath temperature is (melting point + 20 °C) is that the bath temperature needs to be not less than the solidification point in order to perform hot-dip coating treatment, and setting the lower limit to (melting point + 20 °C) is intended to prevent solidification due to a local bath temperature drop in the molten bath. The reason why the upper limit of the bath temperature is 650 °C is that, if the bath temperature is more than 650 °C, it is difficult to rapidly cool the coating, and the interfacial alloy layer formed between the coating and the steel sheet is likely to become thick.

30 **[0063]** The temperature of the base steel sheet entering the molten bath (entering sheet temperature) is not limited, but is preferably within ± 20 °C with

respect to the temperature of the molten bath from the viewpoint of ensuring the coating properties and preventing bath temperature changes in continuous hot-dip coating operation.

5 **[0064]** The immersion time of the base steel sheet in the molten bath is preferably 0.5 sec or more. If the immersion time is less than 0.5 sec, there is a possibility that a sufficient coating cannot be formed on the surface of the base steel sheet. Although no upper limit is placed on the immersion time, the immersion time is preferably 8 sec or less because a longer immersion time may cause thickening of the interfacial alloy layer formed between the coating
10 and the steel sheet.

[0065] The hot-dip Al-Zn-Si-Mg coated steel sheet may have a painting layer formed on the coating directly or with an intermediate layer therebetween, depending on the required performance.

[0066] The method of forming the painting layer is not limited, and may be
15 selected as appropriate depending on the required performance. Examples include formation methods such as roll coater painting, curtain flow painting, and spray painting. After applying paint containing organic resin, the paint may be heated and dried by a method such as hot blast drying, infrared heating, or induction heating to form a painting layer.

20 **[0067]** The intermediate layer is not limited, and may be any layer that is formed between the coating of the hot-dip coated steel sheet and the painting layer.

[0068] (Surface-treated steel sheet)

25 A surface-treated steel sheet according to the present disclosure comprises a coating on a surface of a steel sheet, and a chemical conversion layer formed on the coating.

The structure of the coating is the same as that of the above-described coating of the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure.

30 **[0069]** In the surface-treated steel sheet according to the present disclosure, the chemical conversion layer is formed on the coating.

The chemical conversion layer is formed on at least one side of the surface-treated steel sheet, and may be formed on both sides of the surface-treated steel sheet depending on the intended use or required performance.

35 **[0070]** In the surface-treated steel sheet according to the present disclosure, the chemical conversion layer contains at least one resin selected from the

group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin, an amino resin, and a fluororesin, and at least one metallic compound selected from the group consisting of a P compound, a Si compound, a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

By forming such a chemical conversion layer on the coating, the affinity with the coating can be enhanced and the chemical conversion layer can be uniformly formed on the coating, and also the rust prevention effect and barrier effect of the chemical conversion layer can be enhanced. The surface-treated steel sheet according to the present disclosure thus has stable corrosion resistance and white rust resistance.

[0071] As the resin contained in the chemical conversion layer, at least one selected from the group consisting of epoxy resin, urethane resin, acrylic resin, acrylic silicon resin, alkyd resin, polyester resin, polyalkylene resin, amino resin, and fluororesin is used from the viewpoint of corrosion resistance improvement. From the same viewpoint, the resin preferably includes at least one of urethane resin and acrylic resin. Examples of the resin contained in the chemical conversion layer also include addition polymers of the foregoing resins.

[0072] Examples of the epoxy resin include glycidyl-etherified epoxy resin such as bisphenol A type, bisphenol F type, and novolac type, glycidyl-etherified epoxy resin of bisphenol A type to which propylene oxide, ethylene oxide, or polyalkylene glycol is added, aliphatic epoxy resin, alicyclic epoxy resin, and polyether-based epoxy resin.

[0073] Examples of the urethane resin include oil-modified polyurethane resin, alkyd-based polyurethane resin, polyester-based polyurethane resin, polyether-based polyurethane resin, and polycarbonate-based polyurethane resin.

[0074] Examples of the acrylic resin include polyacrylic acid and its copolymer, polyacrylic acid ester and its copolymer, polymethacrylic acid and its copolymer, polymethacrylic acid ester and its copolymer, urethane-acrylic acid copolymer (or urethane-modified acrylic resin), styrene-acrylic acid copolymer, and modification products of these resins with other alkyd resin, epoxy resin, phenol resin, etc.

[0075] Examples of the acrylic silicon resin include resin that has a hydrolyzable alkoxysilyl group at a side chain or end of an acrylic-based

copolymer as base resin and to which a curing agent is added. In the case where acrylic silicon resin is used, excellent atmospheric corrosion resistance can be expected in addition to corrosion resistance.

5 **[0076]** Examples of the alkyd resin include oil-modified alkyd resin, rosin-modified alkyd resin, phenol-modified alkyd resin, styrenated alkyd resin, silicon-modified alkyd resin, acrylic-modified alkyd resin, oil-free alkyd resin, and high molecular weight oil-free alkyd resin.

10 **[0077]** The polyester resin is a polycondensate synthesized by dehydration condensation of polycarboxylic acid and polyalcohol to form an ester bond. Examples of the polycarboxylic acid include terephthalic acid and 2,6-naphthalenedicarboxylic acid. Examples of the polyalcohol include ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,4-cyclohexanedimethanol. Specific examples of the polyester include polyethylene terephthalate, polytrimethylene terephthalate, polyethylene naphthalate, polybutylene
15 naphthalate, and acrylic modification products of these polyester resins.

20 **[0078]** Examples of the polyalkylene resin include ethylene-based copolymers such as ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, and carboxyl-modified polyolefin resin, ethylene-unsaturated carboxylic acid copolymers, ethylene-based ionomers, and modification products of these
resins with other alkyd resin, epoxy resin, phenol resin, etc.

25 **[0079]** The amino resin is a thermosetting resin produced by reaction of amine or amide compound and aldehyde, and examples include melamine resin, guanamine resin, and thiourea resin. Melamine resin is preferable from the viewpoint of corrosion resistance, atmospheric corrosion resistance, adhesion, etc. The melamine resin is not limited, and examples include butylated
melamine resin, methylated melamine resin, and aqueous melamine resin.

30 **[0080]** Examples of the fluororesin include fluoroolefin-based polymers and copolymers of fluoroolefin with alkyl vinyl ether, synchroalkyl vinyl ether, carboxylic acid-modified vinyl ester, hydroxyalkyl allyl ether, tetrafluoropropyl vinyl ether, etc. In the case where these fluororesins are used, excellent atmospheric corrosion resistance and excellent hydrophobicity can be expected in addition to corrosion resistance.

35 **[0081]** For the resin contained in the chemical conversion layer, it is particularly preferable to use a curing agent for the purpose of improving the corrosion resistance and the workability. As the curing agent, urea resin (butylated urea resin, etc.), melamine resin (butylated melamine resin, butyl

etherified melamine resin, etc.), butylated urea-melamine resin, amino resin such as benzoguanamine resin, blocked isocyanate, oxazoline compound, phenol resin, etc. may be used as appropriate.

[0082] As the metallic compound contained in the chemical conversion layer,
5 at least one selected from the group consisting of a P compound, a Si compound, a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound is used. From the same viewpoint, the metallic compound preferably includes at least one of a P compound, a Si compound, and a V
10 compound.

[0083] The P compound, when contained in the chemical conversion layer, can improve the corrosion resistance and the perspiration resistance. The P compound is a compound containing P, and may contain, for example, one or more selected from the group consisting of inorganic phosphoric acid, organic
15 phosphoric acid, and their salts.

[0084] The inorganic phosphoric acid, the organic phosphoric acid, and their salts are not limited, and any compounds may be used. For example, the inorganic phosphoric acid is preferably one or more selected from the group consisting of phosphoric acid, primary phosphate, secondary phosphate, tertiary phosphate, pyrophosphoric acid, pyrophosphate, tripolyphosphoric
20 acid, tripolyphosphate, phosphorus acid, phosphite, hypophosphorus acid, and hypophosphite. The organic phosphoric acid is preferably phosphonic acid (phosphonic acid compound). The phosphonic acid is preferably one or more selected from the group consisting of nitrilotrismethylenephosphonic acid, phosphonobutanetricarboxylic acid, methyldiphosphonic acid, methylenephosphonic acid, and ethylenediphosphonic acid.
25

In the case where the P compound is a salt, the salt is preferably a salt of an element from groups 1 to 13 in the periodic table, and more preferably a metal salt. Preferably, the salt is one or more selected from the group consisting
30 of alkali metal salts and alkaline earth metal salts.

[0085] When a chemical conversion treatment liquid containing the P compound is applied to the hot-dip Al-Zn-Si-Mg coated steel sheet, the surface of the coating is etched by the action of the P compound, and an enriched layer containing Al, Zn, Si, and Mg which are constituent elements of the coating is
35 formed on the coating side of the chemical conversion layer. As a result of the formation of the enriched layer, the bond between the chemical conversion

layer and the surface of the coating is strengthened, and the adhesion of the chemical conversion layer is improved.

The concentration of the P compound in the chemical conversion treatment liquid is not limited, but may be 0.25 mass% to 5 mass%. If the
5 concentration of the P compound is less than 0.25 mass%, the etching effect is insufficient, and the adhesion to the coating interface decreases. There is thus a possibility that not only the corrosion resistance of flat parts decreases but also the corrosion resistance of defective parts, cut end surface parts, and damaged parts of the coating or layer caused by working or the like decrease
10 and perspiration resistance. From the same viewpoint, the concentration of the P compound is preferably 0.35 mass% or more, and more preferably 0.50 mass% or more. If the concentration of the P compound is more than 5 mass%, not only the life of the chemical conversion treatment liquid is shortened, but also the appearance of the layer formed tends to be not uniform. Moreover, the
15 amount of P eluted from the chemical conversion layer increases, which may cause a decrease in blackening resistance. From the same viewpoint, the concentration of the P compound is preferably 3.5 mass% or less, and more preferably 2.5 mass% or less. Regarding the content of the P compound in the chemical conversion layer, for example, applying and drying a chemical
20 conversion treatment liquid in which the concentration of the P compound is 0.25 mass% to 5 mass% can cause the coating weight of P in the chemical conversion layer after the drying to be 5 mg/m² to 100 mg/m².

[0086] The Si compound is a component that serves as a skeleton for forming the chemical conversion layer together with the resin, and enhances the affinity
25 with the coating and enables uniform formation of the chemical conversion layer. The Si compound is a compound containing Si, and preferably contains one or more selected from the group consisting of silica, trialkoxysilane, tetraalkoxysilane, and a silane coupling agent.

[0087] Any silica may be used without limitation. As the silica, for example,
30 at least one of wet silica and dry silica may be used. As colloidal silica which is one type of wet silica, for example, SNOWTEX O, C, N, S, 20, OS, OXS, NS, etc. produced by Nissan Chemical Corporation can be suitably used. As dry silica, for example, AEROSIL 50, 130, 200, 300, 380, etc. produced by Nippon Aerosil Co., Ltd. can be suitably used.

35 **[0088]** Any trialkoxysilane may be used without limitation. For example, trialkoxysilane represented by general formula: R₁Si(OR₂)₃ (where R₁ is

hydrogen or an alkyl group having 1 to 5 carbon atoms, and R₂ is the same or different alkyl group having 1 to 5 carbon atoms) is preferably used. Examples of such trialkoxysilane include trimethoxysilane, triethoxysilane, and methyltriethoxysilane.

5 [0089] Any tetraalkoxysilane may be used without limitation. For example, tetraalkoxysilane represented by general formula: Si(OR)₄ (where R is the same or different alkyl group having 1 to 5 carbon atoms) is preferably used. Examples of such tetraalkoxysilane include tetramethoxysilane, tetraethoxysilane, and tetrapropoxysilane.

10 [0090] Any silane coupling agent may be used without limitation. Examples include γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldiethoxysilane, γ -glycidoxypentyltriethoxysilane, γ -aminopentyltrimethoxysilane, γ -aminopentylmethyldiethoxysilane, γ -aminopentyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -mercaptopentylmethyldimethoxysilane, γ -mercaptopentyltrimethoxysilane, vinyltriethoxysilane, and γ -isocyanatepropyltriethoxysilane.

[0091] The Si compound, when contained in the chemical conversion layer, undergoes dehydration condensation to form an amorphous chemical conversion layer having a siloxane bond with a high barrier effect of blocking corrosion factors. Moreover, as a result of the Si compound combining with the foregoing resin, a chemical conversion layer having higher barrier property is formed. In a corrosion environment, dense and stable corrosion products are formed in defective parts and damaged parts of the coating or layer caused by working or the like, and the combination with the coating produces the effect of suppressing corrosion of the base steel sheet. As the Si compound, at least one of colloidal silica and dry silica is preferable from the viewpoint of being highly effective in forming stable corrosion products.

