

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 PREPAINTED 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 having consistently excellent corrosion resistance and a production
method therefor, a surface-treated steel sheet and a production method therefor,
and a prepainted 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 have high corrosion resistance among hot-dip galvanized
steel sheets because they have both sacrificial protection performance of Zn
and high corrosion resistance of Al. For their excellent corrosion resistance,
20 hot-dip Al-Zn coated steel sheets are used mainly in the field of building
materials such as roofs and walls exposed outdoors for long periods of time
and in the field of civil engineering and construction such as guardrails, wiring
and piping, and soundproof walls. In particular, due to the growing need for
high corrosion resistant materials and maintenance-free materials in severer
25 operating environments such as acid rain caused by air pollution, spraying of
snow-melting agents for road deicing in snow-covered regions, and coastal area
development, the demand for hot-dip Al-Zn coated steel sheets has increased
in recent years.

[0003] A coating of a hot-dip Al-Zn coated steel sheet is composed of a part
30 (α -Al phase) in which Zn is supersaturatedly contained and Al solidifies as
dendrites and a Zn-Al eutectic structure existing in the dendrite interstices
(interdendrites), and has a structure in which a plurality of layers of 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
35 preventing corrosion 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 further extend the life of such hot-dip Al-Zn coated steel sheets, and hot-dip Al-Zn-Si-Mg coated steel sheets containing Mg have been put to practical use.

5 As such hot-dip Al-Zn-Si-Mg coated steel sheets, for example, JP 5020228 B2 (PTL 1) discloses a hot-dip Al-Zn-Si-Mg coated steel sheet wherein a 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 concentration of
10 Mg is 1 wt% to 5 wt%.

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

15 JP 2002-12959 A (PTL 3) discloses a hot-dip Al-Zn-Si-Mg coated steel sheet comprising 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, wherein intermetallic compounds such as Mg₂Si phase and MgZn₂ phase existing in the coating are 10 μm or less in size in order to
20 improve the corrosion resistance of flat surfaces 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 worked parts.

JP 2019-155872 A (PTL 7) discloses a technique of improving
5 blackening resistance and 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] Prepainted 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
10 layer, a top coat painting layer, and the like are subjected to various works such as 90-degree bending and 180-degree bending by press forming, roll forming, or embossing. Such prepainted steel sheets are required to have long-term painting layer durability. To meet the requirement, prepainted steel sheets are known that are each obtained by forming, on a hot-dip Al-Zn coated steel sheet,
15 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 fluorine-based resin painting layer.

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

As a technique to meet this need, for example, JP 2005-169765 A (PTL
25 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 titanium compounds and
30 zirconium compounds 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

35 Patent Literature

[0008] PTL 1: JP 5020228 B2

PTL 2: JP 5000039 B2

PTL 3: JP 2002-12959 A

PTL 4: JP 3983932 B2

PTL 5: JP 2011-514934 A

5 PTL 6: JP 5751093 B2

PTL 7: JP 2019-155872 A

PTL 8: JP 2005-169765 A

SUMMARY

10 (Technical Problem)

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

With the hot-dip Al-Zn-Si-Mg coated steel sheets disclosed in PTL 1 to PTL 3, improvement in corrosion resistance is sought merely by including Mg
15 in the coating components. Meanwhile, the influence of components other than the four elements (Al, Zn, Si, and Mg) and the characteristics of metallic phase and intermetallic compound phase constituting the coating are not taken into consideration, and the level of corrosion resistance (i.e. whether the corrosion resistance is better) cannot be evaluated in a single uniform way. Hence, even
20 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, the corrosion resistance varies in a corrosion acceleration test, and is not necessarily better than that of an Al-Zn coated steel sheet not containing Mg.

Regarding improvement in coating appearance, too, simply adding Sr
25 to the coating does not necessarily eliminate wrinkle-like irregularity defects. Thus, with 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 form oxides as called “top dross” near
30 the bath surface. Moreover, in the case of hot-dip coating, Fe-Al-based compounds as called “bottom dross” containing iron and 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.

35 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, MgZn₂ phase, and Si phase precipitate in the coating. However, how the precipitation amount and abundance ratio of each phase influence corrosion resistance has not been clarified.

5 [0010] Moreover, 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 worked parts and heated flat parts is mentioned, but white rust resistance in unheated flat parts is not taken into consideration, and achieving stable white rust resistance is still an issue. With the hot-dip Al-Zn-Si-Mg coated steel sheet in PTL 7, too, consistently excellent
10 corrosion resistance and white rust resistance cannot necessarily be achieved, and further improvement is desired.

[0011] Prepainted steel sheets are required to have long-term painting layer durability in a state of being subjected to various works such as 90-degree bending and 180-degree bending by press forming, roll forming, embossing,
15 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 a prepainted steel sheet is influenced by the corrosion resistance of the coated steel sheet as its base. Regarding the surface appearance, given that the height difference of the irregularities of wrinkle-
20 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 prepainted 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. Thus, in order to obtain a
25 prepainted steel sheet excellent in corrosion resistance and surface appearance, it is important to improve the corrosion resistance and surface appearance of the coated steel sheet as its base.

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

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

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

(Solution to Problem)

[0013] Upon careful examination, we noted 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 appropriately controlling the content of Co among such elements is effective in suppressing degradation in corrosion resistance.

We also found out that Mg_2Si phase and Si phase formed in the coating of the hot-dip Al-Zn-Si-Mg coated steel sheet increase or decrease in their precipitation amounts and their abundance ratio varies 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-Zn-Si-Mg coated steel sheet varies depending on the abundance ratio of these phases and, particularly in the case where Si phase is less than Mg_2Si phase, the corrosion resistance is improved stably. For these Mg_2Si 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 a secondary electron image or reflected electron image of the coating from its surface or cross section 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 abundance ratio of Mg_2Si and Si phase which influences macroscopic information such as corrosion resistance and appearance.

[0014] We then conducted further examination, and, focusing on the X-ray diffraction method, discovered that the use of the intensity ratio of specific diffraction peaks of Mg_2Si phase and Si phase makes it possible to quantitatively specify the abundance ratio of the phases. We also discovered that, as a result of Mg_2Si phase and Si phase in the coating satisfying a specific abundance ratio, consistently excellent corrosion resistance can be achieved.

We further discovered that, by controlling the Co content and the abundance ratio of Mg_2Si phase and Si phase in the coating as mentioned above and also controlling the Sr concentration in the molten bath, it is possible to obtain a coated steel sheet excellent in surface appearance while reliably suppressing wrinkle-like irregularity defects.