20 [0092] The concentration of the Si compound in the chemical conversion treatment liquid for forming the chemical conversion layer is 0.2 mass% to 9.5 mass%. If the concentration of the Si compound in the chemical conversion treatment liquid is 0.2 mass% or more, the barrier effect by siloxane bond can be achieved, as a result of which not only the corrosion resistance of flat parts but also the corrosion resistance and perspiration resistance of defective parts, cut parts, and damaged parts caused by working or the like are improved. If 25 30 35 the concentration of the Si compound is 9.5 mass% or less, the life of the

chemical conversion treatment liquid can be increased. Applying and drying a chemical conversion treatment liquid in which the concentration of the Si compound is 0.2 mass% to 9.5 mass% can cause the coating weight of Si in the chemical conversion layer after the drying to be 2 mg/m² to 95 mg/m².

5 **[0093]** The Co compound and the Ni compound, when contained in the chemical conversion layer, can improve the blackening resistance. This is because Co and Ni have the effect of delaying the elution of water-soluble components from the coating under a corrosion environment. Moreover, Co and Ni are elements less easily oxidizable than Al, Zn, Si, Mg, etc. Accordingly,
10 when at least one of the Co compound and the Ni compound is enriched at the interface between the chemical conversion layer and the coating (i.e. an enriched layer is formed), the enriched layer serves as a barrier against corrosion, and thus the blackening resistance can be improved.

[0094] With use of a chemical conversion treatment liquid containing the Co
15 compound, Co can be contained in the chemical conversion layer and incorporated into the enriched layer. A cobalt salt is preferably used as the Co compound. It is more preferable to use, as the cobalt salt, one or more selected from the group consisting of cobalt sulfate, cobalt carbonate, and cobalt chloride.

20 With use of a chemical conversion treatment liquid containing the Ni compound, Ni can be contained in the chemical conversion layer and incorporated into the enriched layer. A nickel salt is preferably used as the Ni compound. It is more preferable to use, as the nickel salt, one or more selected from the group consisting of nickel sulfate, nickel carbonate, and nickel
25 chloride.

[0095] The concentration of the Co compound and/or the Ni compound in the chemical conversion treatment liquid is not limited, but may be 0.25 mass% to 5 mass% in total. If the concentration of the Co compound and/or the Ni compound is less than 0.25 mass%, the interface enriched layer is not uniform,
30 and there is a possibility that not only the corrosion resistance of flat parts decreases but also the corrosion resistance of defective parts, cut end surface parts, and damaged parts of the coating or layer caused by working or the like decreases. From the same viewpoint, the concentration of the Co compound and/or the Ni compound is preferably 0.5 mass% or more, and more preferably
35 0.75 mass% or more. If the concentration of the Co compound and/or the Ni compound is more than 5 mass%, the appearance of the layer formed tends to

be not uniform, and the corrosion resistance may decrease. From the same viewpoint, the concentration of the Co compound and/or the Ni compound is preferably 4.0 mass% or less, and more preferably 3.0 mass% or less. Applying and drying a chemical conversion treatment liquid in which the total
5 concentration of the Co compound and/or the Ni compound is 0.25 mass% to 5 mass% can cause the total coating weight of Co and Ni in the chemical conversion layer after the drying to be 5 mg/m² to 100 mg/m².

[0096] The Al compound, the Zn compound, and the Mg compound, when contained in the chemical conversion treatment liquid, can form an enriched
10 layer containing at least one of Al, Zn, and Mg on the coating side of the chemical conversion layer. The enriched layer formed can improve the corrosion resistance.

The Al compound, the Zn compound, and the Mg compound are not limited as long as they are compounds containing Al, Zn, and Mg respectively,
15 but are preferably inorganic compounds, and preferably salts, chlorides, oxides, or hydroxides.

[0097] The Al compound is, for example, one or more selected from the group consisting of aluminum sulfate, aluminum carbonate, aluminum chloride, aluminum oxide, and aluminum hydroxide.

20 The Zn compound is, for example, one or more selected from the group consisting of zinc sulfate, zinc carbonate, zinc chloride, zinc oxide, and zinc hydroxide.

The Mg compound is, for example, one or more selected from the group consisting of magnesium sulfate, magnesium carbonate, magnesium chloride,
25 magnesium oxide, and magnesium hydroxide.

[0098] The total concentration of the Al compound, the Zn compound, and/or the Mg compound in the chemical conversion treatment liquid for forming the chemical conversion layer is preferably 0.25 mass% to 5 mass%. If the total concentration is 0.25 mass% or more, the enriched layer can be formed more
30 effectively, so that the corrosion resistance can be further improved. If the total concentration is 5 mass% or less, the appearance of the chemical conversion layer is more uniform, and the corrosion resistance of flat parts, defective parts, and damaged parts of the coating or layer caused by working or the like can be further improved.

35 **[0099]** When the V compound is contained in the chemical conversion layer, V is eluted moderately in a corrosion environment and bonds with zinc ions,

which are coating components equally eluted in a corrosion environment, to form a dense protective layer. The protective layer formed can further improve the corrosion resistance of not only flat parts of the steel sheet but also defective parts and damaged parts of the coating caused by working, for example, against such corrosion progressing from a cut end surface to a flat part.

[0100] The V compound is a compound containing V, and is, for example, one or more selected from the group consisting of sodium metavanadate, vanadyl sulfate, and vanadium acetylacetonate.

[0101] The V compound in the chemical conversion treatment liquid for forming the chemical conversion layer is preferably 0.05 mass% to 4 mass%. If the concentration of the V compound is 0.05 mass% or more, V is easily eluted in a corrosion environment to form a protective layer, and the corrosion resistance of defective parts, cut end surface parts, and damaged parts of the coating caused by working is improved. If the concentration of the V compound is more than 4 mass%, the appearance of the chemical conversion layer formed tends to be not uniform, and the blackening resistance decreases.

[0102] The Mo compound, when contained in the chemical conversion layer, can enhance the blackening resistance of the surface-treated steel sheet. The Mo compound is a compound containing Mo, and can be obtained by adding one or both of molybdic acid and molybdate to the chemical conversion treatment liquid.

The molybdate is, for example, one or more selected from the group consisting of sodium molybdate, potassium molybdate, magnesium molybdate, and zinc molybdate.

[0103] The concentration of the Mo compound in the chemical conversion treatment liquid for forming the chemical conversion layer is preferably 0.01 mass% to 3 mass%. If the concentration of the Mo compound is 0.01 mass% or more, the formation of oxygen-deficient zinc oxide is further suppressed, and the blackening resistance can be further improved. If the concentration of the Mo compound is 3 mass% or less, the life of the chemical conversion treatment liquid can be extended, and the corrosion resistance can be further improved.

[0104] The Zr compound and the Ti compound, when contained in the chemical conversion layer, can prevent the chemical conversion layer from being porous and densify the layer. This prevents corrosion factors from permeating the chemical conversion layer, and thus enhances the corrosion resistance.

[0105] The Zr compound is a compound containing Zr, and is, for example, one or more selected from the group consisting of zirconyl acetate, zirconyl sulfate, potassium zirconyl carbonate, sodium zirconyl carbonate, and ammonium zirconyl carbonate. In particular, an organic titanium chelate compound is preferable because, when the chemical conversion treatment liquid is dried to form the layer, it densifies the layer and contributes to better corrosion resistance.

[0106] The Ti compound is a compound containing Ti, and is, for example, one or more selected from the group consisting of titanium sulfate, titanium chloride, titanium hydroxide, titanium acetylacetonate, titanium octylene glycolate, and titanium ethylacetoacetate.

[0107] The total concentration of the Zr compound and/or the Ti compound in the chemical conversion treatment liquid for forming the chemical conversion layer is preferably 0.2 mass% to 20 mass%. If the total concentration of the Zr compound and/or the Ti compound is 0.2 mass% or more, the corrosion factor permeation suppression effect can be enhanced, and not only the corrosion resistance of flat parts but also the corrosion resistance of defective parts, cut end surface parts, and damaged parts of the coating caused by working can be further improved. If the total concentration of the Zr compound and/or the Ti compound is 20 mass% or less, the life of the chemical conversion treatment liquid can be further extended.

[0108] The Ca compound, when contained in the chemical conversion layer, has the effect of lowering the corrosion rate.

[0109] The Ca compound is a compound containing Ca, and examples include Ca oxides, Ca nitrates, Ca sulfates, and Ca-containing intermetallic compounds. More specific examples of the Ca compound include CaO, CaCO₃, Ca(OH)₂, Ca(NO₃)₂·4H₂O, and CaSO₄·2H₂O. The content of the Ca compound in the chemical conversion layer is not limited.

[0110] The chemical conversion layer may optionally contain various known components commonly used in the paint field. Examples of such components include various surface conditioners such as leveling agents and defoamers, various additives such as dispersants, anti-settling agents, UV absorbers, light stabilizers, silane coupling agents, and titanate coupling agents, various pigments such as coloring pigments, extender pigments, and luster pigments, curing catalysts, organic solvents, and lubricants.

[0111] In the surface-treated steel sheet according to the present disclosure,

the chemical conversion layer preferably does not contain harmful components such as hexavalent chromium, trivalent chromium, and fluorine. The absence of such harmful components in the chemical conversion treatment liquid for forming the chemical conversion layer contributes to higher safety and environmental friendliness.

[0112] The coating weight of the chemical conversion layer is not limited. For example, the coating weight of the chemical conversion layer is preferably 0.1 g/m² to 3.0 g/m² and more preferably 0.5 g/m² to 2.5 g/m², from the viewpoint of preventing peeling, etc. of the chemical conversion layer while ensuring the corrosion resistance more reliably. If the coating weight of the chemical conversion layer is 0.1 g/m² or more, the corrosion resistance can be ensured more reliably. If the coating weight of the chemical conversion layer is 3.0 g/m² or less, cracking and peeling of the chemical conversion layer can be prevented.

The coating weight of the chemical conversion layer may be determined by a method appropriately selected from existing methods, such as a method of subjecting the layer to fluorescent X-ray analysis and measuring the existence amount of each element whose content in the layer is known beforehand.

[0113] The method of forming the chemical conversion layer is not limited, and may be selected as appropriate depending on the required performance, the production line, etc. For example, the chemical conversion layer may be formed by continuously applying the chemical conversion treatment liquid onto the coating with a roll coater or the like and then drying it with a peak metal temperature (PMT) of about 60 °C to 200 °C using hot blast, induction heating, or the like. For the application of the chemical conversion treatment liquid, a known method other than a roll coater, such as an airless spray, an electrostatic spray, and a curtain flow coater, may also be used as appropriate. The chemical conversion layer may be any of monolayer and multilayer as long as it contains the resin and the metal compound, and is not limited.

[0114] The surface-treated steel sheet according to the present disclosure may optionally comprise a painting layer on the chemical conversion layer.

[0115] (Production method for surface-treated steel sheet)

A production method for a surface-treated steel sheet according to the present disclosure is a production method for a surface-treated steel sheet that includes a coating and a chemical conversion layer formed on the coating.

In the production method according to the present disclosure, the chemical conversion layer contains at least one resin selected from the group consisting of epoxy resin, urethane resin, acrylic resin, acrylic silicon resin, alkyd resin, polyester resin, polyalkylene resin, amino resin, and fluororesin and at least one metallic compound selected from the group consisting of a P compound, a Si compound, a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound, and the coating is formed under the same conditions as the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure.

[0116] Ni contained in the coating may degrade the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet, as mentioned above. By appropriately controlling the contents of Al, Zn, Si, and Mg in the molten bath and further reducing the Ni content as an inevitable impurity, degradation in corrosion resistance can be suppressed.

[0117] The conditions of the hot-dip coating treatment process are the same as those described with regard to the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure.

The structure of the chemical conversion layer is the same as that described with regard to the chemical conversion layer of the surface-treated steel sheet according to the present disclosure.

[0118] (Painted steel sheet)

A painted steel sheet according to the present disclosure is a painted steel sheet obtained by forming a painting layer on a coating directly or with a chemical conversion layer therebetween.

The structure of the coating is the same as that of the coating of the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure.

[0119] In the painted steel sheet according to the present disclosure, a chemical conversion layer may be formed on the coating.

The chemical conversion layer is formed on at least one side of the painted steel sheet, and may be formed on both sides of the painted steel sheet depending on the intended use or required performance.

[0120] In a production method according to the present disclosure, the chemical conversion layer contains: a resin component that contains (a): an anionic polyurethane resin having an ester bond and (b): an epoxy resin having a bisphenol skeleton in a total amount of 30 mass% to 50 mass% and in which

the content ratio of (a) and (b) ((a):(b)) is in the range of 3:97 to 60:40 in mass ratio; and an inorganic compound that contains 2 mass% to 10 mass% of a vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound, the painting layer includes at least a primer painting layer that contains: a polyester resin having a urethane bond; and an inorganic compound including a vanadium compound, a phosphate compound, and magnesium oxide, and the coating is formed under the same conditions as the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure.