[0015] We also studied the chemical conversion layer formed on the coating, and discovered that, by forming the chemical conversion layer of at least one

specific resin and at least one specific metallic compound, the compatibility of the chemical conversion layer with the coating, the rust prevention effect, etc. can be enhanced to thus stably improve 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 specific resins and specific inorganic compounds and also forming the primer painting layer of a specific polyester resin and inorganic compounds, 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.

[0016] 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 Co content in the inevitable impurities is 0.080 mass% or less with respect to a total mass of the coating, and respective diffraction intensities of Si and Mg₂Si in the coating by an X-ray diffraction method satisfy the following relationship (1):

$$\text{Si (111)}/\text{Mg}_2\text{Si (111)} \leq 0.8 \quad \dots (1)$$

where Si (111) is a diffraction intensity of (111) plane of Si with interplanar spacing $d = 0.3135 \text{ nm}$, and Mg₂Si (111) is a diffraction intensity of (111) plane of Mg₂Si with interplanar spacing $d = 0.3668 \text{ nm}$.

[0017] 2. The hot-dip Al-Zn-Si-Mg coated steel sheet according to 1., wherein a diffraction intensity of Si in the coating by the X-ray diffraction method satisfies the following relationship (2):

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

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

[0018] 3. The hot-dip Al-Zn-Si-Mg coated steel sheet according to 1. or 2., wherein the coating further contains Sr: 0.01 mass% to 1.0 mass%.

[0019] 4. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 3., wherein Al content in the coating is 50 mass% to 60 mass%.

[0020] 5. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 4., wherein Si content in the coating is 1.0 mass% to 3.0 mass%.

[0021] 6. The hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 5., wherein Mg content in the coating is 1.0 mass% to 5.0 mass%.

[0022] 7. 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 Co content in the inevitable impurities in the molten bath is controlled to be 0.080 mass% or less with respect to a total mass of the molten bath.

[0023] 8. The production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to 7., wherein the molten bath further contains Sr: 0.01 mass% to 1.0 mass%.

[0024] 9. A surface-treated steel sheet comprising: the coating of the hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 6.; 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.

[0025] 10. 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 7. or 8.; 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.

[0026] 11. A prepainted steel sheet comprising: the coating of the hot-dip Al-Zn-Si-Mg coated steel sheet according to any one of 1. to 6.; and a painting layer formed on the coating directly or with a chemical conversion layer therebetween, wherein the chemical conversion layer contains: resin

components that include (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 inorganic compounds that include
5 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 inorganic compounds including a vanadium compound, a phosphate compound, and magnesium oxide.

10 **[0027]** 12. A production method for a prepainted steel sheet that includes: a coating formed by the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to 7. or 8.; and a painting layer formed on the coating directly or with a chemical conversion layer therebetween, wherein the chemical conversion layer contains: resin components that include (a) an
15 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 inorganic compounds that include 2 mass% to 10 mass% of a vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and
20 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 inorganic compounds including a vanadium compound, a phosphate compound, and magnesium oxide.

(Advantageous Effect)

25 **[0028]** It is thus possible to provide a hot-dip Al-Zn-Si-Mg coated steel sheet having consistently excellent corrosion resistance.

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

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

BRIEF DESCRIPTION OF THE DRAWINGS

35 **[0029]** 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

[0030] (Hot-dip Al-Zn-Si-Mg coated steel sheet)

5 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.

10 **[0031]** 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 microstructure of α -Al phase can
15 be obtained. As a result of the dendritic solidification microstructure 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
20 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 microstructure changes to a microstructure 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
25 degrades. The Al content in the coating therefore needs to be 65 mass% or less, and is preferably 60 mass% or less.

[0032] 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
30 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
35 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 mass% or less. The Si content in the coating is preferably 3.0 mass% 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 Mg content, too, the Si content is preferably 1.0 mass% to 3.0 mass%.

10 **[0033]** The Mg content in the coating is 1.0 mass% to 10.0 mass%. 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 solid solution in $\alpha\text{-Al}$ phase which is a main phase rather than for the formation of the intermetallic compounds (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 $\alpha\text{-Al}$ phase. The Mg content is therefore 10.0 mass% 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%. The Mg content is more preferably 3.0 mass% to 5.0 mass%, in terms of both satisfying the relational formula (1) and suppressing dross.

30 **[0034]** The coating contains Zn and inevitable impurities. The inevitable impurities include 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, Cu, Co,

and W. These components are inevitably contained in the coating as a result of elution from the base steel sheet, stainless-steel in-bath equipment, or a W-C-based or Co-Cr-W-based thermal sprayed coating formed on 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 that has been used in the production of coated steel sheets to which these components are intentionally added.

[0035] In the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the Co content in the inevitable impurities is 0.080 mass% or less with respect to the total mass of the coating. Co 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 and further reducing the content of Co as an inevitable impurity in the coating, degradation in corrosion resistance can be suppressed. From the same viewpoint, the Co content in the inevitable impurities is preferably 0.020 mass% or less, more preferably 0.001 mass% or less, and most preferably 0 mass% with respect to the total mass of the coating.

[0036] Co contained in the coating exists mainly as a solid solution element in α -Al. In the case where the concentration of Co exceeds the solubility limit, a Fe-Co-Al compound or a Fe-Co-Al-Si compound may precipitate in the alloy layer formed at the interface between the steel substrate and the coating.

Although the mechanism whereby the corrosion resistance degrades due to the presence of Co as an impurity is uncertain, mechanisms that are presumed include: a mechanism in which the corrosion rate increases as a result of a decrease in the barrier property of α -Al phase in which Co is dissolved; and a mechanism in which the corrosion rate increases as a result of Co-containing compounds functioning as a cathode in a corrosion environment and forming a local battery with surrounding solidification microstructure.

[0037] 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.

[0038] In the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the respective diffraction intensities of Si and Mg_2Si in the coating by the X-ray diffraction method need to satisfy the following relationship (1):

$$\text{Si (111)}/\text{Mg}_2\text{Si (111)} \leq 0.8 \quad \dots (1)$$

where Si (111) is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135 \text{ nm}$) of Si, and $\text{Mg}_2\text{Si (111)}$ is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668 \text{ nm}$) of Mg_2Si .

5 **[0039]** It is important to, in the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, control the abundance ratio of Mg_2Si phase and Si phase formed in the coating as a result of inclusion of Mg and Si to a specific ratio, as mentioned above. The influence of such a factor on the corrosion resistance is largely unknown and is currently under investigation,
10 but the following mechanism is presumed.

[0040] 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 $\alpha\text{-Al}$ 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
15 products formed are difficult to decompose, and consequently the protective effect of the coating increases. Since the protective effect of the coating is improved more reliably when Si in the coating exists not as Si phase but as Mg_2Si phase, lowering the abundance ratio of Si phase to Mg_2Si phase is effective.

20 **[0041]** The abundance ratio of Si and Mg_2Si in the coating needs to satisfy the relationship (1): $\text{Si (111)}/\text{Mg}_2\text{Si (111)} \leq 0.8$, in terms of the diffraction peak intensities obtained by the X-ray diffraction method. If the abundance ratio of Si and Mg_2Si in the coating does not satisfy the relationship (1), that is, $\text{Si (111)}/\text{Mg}_2\text{Si (111)} > 0.8$, more Si phase exists in the coating, so that the
25 foregoing Mg-rich environment cannot be created in the vicinity of the corrosion products. This hinders the improvement of the protective effect of the coating. From the same viewpoint, the abundance ratio of Si to Mg_2Si ($\text{Si (111)}/\text{Mg}_2\text{Si (111)}$) is preferably 0.5 or less, more preferably 0.3 or less, and particularly preferably 0.2 or less.

30 **[0042]** In the relationship (1), Si (111) is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135 \text{ nm}$) of Si, and $\text{Mg}_2\text{Si (111)}$ is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668 \text{ nm}$) of Mg_2Si .

For example, the measurement of Si (111) and $\text{Mg}_2\text{Si (111)}$ by X-ray
35 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 Si corresponding to interplanar spacing $d = 0.3135$ nm and the diffraction peak intensity of Mg_2Si corresponding to interplanar spacing $d = 0.3668$ nm are measured. Calculating the ratio between these diffraction peak intensities can yield Si (111)/ Mg_2Si (111).

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 Si (111) and Mg_2Si (111). 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, thus 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 microstructure.

[0043] In the hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, in addition to the foregoing control of the concentrations of Al, Zn, Si, and Mg, and Co as an inevitable impurity, it is preferable that 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:

$$Si(111) = 0 \quad \dots (2)$$

where Si (111) is the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135$ 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 is as described above.

[0044] The method of satisfying the relationship (1) or the relationship (2) is not limited. For example, to satisfy the relationship (1) or 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 abundance ratio of Si and Mg₂Si (the diffraction intensities of Si (111) and Mg₂Si (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) or the relationship (2), and, for example, the content ratios of Mg and Al need to be changed depending on the Si content (mass%).

Apart from 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 diffraction intensities of Si (111) and Mg₂Si (111) so as to satisfy the relationship (1) or the relationship (2).

[0045] 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 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 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.

[0046] The coating preferably further contains one or more selected from the group consisting of Cr, Mn, V, Mo, Ti, Ca, Sb, and B in a total amount of 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.

[0047] 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 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

weight of the coating is more preferably 45 g/m² to 100 g/m².

[0048] 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 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.

[0049] The chemical composition of the coating can be determined by 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 Co 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.

[0050] The coating of the hot-dip Al-Zn-Si-Mg coated steel sheet obtained 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.

[0051] The base steel sheet of the hot-dip Al-Zn-Si-Mg coated steel sheet 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.

[0052] 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 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.

[0053] (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 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

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 recrystallization annealing and the like for controlling the microstructure 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.

5
10 **[0054]** The molten bath that can be used in the hot-dip coating treatment 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.

15 **[0055]** In the production method for a hot-dip Al-Zn-Si-Mg coated steel sheet according to the present disclosure, the Co content in the inevitable impurities in the molten bath is controlled to 0.080 mass% or less with respect to the total mass of the molten bath. Co 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 and further reducing the content of Co as an inevitable impurity in the molten bath, degradation in corrosion resistance can be suppressed.

20 The content of Co as an inevitable impurity in the molten bath needs to be 0.080 mass% or less and is more preferably 0.020 mass% or less and further preferably 0.001 mass% or less, with respect to the total mass of the molten bath. If the Co content in the molten bath is 0.080 mass% or less, the hot-dip Al-Zn-Si-Mg coated steel sheet produced has sufficiently excellent corrosion resistance. If the Co content in the molten bath is 0.020 mass% or less, the hot-dip Al-Zn-Si-Mg coated steel sheet has better corrosion resistance. If the Co content in the molten bath is 0.001 mass% or less, the hot-dip Al-Zn-Si-Mg coated steel sheet has particularly excellent corrosion resistance.

25 Thus, the corrosion resistance of the hot-dip Al-Zn-Si-Mg coated steel sheet is better when the Co content in the molten bath is lower. Accordingly, no lower limit is placed on the Co content in the molten bath, and the Co content in the molten bath is most preferably 0 %.

[0056] The means of reducing the Co content in the molten bath is not limited.

For example, given that suppressing elution of a Co-Cr-W thermal sprayed coating formed on in-bath equipment into the molten bath is effective, it is preferable to use a thermal sprayed coating not containing Co.

5 **[0057]** As another means of reducing the Co content in the molten bath, it is preferable to use, as the material of the molten bath, metal lumps having low Co 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 that has been used in the
10 production of coated steel sheets to which Co is intentionally added. A situation in which metal lumps containing Co adhering to such pot or in-bath equipment dissolve and mix into the molten bath can thus be suppressed.

[0058] 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.

15 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
20 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.

[0059] The temperature of the base steel sheet entering the molten bath
25 (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.

[0060] The immersion time of the base steel sheet in the molten bath is
30 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
35 and the steel sheet.

[0061] 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.

[0062] The method of forming the painting layer is not limited, and may be selected as appropriate depending on the required performance. Examples
5 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.

[0063] The intermediate layer is not limited, and may be any layer that is
10 formed between the coating of the hot-dip coated steel sheet and the painting layer.

[0064] (Surface-treated steel sheet)

A surface-treated steel sheet according to the present disclosure comprises a coating on a surface of a steel sheet, and a chemical conversion
15 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.

[0065] In the surface-treated steel sheet according to the present disclosure,
20 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.

[0066] In the surface-treated steel sheet according to the present disclosure,
25 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,
30 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 compatibility with the coating can be enhanced and the chemical conversion layer can be uniformly formed on the coating, and also the rust prevention
35 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.

[0067] 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
5 resin, and fluoro-resin 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.

10 **[0068]** 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.

15 **[0069]** 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.

[0070] Examples of the acrylic resin include polyacrylic acid and its copolymer, polyacrylic acid ester and its copolymer, polymethacrylic acid and
20 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.

[0071] Examples of the acrylic silicon resin include resin that has a
25 hydrolyzable alkoxy-silyl 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.

[0072] Examples of the alkyd resin include oil-modified alkyd resin, rosin-
30 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.