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10 **[0121]** Ni contained in the coating may degrade the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet, as mentioned above. By appropriately controlling the contents of Al, Zn, Si, and Mg in the molten bath and further reducing the Ni content as an inevitable impurity, degradation in corrosion resistance can be suppressed.

15 **[0122]** The conditions of the hot-dip coating treatment process are the same as those described with regard to the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure.

The structures of the chemical conversion layer and the painting layer are the same as those described with regard to the chemical conversion layer and the painting layer of the painted steel sheet according to the present disclosure.

EXAMPLES

[0123] <Example 1: Samples 1 to 62>

25 Cold-rolled steel sheets of 0.8 mm in thickness produced by a conventional method were used as base steel sheets, and subjected to annealing treatment and coating treatment by a hot-dip coating simulator produced by Rhesca Co., Ltd. to produce Samples 1 to 62 of hot-dip coated steel sheets under the conditions shown in Table 1.

30 The composition of the molten bath used in the hot-dip coated steel sheet production was changed in the range of Al: 5 mass% to 75 mass%, Si: 0.0 mass% to 4.5 mass%, Mg: 0 mass% to 10 mass%, and Ni: 0.000 mass% to 0.025 mass% so as to be the composition of the coating of each sample shown in Table 1. The bath temperature of the molten bath was 450 °C in the case of Al: 5 mass%, 480 °C in the case of Al: 15 mass%, 590 °C in the case of Al: 30 mass% to 60 mass%, and 630 °C in the case of Al: more than 60 mass%, and

the coating entering sheet temperature of the base steel sheet was controlled to be equal to the molten bath temperature. In the case of Al: 30 mass% to 60 mass%, the coating treatment was performed under the conditions that the sheet temperature was lowered (i.e. the sheet was cooled) to the temperature range of 520 °C to 500 °C in 3 sec.

The coating weight of the coating was controlled to be $85 \pm 5 \text{ g/m}^2$ per side in Samples 1 to 59, $50 \pm 5 \text{ g/m}^2$ per side in Sample 60, $100 \pm 5 \text{ g/m}^2$ per side in Sample 61, and $125 \pm 5 \text{ g/m}^2$ per side in Sample 62.

[0124] (Evaluation)

Each sample of hot-dip coated steel sheet obtained as described above was evaluated as follows. The evaluation results are shown in Table 1.

[0125] (1) Coating (composition, coating weight, Ni-based compound, X-ray diffraction intensity)

Each sample after the coating was subjected to 100 mmφ blanking. After sealing the non-measurement surface with tape, the coating was dissolved and peeled with a liquid mixture of hydrochloric acid and hexamethylenetetramine as described in JIS H 0401: 2013, and the coating weight of the coating was calculated from the difference in the mass of the sample between before and after the peeling. The calculated coating weight of the coating is shown in Table 1.

After this, the peeling liquid was filtered, and the filtrate and the solid content were each analyzed. Specifically, ICP optical emission spectrometry was performed on the filtrate to quantify the components other than insoluble Si.

The solid content was dried and incinerated in a heating furnace at 650 °C, and then melted by adding sodium carbonate and sodium tetraborate. Further, the melt was dissolved with hydrochloric acid, and ICP optical emission spectrometry was performed on the solution to quantify insoluble Si. The Si concentration in the coating was obtained by adding the insoluble Si concentration obtained by solid content analysis to the soluble Si concentration obtained by filtrate analysis. The composition of the coating obtained as a result of the calculation is shown in Table 1.

Moreover, after shearing each sample to a size of 15 mm × 15 mm, it was mechanically polished in a state of being embedded in a conductive resin so that a cross section of the steel sheet could be observed. After this, for randomly selected serial sections of the coating having a length of 2 mm or

more in the direction parallel to the surface of the base steel sheet, reflected electron images were taken continuously at a width of 100 μm with an accelerating voltage of 3 kv using a scanning electron microscope (ULTRA55 produced by Carl Zeiss AG). Further, in the same apparatus, elemental mapping analysis (Al, Zn, Si, Mg, Fe, Sr, and Ni) of each section was performed with an accelerating voltage of 3 kv using an energy-dispersive X-ray spectrometer (Ultim Extreme produced by Oxford Instruments). Each part where high Ni intensity was detected in this analysis was subjected to point analysis with an accelerating voltage of 3 kv using the same spectrometer, and the substance was identified from the obtained semi-quantitative values of the components. The major axis length was measured for all Ni-based compounds observed in the observation field, and the maximum major axis length was obtained. In addition, the number of all Ni-based compounds present in the observed serial sections was counted, and the counted number was divided by the observed section length (mm) to calculate the number of Ni-based compounds per 1 mm (/mm) in the direction parallel to the surface of the base steel sheet. Each part where high Ni intensity was detected in this analysis was subjected to point analysis with an accelerating voltage of 3 kv using the same spectrometer, and the substance was identified from the obtained semi-quantitative values of the components. The analysis results are shown in Table 1.

In addition, after shearing each sample to a size of 100 mm $\times$ 100 mm, the coating on the surface to be evaluated was mechanically scraped off until the base steel sheet appeared, and the obtained powder was mixed well and then 0.3 g was taken out. Using an X-ray diffractometer (SmartLab produced by Rigaku Corporation), qualitative analysis was performed on the powder under the conditions of X-rays used: Cu-K α (wavelength = 1.54178 $\text{\AA}$), removal of K β rays: Ni filter, tube voltage: 40 kV, tube current: 30 mA, scanning speed: 4 $^\circ$ /min, sampling interval: 0.020 $^\circ$, divergence slit: 2/3 $^\circ$, solar slit: 5 $^\circ$, and detector: high-speed one-dimensional detector (D/teX Ultra). The intensity obtained by subtracting the base intensity from each peak intensity was taken to be diffraction intensity (cps), and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668 \text{ nm}$) of Mg_2Si , the diffraction intensity of (100) plane (interplanar spacing $d = 0.4510 \text{ nm}$) of MgZn_2 , and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135 \text{ nm}$) of Si were measured. The measurement results are shown in Table 1.

[0126] (2) Evaluation of corrosion resistance

After shearing each obtained sample of hot-dip coated steel sheet to a size of 120 mm × 120 mm, the range of 10 mm from each edge of the surface to be evaluated, the end surface of the sample, and the surface not to be evaluated were sealed with tape, and the surface to be evaluated was exposed in a size of 100 mm × 100 mm to obtain an evaluation sample. Three identical evaluation samples were produced.

A corrosion acceleration test was performed on the three evaluation samples produced as described above, with the cycle illustrated in FIG. 1. The corrosion acceleration test was started from wetting. After 300 cycles, the corrosion weight loss of each sample was measured by the method described in JIS Z 2383 and ISO 8407, and evaluated based on the following criteria. The evaluation results are shown in Table 1.

◎: The corrosion weight loss of all three samples was 45 g/m² or less.

O: The corrosion weight loss of all three samples was 95 g/m² or less.

X: The corrosion weight loss of one or more samples was more than 95 g/m².

[0127] (3) Surface appearance

For each obtained sample of hot-dip coated steel sheet, the surface of the coating was visually observed.

The observation results were evaluated based on the following criteria. The evaluation results are shown in Table 1.

◎: No wrinkle-like defects were observed.

O: Wrinkle-like defects were observed only in the range of 50 mm from the edge.

X: Wrinkle-like defects were observed outside the range of 50 mm from the edge.

[0128] (4) Workability

After shearing each obtained sample of hot-dip coated steel sheet to a size of 70 mm × 150 mm, 180° bending (8T bending) was performed with eight sheets of the same thickness sandwiched inside. Cellotape® (Cellotape is a registered trademark in Japan, other countries, or both) was firmly attached to the outer surface of the bent portion after the bending, and then peeled off. The surface state of the coating on the outer surface of the bent portion and whether the coating adhered to the surface of the tape used (i.e. whether the coating peeled off (came off)) were visually observed, and the workability was evaluated based on the following criteria. The evaluation results are shown in

Table 1.

O: Neither cracking nor peeling of the coating was observed.

Δ : Cracking of the coating was observed but no peeling was observed.

X: Both cracking and peeling of the coating were observed.

5 **[0129]** (5) Bath stability

During the production of each sample of hot-dip coated steel sheet, the state of the bath surface of the molten bath was visually checked, and compared with the bath surface (bath surface without Mg-containing oxides) of a molten bath used when producing hot-dip Al-Zn coated steel sheets. Evaluation was
10 made based on the following criteria. The evaluation results are shown in Table 1.

O: Similar to hot-dip Al-Zn molten bath (55 mass% Al-balance Zn-1.6 mass% bath).

Δ : More white oxides were present than in hot-dip Al-Zn molten bath
15 (55 mass% Al-balance Zn-1.6 mass% bath).

X: Formation of black oxides was observed in the molten bath.

[0130] [Table 1]

Table 1																		
No.	Composition (mass%)					Coating weight (g/m ²)	Coating			Corrosion resistance					Surface appearance	Workability	Bath stability	Remarks
							Ni-based compound			Corrosion weight loss (g/m ²)			Evaluation					
Al	Si	Mg	Fe	Sr	Ni	Type	Existence amount (particles/mm)	Maximum major axis length (μm)	Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (kcps)	N1	N2	N3					
1	55	0.5	4.4	1.05	0.11	0.003	-	0.0	-	0.00	0.00	97	98	95	⊙	×	○	Comparative Example
2	55	1.0	4.4	0.68	0.11	0.003	-	0.0	-	0.22	0.00	42	43	45	⊙	△	○	Example
3	55	1.5	0.0	0.51	0.00	0.003	-	0.0	-	No Mg ₂ Si No MgZn ₂	1.19	111	105	102	⊙	○	○	Comparative Example
4	55	1.5	0.0	0.51	0.11	0.003	-	0.0	-	No Mg ₂ Si No MgZn ₂	1.18	104	99	100	⊙	○	○	Comparative Example
5	55	1.5	1.1	0.58	0.10	0.003	-	0.0	-	0.00	0.88	80	82	78	⊙	△	○	Example
6	55	1.6	1.5	0.63	0.10	0.003	-	0.0	-	0.21	0.75	75	77	66	⊙	△	○	Example
7	54	1.5	1.9	0.39	0.00	0.003	-	0.0	-	0.38	0.62	45	44	51	⊙	×	○	Example
8	55	1.5	2.0	0.43	0.05	0.003	-	0.0	-	0.42	0.62	46	48	50	⊙	△	○	Example
9	55	1.5	1.9	0.62	0.11	0.003	-	0.0	-	0.46	0.63	49	40	50	⊙	△	○	Example
10	55	1.5	3.4	0.59	0.09	0.003	-	0.0	-	0.60	0.00	45	43	45	⊙	△	○	Example
11	5	0.0	0.5	0.39	0.00	0.000	-	0.0	-	No Mg ₂ Si	0.00	251	246	210	⊙	×	○	Comparative Example
12	15	0.3	3.0	0.42	0.00	0.001	-	0.0	-	No Mg ₂ Si	0.00	216	241	198	⊙	×	○	Comparative Example
13	32	1.5	4.5	0.58	0.10	0.001	-	0.0	-	0.36	0.00	89	98	90	⊙	×	○	Comparative Example
14	48	1.5	4.5	0.60	0.10	0.002	-	0.0	-	0.33	0.00	42	44	43	⊙	△	○	Example
15	50	1.5	4.5	0.59	0.01	0.003	-	0.0	-	0.32	0.00	40	39	37	⊙	△	○	Example
16	55	1.5	4.4	0.54	0.10	0.001	-	0.0	-	0.30	0.00	40	37	36	⊙	△	○	Example
17	55	1.5	4.4	0.55	0.10	0.003	-	0.0	-	0.28	0.00	39	41	40	⊙	△	○	Example
18	55	1.5	4.4	0.56	0.10	0.005	-	0.0	-	0.28	0.00	42	37	41	⊙	△	○	Example
19	55	1.5	4.4	0.64	0.10	0.008	Ni-Al	1.5	1.7	0.29	0.00	38	49	47	○	△	○	Example
20	55	1.5	4.4	0.55	0.10	0.008	Ni-Al	1.8	2.7	0.29	0.00	54	46	51	○	△	○	Example
21	55	1.5	4.4	0.54	0.10	0.008	Ni-Al	3.7	2.5	0.33	0.00	55	53	56	○	△	○	Example
22	55	1.5	4.4	0.62	0.10	0.009	Ni-Al Ni-Al-Fe	5.4	3.0	0.31	0.00	57	63	61	⊙	△	○	Example
23	55	1.5	4.4	0.51	0.10	0.009	Ni-Al	3.1	3.9	0.30	0.00	68	62	64	⊙	△	○	Example
24	55	1.5	4.4	0.57	0.10	0.010	Ni-Al	5.8	3.6	0.30	0.00	67	70	74	⊙	△	○	Example
25	55	1.5	4.4	0.55	0.10	0.010	Ni-Al	4.9	4.0	0.27	0.00	77	80	78	⊙	△	○	Example
26	55	1.5	4.4	0.56	0.10	0.010	Ni-Al	2.5	4.3	0.28	0.00	75	73	77	⊙	△	○	Example
27	55	1.5	4.4	0.63	0.10	0.010	Ni-Al Ni-Al-Fe	5.1	4.5	0.32	0.00	81	79	84	⊙	△	○	Example
28	55	1.5	4.4	0.56	0.10	0.015	Ni-Al Ni-Al-Fe	5.7	5.8	0.32	0.00	92	97	86	⊙	×	○	Comparative Example
29	55	1.5	4.4	0.55	0.10	0.025	Ni-Al	8.3	6.4	0.32	0.00	121	109	114	⊙	×	○	Comparative Example
30	60	1.5	4.5	0.63	0.10	0.003	-	0.0	-	0.37	0.00	38	44	39	⊙	△	○	Example
31	64	1.6	4.3	0.61	0.02	0.004	-	0.0	-	0.33	0.00	44	43	44	⊙	△	○	Example