[0073] The polyester resin is a polycondensate synthesized by dehydration
condensation of polycarboxylic acid and polyalcohol to form an ester bond.
35 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 naphthalate, and acrylic modification products of these polyester resins.

5 **[0074]** 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.

10 **[0075]** 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
15 melamine resin, methylated melamine resin, and aqueous melamine resin.

[0076] Examples of the fluororesin include fluoroolefin-based polymers and copolymers of fluoroolefin with alkyl vinyl ether, cycloalkyl vinyl ether, carboxylic acid-modified vinyl ester, hydroxyalkyl allyl ether, tetrafluoropropyl vinyl ether, etc. In the case where these fluororesins are used,
20 excellent atmospheric corrosion resistance and excellent hydrophobicity can be expected in addition to corrosion resistance.

[0077] 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
25 (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.

[0078] As the metallic compound contained in the chemical conversion layer,
30 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
35 compound.

[0079] 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 phosphoric acid, and their salts.

5 **[0080]** 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 acid, tripolyphosphate, phosphorus acid, phosphite, hypophosphorus acid, and
10 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,
15 methylenephosphonic acid, and ethylenediphosphonic acid.

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 of alkali metal salts and alkaline earth metal salts.

20 **[0081]** When a chemical conversion treatment liquid containing the P compound is applied to the 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 formed on the coating side of the chemical conversion layer. As a result of the formation of
25 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
30 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 and perspiration resistance of defective parts, cut end surface parts, and damaged parts of the coating or layer caused by working
35 or the like decrease. 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 amount of P eluted from the chemical conversion layer increases, which may
5 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 conversion treatment liquid in which the concentration of the P compound is
10 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.

[0082] The Si compound is a component that serves as a skeleton for forming the chemical conversion layer together with the resin, and enhances the compatibility with the coating and enables uniform formation of the chemical
15 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.

[0083] Any silica may be used without limitation. As the silica, for example, at least one of wet silica and dry silica may be used. As colloidal silica which
20 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.

[0084] Any trialkoxysilane may be used without limitation. For example,
25 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.

[0085] Any tetraalkoxysilane may be used without limitation. For example,
30 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.

[0086] Any silane coupling agent may be used without limitation. Examples
35 include γ -glycidoxypopyltrimethoxysilane, γ -

glycidoxypropylmethyldiethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropylmethyldiethoxysilane, γ -aminopropyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropyltrimethoxysilane, vinyltriethoxysilane, and γ -isocyanatepropyltriethoxysilane.

[0087] 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.

[0088] 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 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.

[0089] 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, 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.

[0090] With use of a chemical conversion treatment liquid containing the Co 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.

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 chloride.

[0091] 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, 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 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 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.

[0092] The Al compound, the Zn compound, and the Mg compound, when contained in the chemical conversion treatment liquid, can form an enriched 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, but are preferably inorganic compounds, and preferably salts, chlorides, oxides, or hydroxides.

[0093] 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.

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, magnesium oxide, and magnesium hydroxide.

[0094] 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 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.

[0095] When the V compound is contained in the chemical conversion layer, V is eluted moderately in a corrosion environment and bonds with, for example, zinc ions of 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 cut end surfaces to flat parts.

[0096] 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.

[0097] 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.

[0098] 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.

[0099] 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.

[0100] 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.

[0101] 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.

[0102] 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.

[0103] 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.

10 **[0104]** The Ca compound, when contained in the chemical conversion layer, has the effect of lowering the corrosion rate.

[0105] 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,
15 Ca(NO₃)₂·4H₂O, and CaSO₄·2H₂O. The content of the Ca compound in the chemical conversion layer is not limited.

[0106] 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
20 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.

[0107] 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.

30 **[0108]** 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
35 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
5 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.

[0109] The method of forming the chemical conversion layer is not limited, and may be selected as appropriate depending on the required performance, the
10 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 sheet 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
15 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 at least one of the foregoing resins and at least one of the foregoing metallic compounds, and is not limited.

[0110] The surface-treated steel sheet according to the present disclosure may optionally comprise a painting layer on the chemical conversion layer.

[0111] (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
25 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
30 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. The production method comprises a hot-dip coating treatment process of immersing a base steel sheet
35 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 and inevitable impurities, to form the coating, wherein the Co content in the inevitable impurities in the molten bath is controlled to be 0.080 mass% or less.

5 **[0112]** Co contained in the coating may degrade the corrosion resistance of the surface-treated steel sheet, as mentioned above. By appropriately controlling the contents of Al, Zn, Si, and Mg and further reducing the content of Co as an inevitable impurity in the molten bath, degradation in corrosion resistance can be suppressed.

10 **[0113]** The conditions of the hot-dip coating treatment process are the same as those described with regard to the coating of the surface-treated 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.

15 **[0114]** (Prepainted steel sheet)

A prepainted steel sheet according to the present disclosure is a prepainted steel sheet that comprises: a coating; and a painting layer formed on the coating directly or with a chemical conversion layer therebetween.

20 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.

[0115] In the prepainted steel sheet according to the present disclosure, a chemical conversion layer may be formed on the coating.

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

[0116] - Chemical conversion layer

30 In the prepainted steel sheet according to the present disclosure, the chemical conversion layer contains: resin components that include (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 inorganic compounds that include 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.

35 Such a chemical conversion layer formed on the coating has enhanced strength and adhesion and also contributes to improved corrosion resistance.

[0117] The resin components contained in the chemical conversion layer include (a) an anionic polyurethane resin having an ester bond and (b) an epoxy resin having a bisphenol skeleton.

5 **[0118]** An example of (a) the anionic polyurethane resin having an ester bond is a resin obtained by copolymerizing dimethylol alkyl acid with a reaction product of a polyester polyol and a diisocyanate or polyisocyanate having two or more isocyanate groups. (a) The anionic polyurethane resin having an ester bond can be dispersed in a liquid such as water by a known method to obtain a chemical conversion treatment liquid.

10 **[0119]** Examples of the polyester polyol include polyesters obtained by a dehydration condensation reaction of glycol components and acid components such as ester-forming derivatives of hydroxyl carboxylic acid, polyesters obtained by a ring-opening polymerization reaction of cyclic ester compounds such as ϵ -caprolactone, and their copolyesters.

15 Examples of the polyisocyanate include aromatic polyisocyanates, aliphatic polyisocyanates, and alicyclic polyisocyanates. Examples of the aromatic polyisocyanates include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, m-xylene diisocyanate, diphenylmethane diisocyanate, 2,4-diphenylmethane diisocyanate, 2,2-diphenylmethane diisocyanate, 20 triphenylmethane triisocyanate, polymethylene polyphenyl polyisocyanate, naphthalene diisocyanate, and their derivatives (for example, prepolymers obtained through reaction with polyols, modified polyisocyanates such as carbodiimide compounds of diphenylmethane diisocyanate, etc.).

[0120] When the polyester polyol is reacted with the diisocyanate or 25 polyisocyanate to synthesize urethane, for example, (a) the anionic polyurethane resin having an ester bond can be obtained by copolymerizing dimethylol alkyl acid and self-emulsifying it to make it water-soluble (water-dispersed). In this case, the dimethylol alkyl acid is, for example, dimethylol alkyl acid having 2 to 6 carbon atoms. More specific examples include 30 dimethylol ethanoic acid, dimethylol propanoic acid, dimethylol butanoic acid, dimethylol heptanoic acid, and dimethylol hexanoic acid.

[0121] As (b) the epoxy resin having a bisphenol skeleton, a known epoxy resin may be used. Examples include bisphenol A type epoxy resin, bisphenol F type epoxy resin, bisphenol AD type epoxy resin, and bisphenol S type epoxy 35 resin. These epoxy resins can be obtained by reacting bisphenol compounds such as bisphenol A, bisphenol F, bisphenol AD, and bisphenol S with

epichlorohydrin in the presence of an alkali catalyst. Among these, component [A] preferably contains bisphenol A type epoxy resin or bisphenol F type epoxy resin, and more preferably contains bisphenol A type epoxy resin. (b) The epoxy resin having a bisphenol skeleton can be dispersed in a liquid such as water by a known method to obtain a chemical conversion treatment liquid.

[0122] The resin components act as a binder of the chemical conversion layer.

(a) The anionic polyurethane resin having an ester bond included in the binder is flexible and therefore has the effect of preventing the chemical conversion layer from fracturing (peeling) when subjected to working. (b) The epoxy resin having a bisphenol skeleton included in the binder has the effect of improving the adhesion between the base zinc alloy coated steel sheet and the upper primer painting layer.

The total content of the resin components in the chemical conversion layer is 30 mass% to 50 mass%. If the content of the resin components is less than 30 mass%, the binder effect of the chemical conversion layer decreases. If the content of the resin components is more than 50 mass%, the functions of the below-described inorganic components, such as the inhibitor action, decrease. From the same viewpoint, the content of the resin components in the chemical conversion layer is preferably 35 mass% to 45 mass%.

[0123] In the resin components, the content ratio ((a):(b)) of (a) the anionic polyurethane resin having an ester bond and (b) the epoxy resin having a bisphenol skeleton needs to be in the range of 3:97 to 60:40 in mass ratio. If (a):(b) is outside this range, the flexibility and adhesion of the chemical conversion layer decrease and sufficient corrosion resistance cannot be obtained. From the same viewpoint, (a):(b) is preferably 10:90 to 55:45.

[0124] The resin components may include resins (other resin components) other than (a) the anionic polyurethane resin having an ester bond and (b) the epoxy resin having a bisphenol skeleton, depending on the required performance. The other resin components are not limited, and, for example, one or more selected from acrylic resin, acrylic silicon resin, alkyd resin, polyester resin, polyalkylene resin, amino resin, and fluororesin may be used in combination.

In the case where the resin components include other resins, the total content of (a) the anionic polyurethane resin having an ester bond and (b) the epoxy resin having a bisphenol skeleton is preferably 50 mass% or more and more preferably 75 mass% or more, in order to further ensure the flexibility

and adhesion of the chemical conversion layer.

[0125] The chemical conversion layer also contains, as inorganic compounds, 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.

5 The inclusion of these compounds can enhance the corrosion resistance of the chemical conversion layer.

[0126] The vanadium compound is added to the chemical conversion treatment liquid and acts as a rust preventive agent (inhibitor). As a result of the vanadium compound being contained in the chemical conversion layer, the
10 vanadium compound is eluted moderately in a corrosion environment and bonds with, for example, zinc ions of 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 surfaces of the steel sheet but also defective parts and damaged parts of the coating
15 caused by working, for example, against such corrosion that progresses from cut end surfaces to flat surfaces.

Examples of the vanadium compound include vanadium pentoxide, metavanadate, ammonium metavanadate, vanadium oxytrichloride, vanadium trioxide, vanadium dioxide, magnesium vanadate, vanadyl acetylacetonate, and
20 vanadium acetylacetonate. Among these, it is particularly desirable to use a tetravalent vanadium compound or a tetravalent vanadium compound obtained by reduction or oxidation.

[0127] The content of the vanadium compound in the chemical conversion layer is 2 mass% to 10 mass%. If the content of the vanadium compound in the
25 chemical conversion layer is less than 2 mass%, the inhibitor effect is insufficient and the corrosion resistance decreases. If the content of the vanadium compound in the chemical conversion layer is more than 10 mass%, the moisture resistance of the chemical conversion layer decreases.

[0128] The zirconium compound is contained in the chemical conversion layer,
30 and is expected to improve the strength and corrosion resistance of the chemical conversion layer by reacting with the coating metal or coexisting with the resin components. Moreover, the zirconium compound itself contributes to the formation of a dense chemical conversion layer and has excellent coatability, and therefore is expected to have a barrier effect.

35 Examples of the zirconium compound include neutralized salts such as zirconium sulfate, zirconium carbonate, zirconium nitrate, zirconium lactate,

zirconium acetate, and zirconium chloride.

[0129] The content of the zirconium compound in the chemical conversion layer is 40 mass% to 60 mass%. If the content of the zirconium compound in the chemical conversion layer is less than 40 mass%, the strength and corrosion resistance of the chemical conversion layer decrease. If the content of the zirconium compound in the chemical conversion layer is more than 60 mass%, the chemical conversion layer becomes brittle, and fractures or peels when subjected to severe working.

[0130] The fluorine compound is contained in the chemical conversion layer and acts to impart adhesion with the coating. This can enhance the corrosion resistance of the chemical conversion layer.

Examples of the fluorine compound include fluoride salts such as ammonium salts, sodium salts, and potassium salts, and fluorine compounds such as ferrous fluoride and ferric fluoride. Among these, it is preferable to use fluoride salts such as ammonium fluoride, sodium fluoride, and potassium fluoride.

[0131] The content of the fluorine compound in the chemical conversion layer is 0.5 mass% to 5 mass%. If the content of the fluorine compound in the chemical conversion layer is less than 0.5 mass%, the adhesion at worked parts is insufficient. If the content of the fluorine compound in the chemical conversion layer is more than 5 mass%, the moisture resistance of the chemical conversion layer decreases.