Table 1(cont'd)

No.	Coating										Corrosion resistance				Surface appearance	Workability	Bath stability	Remarks		
	Composition (mass%)					Coating weight (g/m ²)	Ni-based compound			Corrosion weight loss (g/m ²)			Evaluation							
	Al	Si	Mg	Fe	Sr		Ni	Type	Existence amount (particles/mm)	Maximum major axis length (μm)	Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (keps)		N1					N2	N3
32	68	1.5	4.5	0.60	0.10	0.003	85	-	0.0	-	0.32	0.00	96	88	82	×	⊙	△	○	Comparative Example
33	73	1.6	4.5	0.58	0.10	0.004	86	-	0.0	-	0.30	0.00	99	94	92	×	⊙	△	○	Comparative Example
34	55	1.5	5.9	0.63	0.09	0.003	85	-	0.0	-	0.25	0.00	29	26	31	⊙	⊙	△	△	Example
35	55	2.3	0.0	0.57	0.00	0.003	86	-	0.0	-	No Mg ₂ Si No MgZn ₂	4.21	105	103	97	×	⊙	○	○	Comparative Example
36	55	2.3	0.0	0.60	0.09	0.003	85	-	0.0	-	No Mg ₂ Si No MgZn ₂	3.98	104	113	104	×	⊙	○	○	Comparative Example
37	55	2.3	0.9	0.58	0.11	0.003	83	-	0.0	-	0.00	3.13	111	98	96	×	⊙	△	○	Comparative Example
38	55	2.2	2.0	0.55	0.10	0.003	85	-	0.0	-	0.24	2.15	81	64	72	○	⊙	△	○	Example
39	55	2.3	2.7	0.58	0.10	0.003	87	-	0.0	-	0.56	1.23	68	83	79	○	⊙	△	○	Example
40	55	2.2	3.1	0.55	0.10	0.003	85	-	0.0	-	1.36	0.75	83	67	76	○	⊙	△	○	Example
41	55	2.2	3.4	0.61	0.10	0.003	85	-	0.0	-	1.40	0.30	62	59	60	○	⊙	△	○	Example
42	55	2.2	4.3	0.56	0.00	0.003	82	-	0.0	-	1.20	0.13	55	56	51	○	×	△	○	Example
43	55	2.3	4.4	0.60	0.03	0.003	85	-	0.0	-	1.64	0.15	43	31	63	○	⊙	△	○	Example
44	55	2.3	4.3	0.59	0.09	0.003	83	-	0.0	-	1.73	0.16	53	60	49	○	⊙	△	○	Example
45	55	2.2	4.3	0.60	0.11	0.003	86	-	0.0	-	1.62	0.12	54	58	60	○	⊙	△	○	Example
46	55	2.2	4.6	0.54	0.09	0.008	83	Ni-Al	1.0	2.9	1.41	0.00	37	49	47	○	⊙	△	○	Example
47	55	2.2	4.6	0.55	0.09	0.010	81	Ni-Al	4.8	3.5	1.19	0.00	64	67	69	○	⊙	△	○	Example
48	55	2.2	4.6	0.55	0.09	0.019	84	Ni-Al, Ni-Al-Fe	7.1	8.2	1.29	0.00	106	102	99	×	⊙	△	○	Comparative Example
49	55	2.2	5.9	0.57	0.10	0.003	85	-	0.0	-	1.53	0.10	59	56	55	○	⊙	△	△	Example
50	55	2.2	6.4	0.55	0.00	0.003	82	-	0.0	-	1.23	0.99	60	54	48	○	×	△	△	Example
51	55	2.9	2.0	0.60	0.00	0.003	85	-	0.0	-	2.06	3.24	89	94	87	○	×	△	○	Example
52	55	2.9	3.2	0.61	0.10	0.003	85	-	0.0	-	2.11	0.85	95	91	80	○	○	△	○	Example
53	55	2.9	5.5	0.60	0.11	0.003	85	-	0.0	-	1.68	0.13	41	45	50	○	⊙	△	△	Example
54	55	3.1	4.5	0.62	0.10	0.003	87	-	0.0	-	1.71	0.87	55	43	48	○	⊙	△	○	Example
55	55	3.6	4.4	0.63	0.09	0.003	86	-	0.0	-	1.64	1.22	61	55	60	○	⊙	△	○	Example
56	55	3.9	3.6	0.61	0.10	0.003	85	-	0.0	-	2.10	1.81	93	85	82	○	○	△	○	Example
57	55	3.9	6.0	0.60	0.11	0.003	85	-	0.0	-	1.85	1.44	65	78	71	○	⊙	△	△	Example
58	55	4.1	4.4	0.58	0.09	0.003	82	-	0.0	-	2.07	1.49	96	89	82	×	○	△	○	Comparative Example
59	55	2.9	9.7	0.61	0.09	0.003	86	-	0.0	-	0.52	0.00	61	43	43	○	⊙	△	△	Example
60	55	1.5	4.4	0.55	0.10	0.003	51	-	0.0	-	0.31	0.00	39	44	39	⊙	⊙	△	○	Example
61	55	1.5	4.4	0.55	0.10	0.003	100	-	0.0	-	0.33	0.00	40	41	43	⊙	⊙	△	○	Example
62	55	1.5	4.4	0.55	0.10	0.003	125	-	0.0	-	0.30	0.00	39	41	39	⊙	⊙	×	○	Example

[0131] As can be understood from the results in Table 1, the sample of each Example was superior to the sample of each Comparative Example in all of corrosion resistance, surface appearance, workability, and bath stability in a well-balanced manner.

5 **[0132]** <Example 2: Samples 1 to 148>

(1) Cold-rolled steel sheets of 0.8 mm in thickness produced by a conventional method were used as base steel sheets, and subjected to annealing treatment and coating treatment by a hot-dip coating simulator produced by Rhesca Co., Ltd. to produce samples of hot-dip coated steel sheets under the
10 coating conditions shown in Tables 3 and 4.

The composition of the molten bath used in the hot-dip coated steel sheet production was changed in the range of Al: 5 mass% to 75 mass%, Si: 0.0 mass% to 4.5 mass%, Mg: 0 mass% to 10 mass%, and Ni: 0.000 mass% to 0.025 mass% so as to be the composition of the coating of each sample shown
15 in Tables 3 and 4. The bath temperature of the molten bath was 450 °C in the case of Al: 5 mass%, 480 °C in the case of Al: 15 mass%, 590 °C in the case of Al: 30 mass% to 60 mass%, and 630 °C in the case of Al: more than 60 mass%, and the coating entering sheet temperature of the base steel sheet was controlled to be equal to the molten bath temperature. In the case of Al: 30
20 mass% to 60 mass%, the coating treatment was performed under the conditions that the sheet temperature was lowered (i.e. the sheet was cooled) to the temperature range of 520 °C to 500 °C in 3 sec.

The coating weight of the coating was controlled to be 85 ± 5 g/m² per side in Samples 1 to 118 and 131 to 148, 50 ± 5 g/m² per side in Samples 119
25 to 120, 100 ± 5 g/m² per side in Samples 121 to 122, $125 \text{ g/m}^2 \pm 5 \text{ g/m}^2$ per side in Samples 123 to 124, and 70 ± 5 g/m² per side in Samples 125 to 130.

[0133] (2) After this, a chemical conversion treatment liquid was applied onto the coating of each produced sample of hot-dip coated steel sheet using a bar coater, and dried in a hot air oven (heating rate: 60 °C/s, PMT: 120 °C) to form
30 a chemical conversion layer. Each sample of surface-treated steel sheet shown in Tables 3 and 4 was thus produced.

As the chemical conversion treatment liquid, surface-treatment solutions A to F were prepared by dissolving each component in water as a solvent. The types of components (resin, metal compound) contained in each
35 surface-treatment solution are as follows.

(Resin)

Urethane resin: SUPERFLEX 130, SUPERFLEX 126 (DKS Co. Ltd.).

Acrylic resin: VONCOAT EC-740EF (DIC Corporation).

(Metallic compound)

P compound: aluminum dihydrogen triphosphosphate.

5 Si compound: silica.

V compound: sodium metavanadate.

Mo compound: molybdic acid.

Zr compound: potassium zirconyl carbonate.

10 The compositions of the chemical conversion treatment liquids A to F prepared and the coating weights of the chemical conversion layers formed are shown in Table 2. Herein, the concentration of each component in Table 2 is solid content concentration (mass%).

[0134] [Table 2]

Table 2									
Chemical conversion treatment	Chemical conversion treatment liquid								Coating weight of chemical conversion layer (g/m ²)
	Resin (mass%)			Metallic compound (mass%)					
	Urethane resin		Acrylic resin	P compound	Si compound	V compound	Mo compound	Zr compound	
	SUPERFLEX 130	SUPERFLEX 126	VONCOAT EC-740EF	Aluminum dihydrogen triphosphosphate	Silica	Sodium metavanadate	Molybdic acid	Potassium zirconyl carbonate	
A	8.0	-	2.0	0.5	1.0	1.0	0.3	-	1.6
B	8.0	-	2.0	0.5	1.0	1.0	0.5	-	1.6
C	8.0	-	2.0	0.5	1.0	1.0	0.8	-	1.6
D	9.0	1.0	-	0.5	1.0	1.0	0.3	-	1.6
E	-	-	-	1.5	1.0	1.5	-	6.0	0.7
F	10.0	-	-	-	-	-	-	-	2.0

15 **[0135]** (Evaluation)

Each sample of hot-dip coated steel sheet and surface-treated steel sheet obtained as described above was evaluated as follows. The evaluation results are shown in Tables 3 and 4.

20 **[0136]** (1) Coating (composition, coating weight, Ni-based compound, X-ray diffraction intensity)

Each sample of hot-dip coated steel sheet was subjected to 100 mmφ blanking. After sealing the non-measurement surface with tape, the coating was dissolved and peeled with a liquid mixture of hydrochloric acid and hexamethylenetetramine as described in JIS H 0401: 2013, and the coating weight of the coating was calculated from the difference in the mass of the sample between before and after the peeling. The calculated coating weight of the coating is shown in Tables 3 and 4.

After this, the peeling liquid was filtered, and the filtrate and the solid content were each analyzed. Specifically, ICP optical emission spectrometry

was performed on the filtrate to quantify the components other than insoluble Si.

The solid content was dried and incinerated in a heating furnace at 650 °C, and then melted by adding sodium carbonate and sodium tetraborate. Further, the melt was dissolved with hydrochloric acid, and ICP optical emission spectrometry was performed on the solution to quantify insoluble Si. The Si concentration in the coating was obtained by adding the insoluble Si concentration obtained by solid content analysis to the soluble Si concentration obtained by filtrate analysis. The composition of the coating obtained as a result of the calculation is shown in Tables 3 and 4.

Moreover, after shearing each sample to a size of 15 mm × 15 mm, it was mechanically polished in a state of being embedded in a conductive resin so that a cross section of the steel sheet could be observed. After this, for randomly selected serial sections of the coating having a length of 2 mm or more in the direction parallel to the surface of the base steel sheet, reflected electron images were taken continuously at a width of 100 μm with an accelerating voltage of 3 kv using a scanning electron microscope (ULTRA55 produced by Carl Zeiss AG). Further, in the same apparatus, elemental mapping analysis (Al, Zn, Si, Mg, Fe, Sr, and Ni) of each section was performed with an accelerating voltage of 3 kv using an energy-dispersive X-ray spectrometer (Ultim Extreme produced by Oxford Instruments). Each part where high Ni intensity was detected in this analysis was subjected to point analysis with an accelerating voltage of 3 kv using the same spectrometer, and the substance was identified from the obtained semi-quantitative values of the components. The major axis length was measured for all Ni-based compounds observed in the observation field, and the maximum major axis length was obtained. In addition, the number of all Ni-based compounds present in the observed serial sections was counted, and the counted number was divided by the observed section length (mm) to calculate the number of Ni-based compounds per 1 mm (/mm) in the direction parallel to the surface of the base steel sheet. Each part where high Ni intensity was detected in this analysis was subjected to point analysis with an accelerating voltage of 3 kv using the same spectrometer, and the substance was identified from the obtained semi-quantitative values of the components. The analysis results are shown in Tables 3 and 4.

In addition, after shearing each sample to a size of 100 mm × 100 mm, the coating on the surface to be evaluated was mechanically scraped off until

the base steel sheet appeared, and the obtained powder was mixed well and then 0.3 g was taken out. Using an X-ray diffractometer (SmartLab produced by Rigaku Corporation), qualitative analysis was performed on the powder under the conditions of X-rays used: Cu-K α (wavelength = 1.54178 Å),
5 removal of K β rays: Ni filter, tube voltage: 40 kV, tube current: 30 mA, scanning speed: 4°/min, sampling interval: 0.020°, divergence slit: 2/3°, solar slit: 5°, and detector: high-speed one-dimensional detector (D/teX Ultra). The intensity obtained by subtracting the base intensity from each peak intensity was taken to be diffraction intensity (cps), and the diffraction intensity of (111)
10 plane (interplanar spacing $d = 0.3668$ nm) of Mg₂Si, the diffraction intensity of (100) plane (interplanar spacing $d = 0.4510$ nm) of MgZn₂, and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135$ nm) of Si were measured. The measurement results are shown in Tables 3 and 4.

[0137] (2) Evaluation of corrosion resistance

15 After shearing each sample of hot-dip coated steel sheet and surface-treated steel sheet to a size of 120 mm $\times$ 120 mm, the range of 10 mm from each edge of the surface to be evaluated, the end surface of the sample, and the surface not to be evaluated were sealed with tape, and the surface to be evaluated was exposed in a size of 100 mm $\times$ 100 mm to obtain an evaluation
20 sample. Three identical evaluation samples were produced.

A corrosion acceleration test was performed on the three evaluation samples produced as described above, with the cycle illustrated in FIG. 1. The corrosion acceleration test was started from wetting. After 300 cycles, the corrosion weight loss of each sample was measured by the method described
25 in JIS Z 2383 and ISO 8407, and evaluated based on the following criteria. The evaluation results are shown in Tables 3 and 4.

◎: The corrosion weight loss of all three samples was 30 g/m² or less.

O: The corrosion weight loss of all three samples was 75 g/m² or less.

X: The corrosion weight loss of one or more samples was more than 75
30 g/m².

[0138] (3) White rust resistance

After shearing each sample of hot-dip coated steel sheet and surface-treated steel sheet to a size of 120 mm $\times$ 120 mm, the range of 10 mm from each edge of the surface to be evaluated, the end surface of the sample, and the
35 surface not to be evaluated were sealed with tape, and the surface to be evaluated was exposed in a size of 100 mm $\times$ 100 mm to obtain an evaluation

sample.

The salt spray test described in JIS Z 2371 was performed on the evaluation sample for 90 hr, and evaluation was made based on the following criteria. The evaluation results are shown in Tables 3 and 4.

5 ◎: Flat parts had no white rust.

O: The area of white rust in flat parts was less than 10 %.

X: The area of white rust in flat parts was 10 % or more.

[0139] (4) Surface appearance

10 For each sample of hot-dip coated steel sheet, the surface of the coating was visually observed.

The observation results were evaluated based on the following criteria. The evaluation results are shown in Tables 3 and 4.

◎: No wrinkle-like defects were observed.

15 O: Wrinkle-like defects were observed only in the range of 50 mm from the edge.

X: Wrinkle-like defects were observed outside the range of 50 mm from the edge.

[0140] (5) Workability

20 After shearing each sample of hot-dip coated steel sheet to a size of 70 mm × 150 mm, 180° bending (8T bending) was performed with eight sheets of the same thickness sandwiched inside. Cellotape® (Cellotape is a registered trademark in Japan, other countries, or both) was firmly attached to the outer surface of the bent portion after the bending, and then peeled off. The surface state of the coating on the outer surface of the bent portion and whether the coating adhered to the surface of the tape used (i.e. whether the coating peeled off (came off)) were visually observed, and the workability was evaluated based on the following criteria. The evaluation results are shown in Tables 3 and 4.

O: Neither cracking nor peeling of the coating was observed.

30 Δ : Cracking of the coating was observed but no peeling was observed.

X: Both cracking and peeling of the coating were observed.

[0141] (6) Bath stability

35 During hot-dip coating, the state of the bath surface of the molten bath was visually checked, and compared with the bath surface (bath surface without Mg-containing oxides) of a molten bath used when producing hot-dip Al-Zn coated steel sheets. Evaluation was made based on the following criteria. The

evaluation results are shown in Tables 3 and 4.

O: Similar to hot-dip Al-Zn molten bath (55 mass% Al-balance Zn-1.6 mass% bath).

Δ : More white oxides were present than in hot-dip Al-Zn molten bath
5 (55 mass% Al-balance Zn-1.6 mass% bath).

X: Formation of black oxides was observed in the molten bath.

[0142] [Table 3]

Table 3																					
No.	Coating										Chemical conversion treatment	Corrosion resistance			White rust resistance	Surface appearance	Workability	Bath stability	Remarks		
	Composition (mass%)				Coating weight (g/m ²)	Ni-based compound			Mg ₂ Si(111)/MgZn ₃ (100)	Si(111) (kps)		Corrosion resistance									
	Al	Si	Mg	Fe		Sr	Ni	Type				Existence amount (particles/mm)	Maximum major axis length (μm)	Evaluation							
														N1						N2	N3
1	55	0.5	4.4	1.05	0.11	0.003	85	-	0.0	-	0.00	97	98	95	x	⊙	×	Comparative Example			
2	55	1.0	4.4	0.68	0.11	0.003	85	-	0.0	-	0.22	80	83	75	×	⊙	○	Comparative Example			
3	55	1.0	4.4	0.68	0.11	0.003	85	-	0.0	-	0.00	42	43	45	○	⊙	×	Comparative Example			
4	55	1.0	4.4	0.68	0.11	0.003	85	-	0.0	-	0.00	26	24	27	⊙	⊙	○	Comparative Example			
5	55	1.5	0.0	0.51	0.00	0.003	82	-	0.0	-	No Mg ₂ Si No MgZn ₂	111	105	102	×	⊙	×	Comparative Example			
6	55	1.5	0.0	0.51	0.00	0.003	82	-	0.0	-	No Mg ₂ Si No MgZn ₂	81	80	76	×	⊙	○	Comparative Example			
7	55	1.5	0.0	0.51	0.11	0.003	85	-	0.0	-	No Mg ₂ Si No MgZn ₂	104	99	100	×	⊙	×	Comparative Example			
8	55	1.5	0.0	0.51	0.11	0.003	85	-	0.0	-	No Mg ₂ Si No MgZn ₂	75	73	76	×	⊙	○	Comparative Example			
9	55	1.5	1.1	0.58	0.10	0.003	84	-	0.0	-	0.88	80	82	78	×	⊙	×	Comparative Example			
10	55	1.6	1.5	0.63	0.10	0.003	82	-	0.0	-	0.75	59	61	54	○	⊙	×	Comparative Example			
11	55	1.6	1.5	0.63	0.10	0.003	82	-	0.0	-	0.21	75	77	66	×	⊙	×	Comparative Example			
12	55	1.6	1.5	0.63	0.10	0.003	82	-	0.0	-	0.21	53	56	55	○	⊙	○	Comparative Example			
13	54	1.5	1.9	0.39	0.00	0.003	85	-	0.0	-	0.38	45	44	51	○	×	×	Comparative Example			
14	54	1.5	1.9	0.39	0.00	0.003	85	-	0.0	-	0.38	33	29	38	○	○	○	Comparative Example			
15	55	1.5	2.0	0.43	0.05	0.003	84	-	0.0	-	0.42	46	48	50	○	×	×	Comparative Example			
16	55	1.5	2.0	0.43	0.05	0.003	84	-	0.0	-	0.42	31	36	35	○	○	○	Comparative Example			
17	55	1.5	1.9	0.62	0.11	0.003	81	-	0.0	-	0.46	49	40	50	○	×	×	Comparative Example			
18	55	1.5	1.9	0.62	0.11	0.003	81	-	0.0	-	0.46	35	29	33	○	○	○	Comparative Example			
19	55	1.5	3.4	0.59	0.09	0.003	85	-	0.0	-	0.60	45	43	45	○	×	×	Comparative Example			
20	55	1.5	3.4	0.59	0.09	0.003	85	-	0.0	-	0.60	29	25	24	⊙	⊙	⊙	Comparative Example			
21	5	0.0	0.5	0.39	0.00	0.000	85	-	0.0	-	0.00	251	246	210	×	×	×	Comparative Example			
22	5	0.0	0.5	0.39	0.00	0.000	85	-	0.0	-	No Mg ₂ Si	131	125	116	×	×	×	Comparative Example			
23	15	0.3	3.0	0.42	0.00	0.001	86	-	0.0	-	0.00	216	241	198	×	×	×	Comparative Example			
24	15	0.3	3.0	0.42	0.00	0.001	86	-	0.0	-	0.00	118	129	134	×	×	×	Comparative Example			
25	32	1.5	4.5	0.58	0.10	0.001	85	-	0.0	-	0.36	89	98	90	×	×	×	Comparative Example			
26	32	1.5	4.5	0.58	0.10	0.001	85	-	0.0	-	0.36	68	77	74	×	×	○	Comparative Example			
27	48	1.5	4.5	0.60	0.10	0.002	84	-	0.0	-	0.33	42	44	43	○	×	×	Comparative Example			
28	48	1.5	4.5	0.60	0.10	0.002	84	-	0.0	-	0.33	23	20	27	⊙	⊙	⊙	Comparative Example			
29	50	1.5	4.5	0.59	0.01	0.003	87	-	0.0	-	0.32	40	39	37	○	×	×	Comparative Example			
30	50	1.5	4.5	0.59	0.01	0.003	87	-	0.0	-	0.32	28	28	26	⊙	⊙	⊙	Comparative Example			
31	55	1.5	4.4	0.54	0.10	0.001	86	-	0.0	-	0.30	40	37	36	○	×	×	Comparative Example			
32	55	1.5	4.4	0.54	0.10	0.001	86	-	0.0	-	0.30	24	23	23	⊙	⊙	⊙	Comparative Example			

Table 3(cont'd1)