[0132] The coating weight of the chemical conversion layer is not limited. For example, the coating weight of the chemical conversion layer is preferably 0.025 g/m² to 0.5 g/m² from the viewpoint of ensuring the corrosion resistance more reliably and improving the adhesion, etc. of the chemical conversion layer. If the coating weight of the chemical conversion layer is 0.025 g/m² or more, the corrosion resistance can be ensured more reliably. If the coating weight of the chemical conversion layer is 0.5 g/m² or less, 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.

[0133] 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 sheet 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 resins and the metallic compounds, and is not limited.

[0134] - Painting layer

In the prepainted steel sheet according to the present disclosure, a painting layer is formed on the coating directly or with the chemical conversion layer therebetween, as mentioned above. The painting layer includes at least a primer painting layer.

[0135] In the present disclosure, the primer painting layer contains: a polyester resin having a urethane bond; and inorganic compounds including a vanadium compound, a phosphate compound, and magnesium oxide.

As a result of the primer painting layer containing the polyester resin having a urethane bond and the inorganic compounds, the adhesion of the painting layer can be enhanced and the corrosion resistance can be improved.

[0136] The primer painting layer contains a polyester resin having a urethane bond, as a main component. The polyester resin having a urethane bond has both flexibility and strength, and thus has the effect of preventing cracking of the primer painting layer when subjected to working. The polyester resin having a urethane bond particularly contributes to improving the corrosion resistance of worked parts because of its high compatibility with the chemical conversion layer containing urethane resin.

The term “main component” as used herein means the component with the highest content among the components in the primer painting layer.

[0137] As the polyester resin having a urethane bond, a known resin, such as a resin obtained by reacting a polyester polyol with a diisocyanate or polyisocyanate having two or more isocyanate groups, may be used. A resin obtained by curing, with a blocked polyisocyanate, a resin (urethane-modified polyester resin) obtained by reacting the polyester polyol with the diisocyanate or polyisocyanate in a state in which hydroxyl groups are excessive may also

be used.

[0138] The polyester polyol can be obtained by a known method using a dehydration condensation reaction between a polyhydric alcohol component and a polybasic acid component.

5 Examples of the polyhydric alcohol include glycols and trihydric or higher polyhydric alcohols. Examples of the glycols include ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, neopentyl glycol, hexylene glycol, 1,3-butanediol, 1,4-butanediol, 1, 5-pentanediol, 1,6-
10 hexanediol, 2-butyl-2-ethyl-1,3-propanediol, methylpropanediol, cyclohexanedimethanol, and 3,3-diethyl-1,5-pentanediol. Examples of the trihydric or higher polyhydric alcohols include glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, and dipentaerythritol. These polyhydric alcohols may be used alone or in combination of two or more.

15 As the polybasic acid, a polycarboxylic acid is typically used, and a monovalent fatty acid or the like may be optionally used together with the polycarboxylic acid. Examples of the polycarboxylic acid include phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, 4-methylhexahydrophthalic acid, bicyclo[2,2,1]heptane-2,3-dicarboxylic acid, trimellitic acid, adipic acid,
20 sebacic acid, succinic acid, azelaic acid, fumaric acid, maleic acid, itaconic acid, pyromellitic acid, and dimer acid, and their acid anhydrides, as well as 1,4-cyclohexanedicarboxylic acid, isophthalic acid, tetrahydroisophthalic acid, hexahydroisophthalic acid, and hexahydroterephthalic acid. These polybasic acids may be used alone or in combination of two or more.

25 **[0139]** Examples of the polyisocyanate include aliphatic diisocyanates such as hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, and dimer acid diisocyanate, aromatic diisocyanates such as xylylene diisocyanate (XDI), metaxylylene diisocyanate, tolylene diisocyanate (TDI), and 4,4-diphenylmethane diisocyanate (MDI), cycloaliphatic diisocyanates such as
30 isophorone diisocyanate, hydrogenated XDI, hydrogenated TDI, and hydrogenated MDI, and their adducts, biurets, and isocyanurates. These polyisocyanates may be used alone or in combination of two or more.

[0140] The hydroxyl value of the polyester resin having a urethane bond is not limited, but is preferably 5 mgKOH/g to 120 mgKOH/g, more preferably 7
35 mgKOH/g to 100 mgKOH/g, and further preferably 10 mgKOH/g to 80 mgKOH/g from the viewpoint of solvent resistance, workability, and the like.

The number average molecular weight of the polyester resin having a urethane bond is preferably 500 to 15,000, more preferably 700 to 12,000, and further preferably 800 to 10,000 from the viewpoint of solvent resistance, workability, and the like.

5 **[0141]** The content of the polyester resin having a urethane bond in the primer painting layer is preferably 40 mass% to 88 mass%. If the content of the polyester resin having a urethane bond is less than 40 mass%, the binder function of the primer painting layer may decrease. If the content of the polyester resin having a urethane bond is more than 88 mass%, the functions
10 of the below-described inorganic substances, such as the inhibitor action, may decrease.

[0142] A vanadium compound, which is one of the inorganic compounds, acts as an inhibitor. Examples of the vanadium compound include vanadium pentoxide, metavanadate, ammonium metavanadate, vanadium oxytrichloride,
15 vanadium trioxide, vanadium dioxide, magnesium vanadate, vanadyl acetylacetonate, and vanadium acetylacetonate. Among these, it is particularly desirable to use a tetravalent vanadium compound or a tetravalent vanadium compound obtained by reduction or oxidation.

The vanadium compound added to the primer painting layer may be the
20 same or different from the vanadium compound added to the chemical conversion layer. Vanadium compounds are considered to have the following effect: Vanadate ions gradually eluted by moisture entering from the outside react with ions on the surface of a zinc alloy coated steel sheet to form a passive film having good adhesion, thus protecting exposed metal parts and preventing
25 rust.

[0143] The content of the vanadium compound in the primer painting layer is not limited, but is preferably 4 mass% to 20 mass% from the viewpoint of achieving both corrosion resistance and moisture resistance. If the content of the vanadium compound is less than 4 mass%, the corrosion resistance may
30 decrease due to a decrease of the inhibitor effect. If the content of the vanadium compound is more than 20 mass%, the moisture resistance of the primer painting layer may decrease.

[0144] A phosphate compound, which is one of the inorganic compounds, acts as an inhibitor, too. Examples of the phosphate compound include phosphoric acid, ammonium salts of phosphoric acid, alkali metal salts of phosphoric acid,
35 and alkaline earth metal salts of phosphoric acid. Alkali metal salts of

phosphoric acid, such as calcium phosphate, are particularly suitable.