No.	Coating										Chemical conversion treatment	Corrosion resistance			White rust resistance	Surface appearance	Workability	Bath stability	Remarks		
	Composition (mass%)				Coating weight (g/m ²)	Ni-based compound			Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (kcps)		Corrosion weight loss (g/m ²)		Evaluation							
	Al	Si	Mg	Fe		Sr	Ni	Type				Existence amount (particles/mm)	Maximum major axis length (μm)								
33	55	1.5	4.4	0.55	0.10	0.003	85	-	0.0	-	0.28	0.00	39	41	40	○	×	◎	△	○	Comparative Example
34	55	1.5	4.4	0.56	0.10	0.005	86	-	0.0	-	0.28	0.00	24	25	26	◎	◎	◎	△	○	Comparative Example
35	55	1.5	4.4	0.56	0.10	0.005	86	-	0.0	-	0.28	0.00	42	37	41	○	×	◎	△	○	Comparative Example
36	55	1.5	4.4	0.56	0.10	0.005	86	-	0.0	-	0.28	0.00	28	29	29	◎	◎	◎	△	○	Comparative Example
37	55	1.5	4.4	0.64	0.10	0.008	83	Ni-Al	1.5	1.7	0.29	0.00	38	49	47	○	×	◎	△	○	Comparative Example
38	55	1.5	4.4	0.64	0.10	0.008	83	Ni-Al	1.5	1.7	0.29	0.00	26	31	22	○	○	◎	△	○	Comparative Example
39	55	1.5	4.4	0.55	0.10	0.008	82	Ni-Al	1.8	2.7	0.29	0.00	54	46	51	○	×	◎	△	○	Comparative Example
40	55	1.5	4.4	0.55	0.10	0.008	82	Ni-Al	1.8	2.7	0.29	0.00	31	28	34	○	○	◎	△	○	Comparative Example
41	55	1.5	4.4	0.54	0.10	0.008	82	Ni-Al	3.7	2.5	0.33	0.00	55	53	56	○	×	◎	△	○	Comparative Example
42	55	1.5	4.4	0.54	0.10	0.008	82	Ni-Al	3.7	2.5	0.33	0.00	30	38	37	○	○	◎	△	○	Comparative Example
43	55	1.5	4.4	0.62	0.10	0.009	86	Ni-Al	5.4	3.0	0.31	0.00	57	63	61	○	×	◎	△	○	Comparative Example
44	55	1.5	4.4	0.62	0.10	0.009	86	Ni-Al-Fe	5.4	3.0	0.31	0.00	44	36	39	○	○	◎	△	○	Comparative Example
45	55	1.5	4.4	0.51	0.10	0.009	87	Ni-Al	3.1	3.9	0.30	0.00	68	62	64	○	×	◎	△	○	Comparative Example
46	55	1.5	4.4	0.51	0.10	0.009	87	Ni-Al	3.1	3.9	0.30	0.00	46	45	43	○	○	◎	△	○	Comparative Example
47	55	1.5	4.4	0.57	0.10	0.010	86	Ni-Al	5.8	3.6	0.30	0.00	67	70	74	○	×	◎	△	○	Comparative Example
48	55	1.5	4.4	0.57	0.10	0.010	86	Ni-Al	5.8	3.6	0.30	0.00	51	46	56	○	○	◎	△	○	Comparative Example
49	55	1.5	4.4	0.55	0.10	0.010	86	Ni-Al	4.9	4.0	0.27	0.00	77	80	78	×	×	◎	△	○	Comparative Example
50	55	1.5	4.4	0.55	0.10	0.010	86	Ni-Al	4.9	4.0	0.27	0.00	53	56	61	○	○	◎	△	○	Comparative Example
51	55	1.5	4.4	0.56	0.10	0.010	85	Ni-Al	2.5	4.3	0.28	0.00	75	73	77	×	×	◎	△	○	Comparative Example
52	55	1.5	4.4	0.56	0.10	0.010	85	Ni-Al	2.5	4.3	0.28	0.00	59	50	54	○	○	◎	△	○	Comparative Example
53	55	1.5	4.4	0.63	0.10	0.010	83	Ni-Al	5.1	4.5	0.32	0.00	81	79	84	×	×	◎	△	○	Comparative Example
54	55	1.5	4.4	0.63	0.10	0.010	83	Ni-Al-Fe	5.1	4.5	0.32	0.00	62	58	59	○	○	◎	△	○	Comparative Example
55	55	1.5	4.4	0.56	0.10	0.015	86	Ni-Al	5.7	5.8	0.32	0.00	92	97	86	×	×	◎	△	○	Comparative Example
56	55	1.5	4.4	0.56	0.10	0.015	86	Ni-Al-Fe	5.7	5.8	0.32	0.00	81	76	78	×	○	◎	△	○	Comparative Example
57	55	1.5	4.4	0.55	0.10	0.025	86	Ni-Al	8.3	6.4	0.32	0.00	121	109	114	×	×	◎	△	○	Comparative Example
58	55	1.5	4.4	0.55	0.10	0.025	86	Ni-Al-Fe	8.3	6.4	0.32	0.00	95	96	88	×	○	◎	△	○	Comparative Example
59	60	1.5	4.5	0.63	0.10	0.003	85	-	0.0	-	0.37	0.00	38	44	39	○	×	◎	△	○	Comparative Example
60	60	1.5	4.5	0.63	0.10	0.003	85	-	0.0	-	0.37	0.00	22	23	24	◎	◎	◎	△	○	Comparative Example
61	64	1.6	4.3	0.61	0.02	0.004	83	-	0.0	-	0.33	0.00	44	43	44	○	×	◎	△	○	Comparative Example
62	64	1.6	4.3	0.61	0.02	0.004	83	-	0.0	-	0.33	0.00	25	23	26	◎	◎	◎	△	○	Comparative Example

Table 3(cont'd2)

No.	Coating										Chemical conversion treatment	Corrosion resistance			White rust resistance	Surface appearance	Workability	Bath stability	Remarks	
	Composition (mass%)				Coating weight (g/m ²)	Ni-based compound			Corrosion weight loss (g/m ²)			Evaluation								
	Al	Si	Mg	Fe		Sr	Ni	Type	Existence amount (particles/mm)	Maximum major axis length (μm)			Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (kcps)						
63	68	1.5	4.5	0.60	0.10	0.003	85	-	0.0	-	0.32	0.00	96	88	82	x	⊙	Δ	○	Comparative Example
64											A		66	77	65	x				Comparative Example
65	73	1.6	4.5	0.58	0.10	0.004	86	-	0.0	-	0.30	0.00	99	94	92	x	⊙	Δ	○	Comparative Example
66											A		70	74	76	x				Comparative Example
67	55	1.5	5.9	0.63	0.09	0.003	85	-	0.0	-	0.25	0.00	29	26	31	○	x	Δ	Δ	Comparative Example
68											A		23	21	25	⊙	⊙			Example
69	55	2.3	0.0	0.57	0.00	0.003	86	-	0.0	-	No Mg ₂ Si No MgZn ₂	4.21	105	103	97	x	⊙	○	○	Comparative Example
70											A		78	76	75	x				Comparative Example
71	55	2.3	0.0	0.60	0.09	0.003	85	-	0.0	-	No Mg ₂ Si No MgZn ₂	3.98	104	113	104	x	⊙	○	○	Comparative Example
72											A		80	85	79	x				Comparative Example
73	55	2.3	0.9	0.58	0.11	0.003	83	-	0.0	-	0.00	3.13	111	98	96	x	⊙	Δ	○	Comparative Example
74											-		77	72	75	x				Comparative Example
75	55	2.2	2.0	0.55	0.10	0.003	85	-	0.0	-	0.24	2.15	81	64	72	x	⊙	Δ	○	Comparative Example
76											A		43	45	51	○				Example
77	55	2.3	2.7	0.58	0.10	0.003	87	-	0.0	-	0.56	1.23	68	89	79	x	⊙	Δ	○	Comparative Example
78											-		61	68	55	○				Example
79	55	2.2	3.1	0.55	0.10	0.003	85	-	0.0	-	1.36	0.75	83	67	76	x	⊙	Δ	○	Comparative Example
80											A		54	57	51	○				Example
81	55	2.2	3.4	0.61	0.10	0.003	85	-	0.0	-	1.40	0.30	62	59	60	○	x	Δ	○	Comparative Example
82											A		36	40	42	○				Example
83	55	2.2	4.3	0.56	0.00	0.003	82	-	0.0	-	1.20	0.13	55	56	51	○	x	Δ	○	Comparative Example
84											A		35	41	38	○		×		Example
85	55	2.3	4.4	0.60	0.03	0.003	85	-	0.0	-	1.64	0.15	43	31	63	○	x	Δ	○	Comparative Example
86											A		28	30	35	○		⊙		Example
87	55	2.3	4.3	0.59	0.09	0.003	83	-	0.0	-	1.73	0.16	53	60	49	○	x	Δ	○	Comparative Example
88											A		39	41	38	○		⊙		Example
89	55	2.2	4.3	0.60	0.11	0.003	86	-	0.0	-	1.62	0.12	54	58	60	○	x	⊙	○	Comparative Example
90											A		38	40	42	○		⊙		Example
91	55	2.2	4.6	0.54	0.09	0.008	83	Ni-Al	1.0	2.9	1.41	0.00	37	49	47	○	x	Δ	○	Comparative Example
92											-		33	24	27	○		⊙		Example
93	55	2.2	4.6	0.55	0.09	0.010	81	Ni-Al	4.8	3.5	1.19	0.00	64	67	69	○	x	Δ	○	Comparative Example
94											A		47	49	44	○		⊙		Example

Table 3(cont'd3)

No.	Coating										Chemical conversion treatment	Corrosion resistance			White rust resistance	Surface appearance	Workability	Bath stability	Remarks	
	Composition (mass%)				Coating weight (g/m ²)	Ni-based compound			Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (kcps)		Corrosion weight loss (g/m ²)		Evaluation						
	Al	Si	Mg	Fe		Sr	Ni	Type				Existence amount (particles/mm)	Maximum major axis length (μm)							
95	55	2.2	4.6	0.55	0.09	0.019	84	Ni-Al	7.1	8.2	1.29	0.00	106	102	99	x	⊙	Δ	○	Comparative Example
96								Ni-Al-Fe			A		80	84	87	x	○			Example
97	55	2.2	5.9	0.57	0.10	0.003	85	-	0.0	-	1.53	0.10	59	56	55	○	x	⊙	Δ	Comparative Example
98											A		42	40	39	○	○			Example
99	55	2.2	6.4	0.55	0.00	0.003	82	-	0.0	-	1.23	0.99	60	54	48	○	x	x	Δ	Comparative Example
100											A		38	40	35	○	○			Example
101	55	2.9	2.0	0.60	0.00	0.003	85	-	0.0	-	2.06	3.24	89	94	87	x	x	x	Δ	Comparative Example
102											A		74	72	66	○	○	○		Example
103	55	2.9	3.2	0.61	0.10	0.003	85	-	0.0	-	2.11	0.85	85	91	80	x	x	○	Δ	Comparative Example
104											A		73	65	71	○	○			Example
105	55	2.9	5.5	0.60	0.11	0.003	85	-	0.0	-	1.68	0.13	41	45	50	○	x	⊙	Δ	Comparative Example
106											A		28	31	27	○	○			Example
107	55	3.1	4.5	0.62	0.10	0.003	87	-	0.0	-	1.71	0.87	55	43	48	○	x	⊙	Δ	Comparative Example
108											A		42	40	33	○	○			Example
109	55	3.6	4.4	0.63	0.09	0.003	86	-	0.0	-	1.64	1.22	61	55	60	○	x	⊙	Δ	Comparative Example
110											A		44	39	45	○	○			Example
111	55	3.9	3.6	0.61	0.10	0.003	85	-	0.0	-	2.10	1.81	93	85	82	x	x	○	Δ	Comparative Example
112											A		73	73	65	○	○			Example
113	55	3.9	6.0	0.60	0.11	0.003	85	-	0.0	-	1.85	1.44	65	78	71	x	x	⊙	Δ	Comparative Example
114											A		48	55	51	○	○			Example
115	55	4.1	4.4	0.58	0.09	0.003	82	-	0.0	-	2.07	1.49	96	89	82	x	x	○	Δ	Comparative Example
116											A		71	76	69	x	○			Example
117	55	2.9	9.7	0.61	0.09	0.003	86	-	0.0	-	0.52	0.00	61	43	43	○	x	⊙	Δ	Comparative Example
118											A		39	37	33	○	○			Example
119	55	1.5	4.4	0.55	0.10	0.003	51	-	0.0	-	0.31	0.00	39	44	39	○	x	⊙	Δ	Comparative Example
120											A		21	26	25	⊙	○			Example
121	55	1.5	4.4	0.55	0.10	0.003	121	-	0.0	-	0.33	0.00	40	41	43	○	x	⊙	Δ	Comparative Example
122											A		26	24	27	⊙	○			Example
123	55	1.5	4.4	0.55	0.10	0.003	125	-	0.0	-	0.30	0.00	39	41	39	○	x	⊙	×	Comparative Example
124											A		28	29	25	⊙	○			Example

[0143] [Table 4]

Table 4																			
No.	Composition (mass%)					Coating weight (g/m ²)	Coating				Chemical conversion treatment	Corrosion resistance			Surface appearance	Workability	Bath stability	Remarks	
							Ni-based compound			Corrosion weight loss (g/m ²)		Evaluation							
	Al	Si	Mg	Fe	Sr	Ni	Type	Existence amount (particles/mm)	Maximum major axis length (μm)		Mg ₂ Si(111)/MgZn ₂ (100)			Si(111) (kps)					
125											A	33	39	35	○				Example
126											B	32	37	33	○				Example
127											C	35	36	38	○				Example
128	55	1.7	1.9	0.42	0.03	0.003	71	-	0.0	-	D	39	34	33	○	◎	△	○	Example
129											E	40	39	41	○	×			Comparative Example
130											F	47	43	44	○	×			Comparative Example
131											A	30	35	36	○				Example
132											B	34	35	37	○				Example
133											C	31	38	33	○				Example
134	55	1.6	2.0	0.45	0.00	0.003	80	-	0.0	-	D	34	36	35	○	×	△	○	Example
135											E	38	43	44	○	×			Comparative Example
136											F	42	43	39	○	×			Comparative Example
137											A	24	25	26	◎				Example
138											B	22	23	26	◎				Example
139											C	28	24	25	◎				Example
140	55	1.5	4.4	0.55	0.10	0.003	85	-	0.0	-	D	21	28	25	◎	◎	△	○	Example
141											E	28	27	29	◎				Example
142											F	35	30	33	○				Example
143											A	39	41	38	○				Example
144											B	37	36	33	○				Example
145	55	2.3	4.3	0.59	0.09	0.003	83	-	0.0	-	C	39	38	36	○	◎	△	○	Example
146											D	36	35	32	○				Example
147											E	39	40	37	○				Example
148											F	46	42	48	○				Example

[0144] As can be understood from the results in Tables 3 and 4, the sample of each Example was superior to the sample of each Comparative Example in all of corrosion resistance, white rust resistance, surface appearance, workability, and bath stability in a well-balanced manner.