[0145] The content of the phosphate compound in the primer painting layer is not limited, but is preferably 4 mass% to 20 mass% from the viewpoint of achieving both corrosion resistance and moisture resistance. If the content of the phosphate compound is less than 4 mass%, the corrosion resistance may decrease due to a decrease of the inhibitor effect. If the content of the phosphate compound is more than 20 mass%, the moisture resistance of the primer painting layer may decrease.

[0146] Magnesium oxide, which is one of the inorganic compounds, forms a Mg-containing product during initial corrosion, and, as sparingly soluble magnesium salt, has the effect of stabilization and improving the corrosion resistance.

[0147] The content of magnesium oxide in the primer painting layer is not limited, but is preferably 4 mass% to 20 mass% from the viewpoint of achieving both corrosion resistance and worked part corrosion resistance. If the content of magnesium oxide is less than 4 mass%, the corrosion resistance may decrease due to a decrease of the foregoing effect. If the content of magnesium oxide is more than 20 mass%, the worked part corrosion resistance may decrease due to a decrease of the flexibility of the primer painting layer.

[0148] The primer painting layer may contain components other than the polyester resin having a urethane bond and the inorganic compounds.

One example is a crosslinking agent used when forming a primer painting layer. The crosslinking agent reacts with the polyester resin having a urethane bond to form a crosslinked painting layer. Examples of the crosslinking agent include oxazoline compounds, epoxy compounds, melamine compounds, isocyanate compounds, carbodiimide compounds, and silane coupling compounds. Two or more crosslinking agents may be used in combination. A blocked polyisocyanate compound or the like is particularly preferable from the viewpoint of the worked part corrosion resistance of the resultant prepainted steel sheet. Examples of the blocked polyisocyanate include polyisocyanate compounds whose isocyanate groups are blocked with alcohols such as butanol, oximes such as methyl ethyl ketoxime, lactams such as ϵ -caprolactam, diketones such as acetoacetic acid diester, imidazoles such as imidazole and 2-ethylimidazole, or phenols such as m-cresol.

[0149] The primer painting layer may optionally contain various known components commonly used in the paint field. Specific 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 and extender pigments, luster materials, curing catalysts, and organic solvents.

[0150] The thickness of the primer painting layer is preferably 1.5 μm or more. If the thickness of the primer painting layer is 1.5 μm or more, the effect of improving the corrosion resistance and the effect of improving the adhesion to the chemical conversion layer and to the top coat painting layer formed on the primer painting layer can be further ensured.

[0151] The method of forming the primer painting layer is not limited. As the method of applying the paint composition for forming the primer painting layer, it is preferable to apply the paint composition by roll coater painting, curtain flow painting, or the like. After applying the paint composition, the paint may be baked by a heating means such as hot-air heating, infrared heating, or induction heating to form the primer painting layer. The baking treatment may be typically performed for about 30 sec to 3 min in a temperature range of peak sheet temperature of about 180 °C to 270 °C.

[0152] The painting layer included in the prepainted steel sheet according to the present disclosure preferably further includes a top coat painting layer formed on the primer painting layer.

The top coat painting layer can not only impart aesthetic appearance such as color, gloss, and surface state to the prepainted steel sheet but also enhance various performances such as workability, atmospheric corrosion resistance, chemical resistance, stain resistance, water resistance, and corrosion resistance.

[0153] The structure of the top coat painting layer is not limited, and the material, thickness, etc. can be selected as appropriate depending on the required performance.

For example, the top coat painting layer may be formed using a polyester resin-based paint, a silicon polyester resin-based paint, a polyurethane resin-based paint, an acrylic resin-based paint, a fluororesin-based paint, or the like.

The top coat painting layer may further contain coloring pigments such as titanium oxide, red oxide, mica, and carbon black; metallic pigments such as aluminum powders and mica; extender pigments such as carbonates and

sulfates; fine particles such as silica microparticles, nylon resin beads, and acrylic resin beads; curing catalysts such as p-toluenesulfonic acid and dibutyltin dilaurate; waxes; and other additives in appropriate amounts.

5 **[0154]** The thickness of the top coat painting layer is preferably 5 μm to 30 μm from the viewpoint of achieving both good appearance and workability. If the thickness of the top coat painting layer is 5 μm or more, the color appearance can be stabilized more reliably. If the thickness of the top coat painting layer is 30 μm or less, a decrease in workability (cracking of the top coat painting layer) can be suppressed more reliably.

10 **[0155]** The method of applying the paint composition for forming the top coat painting layer is not limited. For example, the paint composition may be applied by roll coater painting, curtain flow painting, or the like. After applying the paint composition, the paint may be baked by a heating means such as hot-air heating, infrared heating, or induction heating to form the top coat painting
15 layer. The baking treatment may be typically performed for about 30 sec to 3 min in a temperature range of peak sheet temperature of about 180 °C to 270 °C.

[0156] (Production method for prepainted steel sheet)

20 A production method for a prepainted steel sheet according to the present disclosure is a production method for a prepainted steel sheet that includes: a coating; and a painting layer formed on the coating directly or with a chemical conversion layer therebetween.

25 In the production method according to the present disclosure, the chemical conversion layer contains: resin components that include (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 inorganic compounds that include 2 mass% to 10 mass% of a vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and
30 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 inorganic compounds including a vanadium compound, a phosphate compound, and magnesium oxide. The production method comprises a hot-dip coating treatment process of immersing a base steel sheet in a molten
35 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 and inevitable impurities, to form the coating, wherein the Co content in the inevitable impurities in the molten bath is controlled to be 0.080 mass% or less.

5 [0157] Co contained in the coating may degrade the corrosion resistance of the prepainted steel sheet, as mentioned above. By appropriately controlling the contents of Al, Zn, Si, and Mg and further reducing the content of Co as an inevitable impurity in the molten bath, degradation in corrosion resistance can be suppressed.

10 [0158] The conditions of the hot-dip coating treatment process are the same as those described with regard to the coating of the prepainted 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 prepainted steel sheet according to the present
15 disclosure.

EXAMPLES

[0159] [Example 1: Samples 1 to 55]

20 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 55 of hot-dip coated steel sheets under the conditions shown in Table 1.

25 The composition of the molten bath used in the hot-dip coated steel sheet production was varied 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 Co: 0.000 mass% to 0.120 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
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
35 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 52, 50 ± 5 g/m² per side in Sample 53, 100 ± 5 g/m² per side in Sample 54, and 125 ± 5 g/m² per side in Sample 55.

[0160] (Evaluation)

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

[0161] (1) Coating (composition, coating weight, X-ray diffraction intensity)

Each sample after the coating was subjected to 100 mm ϕ blanking.
After sealing the non-measurement surface with tape, the coating was dissolved
and peeled with a liquid mixture of hydrochloric acid and
10 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
15 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.
20 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
25 result of the calculation is 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
30 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
35 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 $d = 0.3135$ nm) of Si and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668$ nm) of Mg_2Si were measured. The measurement results are shown in Table 1.