5 As can be understood from the results in Table 4, each sample subjected to chemical conversion treatments A to D was particularly excellent in white rust resistance.

[0145] <Example 3: Samples 1 to 41>

10 (1) Cold-rolled steel sheets of 0.8 mm in thickness produced by a conventional method were used as base steel sheets, and subjected to annealing treatment and coating treatment by a hot-dip coating simulator produced by Rhesca Co., Ltd. to produce samples of hot-dip coated steel sheets under the coating conditions shown in Table 6.

15 The composition of the molten bath used in the hot-dip coated steel sheet production was changed in the range of Al: 30 mass% to 75 mass%, Si: 0.5 mass% to 4.5 mass%, Mg: 0 mass% to 15 mass%, Ni: 0.001 mass% to 0.025 mass% so as to be the composition of the coating of each sample shown in Table 6. The bath temperature of the molten bath was 590 °C in the case of Al: 30 mass% to 60 mass% and 630 °C in the case of Al: more than 60 mass%, and
20 the coating entering sheet temperature of the base steel sheet was controlled to be equal to the molten bath temperature. Moreover, the coating treatment was performed under the conditions that the sheet temperature was lowered (i.e. the sheet was cooled) to the temperature range of 520 °C to 500 °C in 3 sec.

25 The coating weight of the coating was controlled to be 85 ± 5 g/m² per side in Samples 1 to 38, 50 ± 5 g/m² per side in Sample 39, 100 ± 5 g/m² per side in Sample 40, and 125 ± 5 g/m² per side in Sample 41.

30 **[0146]** (2) After this, the chemical conversion treatment liquid shown in Table 5 was applied onto the coating of each produced sample of hot-dip coated steel sheet using a bar coater, and dried in a hot air drying oven (end-point temperature: 90 °C) to form a chemical conversion layer having a coating weight of 0.1 g/m².

35 The chemical conversion treatment liquid used was prepared by dissolving each component in water as a solvent and had a pH of 8 to 10. The types of components (resin component, inorganic compound) contained in each chemical conversion treatment liquid are as follows.

(Resin components)

Resin A: mixture of (a) an anionic polyurethane resin having an ester bond (SUPERFLEX 210 produced by DKS Co. Ltd.) and (b) an epoxy resin having a bisphenol skeleton (YUKARESIN RE-1050 produced by Yoshimura Oil Chemical Co., Ltd.) at a content mass ratio (a): (b) = 50: 50.

5 Resin B: acrylic resin (VONCOAT EC-740EF produced by DIC Corporation).
(Inorganic compounds)

Vanadium compound: organic vanadium compound chelated with acetylacetone.

10 Zirconium compound: ammonium zirconium carbonate.

Fluorine compound: ammonium fluoride.

[0147] (3) A primer paint was then applied onto the chemical conversion layer formed as described above with a bar coater, and baked under the conditions of a steel sheet end-point temperature of 230 °C and a baking time of 35 sec to
15 form a primer painting layer having the chemical composition shown in Table 5. Atop coat paint composition was then applied onto the primer painting layer formed as described above with a bar coater, and baked under the conditions of a steel sheet end-point temperature of 230 °C to 260 °C and a baking time of 40 sec to form a top coat painting layer having the resin conditions and
20 thickness shown in Table 5. Each sample of painted steel sheet was thus produced.

The primer paint was obtained by mixing the components and then stirring the mixture with a ball mill for about 1 hr. The following resin components and inorganic compounds were used to form the primer painting
25 layer.

(Resin components)

Resin α : obtained by curing urethane-modified polyester resin (obtained by reacting 455 parts by mass of polyester resin and 45 parts by mass of isophorone diisocyanate; resin acid value: 3, number average molecular
30 weight: 5,600, and hydroxyl value: 36) with blocked isocyanate.

The polyester resin to be urethane-modified was produced under the following conditions: 320 parts by mass of isophthalic acid, 200 parts by mass of adipic acid, 60 parts by mass of trimethylolpropane, and 420 parts by mass of cyclohexanedimethanol were charged into a flask equipped with a stirrer, a
35 rectifying column, a water separator, a cooling pipe, and a thermometer, and heated and stirred. The temperature was raised from 160 °C to 230 °C at a

constant rate over 4 hr while distilling off the resulting condensed water. After the temperature reached 230 °C, 20 parts by mass of xylene are gradually added, and the condensation reaction was continued while the temperature was maintained at 230 °C. The reaction was terminated when the acid value reached
5 5 or less. After cooling to 100 °C, 120 parts by mass of SOLVESSO 100 (produced by Exxon Mobil Corporation, trade name, high boiling point aromatic hydrocarbon solvent) and 100 parts by mass of butyl cellosolve were added to obtain a polyester resin solution.

Resin β: urethane-cured polyester resin (EVACLAD 4900 produced by
10 Kansai Paint Co., Ltd.).

(Inorganic compounds)

Vanadium compound: magnesium vanadate.

Phosphate compound: calcium phosphate.

Magnesium oxide compound: magnesium oxide.

15 As the resin used in the top coat painting layer shown in Table 5, the following paints were used.

Resin I: melamine-cured polyester paint (PRECOLOR HD0030HR produced by BASF Japan Ltd.).

20 Resin II: organosol-based baking-type fluororesin-based paint (PRECOLOR No. 8800HR produced by BASF Japan Ltd.) with mass ratio of polyvinylidene fluoride and acrylic resin of 80:20.

[0148] [Table 5]

Painting layer conditions	Chemical conversion layer					Primer painting layer						Top coat painting layer		Remarks
	Resin		Vanadium compound (mass%)	Zirconium compound (mass%)	Fluorine compound (mass%)	Resin		Vanadium compound (mass%)	Phosphate compound (mass%)	Magnesium oxide compound (mass%)	Others (pigment etc.) (mass%)	Resin		
	Type	Content (mass%)				Type	Content (mass%)					Type	Painting layer thickness (μm)	
T1	A	30	6	50	1	α	60	12	12	6	10	I	15	Example
T2	A	30	6	50	1	α	60	12	12	6	10	II	23	Example
T3	B	30	6	50	1	α	60	12	12	6	10	I	15	Comparative Example
T4	A	30	0	50	1	α	60	12	12	6	10	I	15	Comparative Example
T5	A	30	6	0	1	α	60	12	12	6	10	I	15	Comparative Example
T6	A	30	6	50	0	α	60	12	12	6	10	I	15	Comparative Example
T7	A	30	6	50	1	β	60	12	12	6	10	I	15	Comparative Example
T8	A	30	6	50	1	α	60	0	12	6	10	I	15	Comparative Example
T9	A	30	6	50	1	α	60	12	0	6	10	I	15	Comparative Example
T10	A	30	6	50	1	α	60	12	12	0	10	I	15	Comparative Example

Table 5

[0149] (Evaluation)

Each sample of painted steel sheet obtained as described above was evaluated as follows. The evaluation results are shown in Table 6.

[0150] (1) Coating structure (coating weight, composition, Ni-based
5 compound, X-ray diffraction intensity)

Each sample of hot-dip coated steel sheet was subjected to 100 mmφ blanking. After sealing the non-measurement surface with tape, the coating was dissolved and peeled with a liquid mixture of hydrochloric acid and hexamethylenetetramine as described in JIS H 0401: 2013, and the coating
10 weight of the coating was calculated from the difference in the mass of the sample between before and after the peeling. The calculated coating weight of the coating is shown in Table 6.

After this, the peeling liquid was filtered, and the filtrate and the solid content were each analyzed. Specifically, ICP optical emission spectrometry
15 was performed on the filtrate to quantify the components other than insoluble Si.

The solid content was dried and incinerated in a heating furnace at 650 °C, and then melted by adding sodium carbonate and sodium tetraborate. Further, the melt was dissolved with hydrochloric acid, and ICP optical
20 emission spectrometry was performed on the solution to quantify insoluble Si. The Si concentration in the coating was obtained by adding the insoluble Si concentration obtained by solid content analysis to the soluble Si concentration obtained by filtrate analysis. The composition of the coating obtained as a result of the calculation is shown in Table 6.

Moreover, after shearing each sample to a size of 15 mm × 15 mm, it was mechanically polished in a state of being embedded in a conductive resin so that a cross section of the steel sheet could be observed. After this, for randomly selected sections of the coating of 100 μm in width, reflected
25 electron images were taken with an accelerating voltage of 3 kv using a scanning electron microscope (ULTRA55 produced by Carl Zeiss AG). Further, in the same apparatus, elemental mapping analysis (Al, Zn, Si, Mg, Fe, Sr, and Ni) of each section was performed with an accelerating voltage of 3 kv using an energy-dispersive X-ray spectrometer (Ultim Extreme produced by Oxford Instruments). Each part where high Ni intensity was detected in this analysis
30 was subjected to point analysis with an accelerating voltage of 3 kv using the same spectrometer, and the substance was identified from the obtained semi-

quantitative values of the components. The analysis results are shown in Table 6.

In addition, after shearing each sample to a size of 100 mm × 100 mm, the coating on the surface to be evaluated was mechanically scraped off until the base steel sheet appeared, and the obtained powder was mixed well and then 0.3 g was taken out. Using an X-ray diffractometer (SmartLab produced by Rigaku Corporation), qualitative analysis was performed on the powder under the conditions of X-rays used: Cu-K α (wavelength = 1.54178 Å), removal of K β rays: Ni filter, tube voltage: 40 kV, tube current: 30 mA, scanning speed: 4°/min, sampling interval: 0.020°, divergence slit: 2/3°, solar slit: 5°, and detector: high-speed one-dimensional detector (D/teX Ultra). The intensity obtained by subtracting the base intensity from each peak intensity was taken to be diffraction intensity (cps), and the diffraction intensity of (111) plane (interplanar spacing $d = 0.368$ nm) of Mg₂Si, the diffraction intensity of (100) plane (interplanar spacing $d = 0.4510$ nm) of MgZn₂, and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135$ nm) of Si were measured. The measurement results are shown in Table 6.

[0151] (2) Evaluation of corrosion resistance

After shearing each sample of painted steel sheet to a size of 120 mm × 120 mm, the range of 10 mm from each edge of the surface to be evaluated, the end surface of the sample, and the surface not to be evaluated were sealed with tape, and the surface to be evaluated was exposed in a size of 100 mm × 100 mm to obtain an evaluation sample. Three identical evaluation samples were produced.

A corrosion acceleration test was performed on the three evaluation samples produced as described above, with the cycle illustrated in FIG. 1. The corrosion acceleration test was started from wetting. Each sample was taken out every 20 cycles, washed with water, dried, and then visually observed to determine whether red rust occurred on the sheared end surface of one side not tape-sealed.

The number of cycles when red rust was found was evaluated based on the following criteria. The evaluation results are shown in Table 6.

◎: The number of red rust cycles of three samples ≥ 600 cycles.

O: 600 cycles > the number of red rust cycles of three samples ≥ 400 cycles.

X: The number of red rust cycles of at least one sample < 400 cycles.

[0152] (3) Appearance after painting

For each sample of painted steel sheet, the surface was visually observed.

The observation results were evaluated based on the following criteria.

5 The evaluation results are shown in Table 6.

O: No wrinkle-like defects were observed.

X: Wrinkle-like defects were observed in at least one part.

[0153] (4) Workability after painting

10 After shearing each sample of painted steel sheet to a size of 70 mm × 150 mm, 180° bending (8T bending) was performed with eight sheets of the same thickness sandwiched inside. Cellotape was firmly attached to the outer surface of the bent portion after the bending, and then peeled off. The surface state of the painting layer on the outer surface of the bent portion and whether the painting layer adhered to the surface of the tape used (i.e. whether the painting layer peeled off (came off)) were visually observed, and the
15 workability was evaluated based on the following criteria. The evaluation results are shown in Table 6.

O: Neither cracking nor peeling of the painting layer was observed.

Δ : Cracking of the painting layer was observed but no peeling was
20 observed.

X: Both cracking and peeling of the painting layer were observed.

[0154] (5) Bath stability

During hot-dip coating, the state of the bath surface of the molten bath was visually checked, and compared with the bath surface (bath surface without
25 Mg-containing oxides) of a molten bath used when producing hot-dip Al-Zn coated steel sheets. Evaluation was made based on the following criteria. The evaluation results are shown in Table 6.

O: Similar to hot-dip Al-Zn molten bath (55 mass% Al-balance Zn-1.6 mass% bath).

30 Δ : More white oxides were present than in hot-dip Al-Zn molten bath (55 mass% Al-balance Zn-1.6 mass% bath).

X: Formation of black oxides was observed in the molten bath.

[0155] [Table 6]

No.		Coating										Painting layer conditions	Corrosion resistance					Appearance after painting	Workability after painting	Bath stability	Remarks
		Composition (mass%)						Coating weight (g/m ²)	Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (kps)	Ni-based compound										
		Red rust occurrence time (cycle)					Evaluation														
		Al	Si	Mg	Fe	Sr	Ni						N1	N2	N3						
1	55	0.5	4.4	1.01	0.11	0.003	86	0.00	-	-	T1	400	360	340	×	○	×	Comparative Example			
2	55	1.0	4.4	0.65	0.11		83	0.25	-	-	T1	620	640	640	⊙	○	△	Example			
3	55	1.5	0.0	0.49	0.00	0.003	84	No Mg ₂ Si No MgZn ₂	-	-	T1	320	300	320	×	○	○	Comparative Example			
4	55	1.5	0.0	0.48	0.11	0.003	82	No Mg ₂ Si No MgZn ₂	-	-	T1	280	320	320	×	○	○	Comparative Example			
5	55	1.5	1.1	0.55	0.10	0.003	85	0.00	-	-	T1	420	460	460	○	○	△	Example			
6	55	1.6	1.5	0.58	0.10	0.003	86	0.22	-	-	T1	460	480	460	○	○	△	Example			
7	54	1.5	1.9	0.36	0.00	0.003	83	0.36	-	-	T1	540	520	560	○	×	△	Example			
8	55	1.5	2.0	0.41	0.05	0.003	82	0.45	-	-	T1	560	580	580	○	○	△	Example			
9	55	1.5	1.9	0.59	0.11	0.003	83	0.44	0.65	-	T1	620	580	620	○	○	△	○	Example		
										-	T2	580	600	560	○	○	△	○	Example		
										-	T3	420	380	400	×	○	△	○	Comparative Example		
										-	T4	400	400	380	×	○	△	○	Comparative Example		
										-	T5	360	380	420	×	○	△	○	Comparative Example		
										-	T6	320	360	340	×	○	△	○	Comparative Example		
										-	T7	380	320	360	×	○	△	○	Comparative Example		
										-	T8	360	380	360	×	○	△	○	Comparative Example		
										-	T9	340	380	400	×	○	△	○	Comparative Example		
										-	T10	360	380	420	×	○	△	○	Comparative Example		
10	55	1.5	3.4	0.57	0.09	0.003	84	0.62	0.00	-	T1	660	680	680	⊙	○	△	○	Example		
11	32	1.5	4.5	0.55	0.10	0.001	86	0.38	0.00	-	T1	380	400	380	×	○	△	○	Comparative Example		
12	48	1.5	4.5	0.58	0.10	0.002	85	0.35	0.00	-	T1	720	680	680	⊙	○	△	○	Example		
13	50	1.5	4.5	0.56	0.01	0.003	87	0.33	0.00	-	T1	700	680	680	⊙	○	△	○	Example		
										-	T2	680	660	680	⊙	○	△	○	Example		
14	55	1.5	4.4	0.54	0.10	0.001	86	0.30	0.00	-	T1	720	640	660	⊙	○	△	○	Example		
15	55	1.5	4.4	0.52	0.10	0.003	84	0.31	0.00	-	T1	640	700	660	⊙	○	△	○	Example		
16	55	1.5	4.4	0.56	0.10	0.005	84	0.28	0.00	-	T1	660	660	680	⊙	○	△	○	Example		
17	55	1.5	4.4	0.55	0.10	0.010	85	0.27	0.00	-	T1	520	480	480	○	○	△	○	Example		
18	55	1.5	4.4	0.56	0.10	0.015	84	0.32	0.00	NiAl ₃	T1	400	360	340	×	○	△	○	Comparative Example		
19	55	1.5	4.4	0.55	0.10	0.025	84	0.32	0.00	NiAl ₃	T1	320	300	280	×	○	△	○	Comparative Example		
20	60	1.5	4.5	0.59	0.10	0.003	83	0.32	0.00	-	T1	680	660	680	⊙	○	△	○	Example		
21	64	1.6	4.3	0.58	0.02	0.004	86	0.35	0.00	-	T1	660	700	660	⊙	○	△	○	Example		

Table 6(cont'd)

No.	Coating										Painting layer conditions	Corrosion resistance			Appearance after painting	Workability after painting	Bath stability	Remarks	
	Composition (mass%)						Coating weight (g/m ²)	Mg ₂ Si(111)/MgZn ₂ (100)	Si(111) (kps)	Ni-based compound		Red rust occurrence time (cycle)							Evaluation
Al	Si	Mg	Fe	Sr	Ni	420	380	400	×	○	△	○	Comparative Example						
22	73	1.6	4.5	0.55	0.10	0.004	88	0.33	0.00	-	T1	680	680	700	⊙	○	Example		
23	55	1.5	5.9	0.61	0.09	0.003	84	0.29	0.00	-	T1	300	280	340	×	○	Comparative Example		
24	55	2.3	0.0	0.54	0.00	0.003	83	No Mg ₂ Si No MgZn ₂	4.36	-	T1	340	360	300	×	○	Comparative Example		
25	55	2.3	0.0	0.56	0.09	0.003	86	No Mg ₂ Si No MgZn ₂	4.22	-	T1	420	380	400	×	○	Comparative Example		
26	55	2.3	0.9	0.52	0.11	0.003	85	0.00	3.46	-	T1	460	500	480	○	○	Comparative Example		
27	55	2.2	2.0	0.52	0.10	0.003	84	0.26	2.28	-	T1	520	560	500	○	○	Example		
28	55	2.2	3.4	0.58	0.10	0.003	87	1.45	0.35	-	T1	520	540	580	○	○	Example		
29	55	2.2	4.3	0.52	0.00	0.003	86	1.23	0.20	-	T1	560	600	560	○	○	Example		
30	55	2.3	4.4	0.59	0.03	0.003	84	1.68	0.18	-	T1	540	560	580	○	○	Example		
											T2	620	560	600	○		Example		
31	55	2.3	4.3	0.56	0.09	0.003	85	1.69	0.21	-	T1	580	580	600	○	○	Example		
32	55	2.2	4.3	0.57	0.11	0.003	87	1.66	0.15	-	T1	580	560	580	○	○	Example		
33	55	2.2	5.9	0.55	0.10	0.003	84	1.58	0.12	-	T1	560	540	580	○	△	Example		
34	55	2.2	6.4	0.53	0.00	0.003	83	1.34	1.05	-	T1	600	580	600	○	△	Example		
35	55	3.1	4.5	0.54	0.10	0.003	85	1.81	0.98	-	T1	520	560	540	○	○	Example		
36	55	3.6	4.4	0.57	0.09	0.003	87	1.70	1.24	-	T1	420	400	440	○	○	Example		
37	55	4.1	4.4	0.58	0.09	0.003	82	2.02	1.49	-	T1	500	560	520	○	×	Example		
38	55	2.9	9.7	0.57	0.09	0.003	88	0.55	0.00	-	T1	640	620	600	○	△	Example		
39	55	1.5	4.4	0.50	0.10	0.003	52	0.38	0.00	-	T1	660	660	640	⊙	○	Example		
40	55	1.5	4.4	0.52	0.10	0.003	98	0.35	0.00	-	T1	720	720	700	⊙	○	Example		
41	55	1.5	4.4	0.54	0.10	0.003	128	0.32	0.00	-	T1				⊙	×	Example		

[0156] As can be understood from the results in Table 6, the sample of each Example was superior to the sample of each Comparative Example in all of corrosion resistance, appearance after painting, workability after painting, and bath stability in a well-balanced manner.

5

INDUSTRIAL APPLICABILITY

[0157] It is thus possible to provide a hot-dip Al-Zn-Si-Mg coated steel sheet stably having excellent corrosion resistance and a production method therefor.

CLAIMS

[Claim 1] A hot-dip Al-Zn-Si-Mg coated steel sheet comprising
a coating having a composition containing Al: 45 mass% to 65 mass%,
5 Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass% with a balance
consisting of Zn and inevitable impurities,
wherein Ni content in the inevitable impurities is 0.010 mass% or less
with respect to a total mass of the coating.

10 [Claim 2] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
1, wherein a Ni-based compound is contained in the coating, and a major axis
length of the Ni-based compound is 4.0 μm or less.

[Claim 3] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
15 1 or 2, wherein a Ni-based compound is contained in the coating, and the
number of the Ni-based compound present in a direction parallel to a surface
of a base steel sheet is 5 per mm or less.

[Claim 4] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
20 1, wherein a Ni-based compound is not contained in the coating.

[Claim 5] The hot-dip Al-Zn-Si-Mg coated steel sheet according to any
one of claims 1 to 4, wherein respective diffraction intensities of Mg_2Si and
 MgZn_2 in the coating by an X-ray diffraction method satisfy the following
25 relationship (1):

$$\text{Mg}_2\text{Si} (111)/\text{MgZn}_2 (100) \leq 2.0 \quad \dots (1)$$

where $\text{Mg}_2\text{Si} (111)$ is a diffraction intensity of (111) plane of Mg_2Si
with interplanar spacing $d = 0.3668 \text{ nm}$, and $\text{MgZn}_2 (100)$ is a diffraction
intensity of (100) plane of MgZn_2 with interplanar spacing $d = 0.4510 \text{ nm}$.

30

[Claim 6] The hot-dip Al-Zn-Si-Mg coated steel sheet according to any
one of claims 1 to 5, wherein a diffraction intensity of Si in the coating by an
X-ray diffraction method satisfies the following relationship (2):

$$\text{Si} (111) = 0 \quad \dots (2)$$

35 where Si (111) is a diffraction intensity of (111) plane of Si with
interplanar spacing $d = 0.3135 \text{ nm}$.

[Claim 7] The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of claims 1 to 6, wherein the coating further contains Sr: 0.01 mass% to 1.0 mass%.

5

[Claim 8] The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of claims 1 to 7, wherein Al content in the coating is 50 mass% to 60 mass%.

10 [Claim 9] The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of claims 1 to 8, wherein Si content in the coating is 1.0 mass% to 3.0 mass%.

[Claim 10] The hot-dip Al-Zn-Si-Mg coated steel sheet according to any
15 one of claims 1 to 9, wherein Mg content in the coating is 1.0 mass% to 5.0 mass%.

[Claim 11] A production method for a hot-dip Al-Zn-Si-Mg coated steel sheet that includes a coating, the production method comprising
20 a hot-dip coating treatment process of immersing a base steel sheet in a molten bath having a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, and Mg: 1.0 mass% to 10.0 mass% with a balance consisting of Zn and inevitable impurities, to form the coating,
wherein Ni content in the inevitable impurities in the molten bath is
25 controlled to be 0.010 mass% or less with respect to a total mass of the molten bath.

[Claim 12] The production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to claim 11, wherein the molten bath further contains Sr: 0.01
30 mass% to 1.0 mass%.

[Claim 13] A surface-treated steel sheet comprising:
the coating according to any one of claims 1 to 10; and
a chemical conversion layer formed on the coating,
35 wherein the chemical conversion layer contains: at least one resin selected from the group consisting of an epoxy resin, a urethane resin, an

acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin, an amino resin, and a fluororesin; and at least one metallic compound selected from the group consisting of a P compound, a Si compound, a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

[Claim 14] A production method for a surface-treated steel sheet that includes: a coating formed by the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to claim 11 or 12; and a chemical conversion layer formed on the coating,

wherein the chemical conversion layer contains: at least one resin selected from the group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin, an amino resin, and a fluororesin; and at least one metallic compound selected from the group consisting of a P compound, a Si compound, a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

20

[Claim 15] A painted steel sheet comprising:

the coating according to any one of claims 1 to 10; and

a painting layer formed on the coating directly or with a chemical conversion layer therebetween,

wherein the chemical conversion layer contains: a resin component that contains (a): an anionic polyurethane resin having an ester bond and (b): an epoxy resin having a bisphenol skeleton in a total amount of 30 mass% to 50 mass% and in which a content ratio (a):(b) between (a) and (b) is in a range of 3:97 to 60:40 in mass ratio; and an inorganic compound that contains 2 mass% to 10 mass% of a vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound, and

the painting layer includes at least a primer painting layer that contains: a polyester resin having a urethane bond; and an inorganic compound including a vanadium compound, a phosphate compound, and magnesium oxide.

35

[Claim 16] A production method for a painted steel sheet that includes: a

coating formed by the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to claim 11 or 12; and a painting layer formed on the coating directly or with a chemical conversion layer therebetween,

wherein the chemical conversion layer contains: a resin component that
5 contains (a): an anionic polyurethane resin having an ester bond and (b): an epoxy resin having a bisphenol skeleton in a total amount of 30 mass% to 50 mass% and in which a content ratio (a):(b) between (a) and (b) is in a range of 3:97 to 60:40 in mass ratio; and an inorganic compound that contains 2 mass%
10 to 10 mass% of a vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound, and

the painting layer includes at least a primer painting layer that contains: a polyester resin having a urethane bond; and an inorganic compound including a vanadium compound, a phosphate compound, and magnesium oxide.