[0162] (2) Evaluation of corrosion resistance

5 After shearing each obtained sample of hot-dip coated steel sheet to a size of $120 \text{ mm} \times 120 \text{ mm}$, 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 $100 \text{ mm} \times 100 \text{ mm}$ to obtain an evaluation sample. Three identical
10 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
15 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 was 45 g/m^2 or less in all three samples.

○: The corrosion weight loss was 70 g/m^2 or less in all three samples.

×: The corrosion weight loss was more than 70 g/m^2 in one or more
20 samples.

[0163] (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.
25 The evaluation results are shown in Table 1.

◎: No wrinkle-like defects were observed.

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

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

[0164] (4) Workability

After shearing each obtained sample of hot-dip coated steel sheet to a size of $70 \text{ mm} \times 150 \text{ mm}$, 180° bending (8T bending) was performed with eight sheets of the same thickness sandwiched inside. Cellotape® (Cellotape is a
35 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

5 Table 1.

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

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

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

[0165] (5) Bath stability

10 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 made based on the following criteria. The evaluation results are shown in Table

15 1.

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

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

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

[0166] [Table 1]

No.		Coating						Corrosion resistance				Surface appearance	Workability	Bath stability	Remarks				
		Composition (mass%)						Coating weight (g/m ²)		Si(111)/Mg ₂ Si(111)						Si(111) (keps)		Evaluation	
Al	Si	Mg	Fe	Sr	Co			N1	N2	N3									
1	55	0.5	4.4	1.05	0.11	0.0003	85	0.00	0.00	97	98	95	×	⊙	×	Comparative Example			
2	55	1.0	4.4	0.68	0.11	0.0003	85	0.00	0.00	42	43	45	⊙	⊙		Example			
3	55	1.5	0.0	0.51	0.00	0.0001	82	No Mg ₂ Si	1.19	111	105	102	×	⊙		Comparative Example			
4	55	1.5	0.0	0.51	0.11	0.0001	85	No Mg ₂ Si	1.18	104	99	100	×	⊙		Comparative Example			
5	55	1.5	1.1	0.58	0.10	0.0001	84	No Mg ₂ Si	0.88	80	82	78	×	⊙		Comparative Example			
6	55	1.6	1.5	0.63	0.10	0.0003	82	0.85	0.75	75	77	66	×	⊙		Comparative Example			
7	54	1.5	1.9	0.39	0.00	0.0002	85	0.58	0.62	45	44	51	○	×	△	Example			
8	55	1.5	2.0	0.43	0.05	0.0002	84	0.55	0.62	46	48	50	○	⊙	△	Example			
9	55	1.5	1.9	0.62	0.11	0.0002	81	0.60	0.63	49	40	50	○	⊙	△	Example			
10	55	1.5	3.4	0.59	0.09	0.0002	85	0.00	0.00	45	43	45	⊙	⊙	△	Example			
11	5	0.0	0.5	0.39	0.00	0.0001	85	No Mg ₂ Si	0.00	251	246	210	×	⊙		Comparative Example			
12	15	0.3	3.0	0.42	0.00	0.0001	86	No Mg ₂ Si	0.00	216	241	198	×	⊙		Comparative Example			
13	32	1.5	4.5	0.58	0.10	0.0003	85	0.00	0.00	89	98	90	×	⊙		Comparative Example			
14	48	1.5	4.5	0.60	0.10	0.0003	84	0.00	0.00	42	44	43	⊙	⊙		Example			
15	50	1.5	4.5	0.59	0.01	0.0001	87	0.00	0.00	40	39	37	⊙	⊙		Example			
16	55	1.5	4.4	0.54	0.10	0.0002	86	0.00	0.00	40	37	36	⊙	⊙		Example			
17	55	1.5	4.4	0.55	0.10	0.0003	85	0.00	0.00	39	41	40	⊙	⊙		Example			
18	55	1.5	4.4	0.56	0.10	0.0003	84	0.00	0.00	42	37	41	⊙	⊙		Example			
19	55	1.5	4.5	0.54	0.11	0.0014	82	0.00	0.00	46	48	39	○	⊙		Example			
20	55	1.5	4.5	0.49	0.11	0.0194	86	0.00	0.00	49	50	47	○	⊙		Example			
21	55	1.5	4.5	0.54	0.11	0.0811	85	0.00	0.00	71	76	82	×	⊙		Comparative Example			
22	60	1.5	4.5	0.63	0.10	0.0002	85	0.00	0.00	38	44	39	⊙	⊙		Example			
23	64	1.6	4.3	0.61	0.02	0.0002	83	0.00	0.00	44	43	44	⊙	⊙		Example			
24	68	1.5	4.5	0.60	0.10	0.0002	85	0.00	0.00	96	88	82	×	⊙		Comparative Example			
25	73	1.6	4.5	0.58	0.10	0.0002	86	0.00	0.00	99	94	92	×	⊙		Comparative Example			
26	55	1.5	5.9	0.63	0.09	0.0002	85	0.00	0.00	29	26	31	⊙	⊙	△	Example			
27	55	2.3	0.0	0.57	0.00	0.0003	86	No Mg ₂ Si	4.21	105	103	97	×	⊙		Comparative Example			
28	55	2.3	0.0	0.60	0.09	0.0003	85	No Mg ₂ Si	3.98	104	113	104	×	⊙		Comparative Example			

Table 1 (cont'd)

No.	Coating						Corrosion resistance			Surface appearance	Workability	Bath stability	Remarks				
	Composition (mass%)						Evaluation										
Al	Si	Mg	Fe	Sr	Co	Coating weight (g/m ²)	Si(111)/Mg ₂ Si(111)	Si(111) (kps)	Corrosion weight loss (g/m ²)	N1	N2	N3					
29	55	2.3	0.9	0.58	0.11	0.0003	83	No Mg ₂ Si	3.13	111	98	96	×	⊙	△	○	Comparative Example
30	55	2.2	2.0	0.55	0.10	0.0001	85	3.26	2.15	81	64	72	×	⊙	△	○	Comparative Example
31	55	2.3	2.7	0.58	0.10	0.0001	87	1.67	1.23	68	83	79	×	⊙	△	○	Comparative Example
32	55	2.2	3.1	0.55	0.10	0.0002	85	0.87	0.75	83	67	76	×	⊙	△	○	Comparative Example
33	55	2.2	3.4	0.61	0.10	0.0001	85	0.12	0.30	62	59	60	○	⊙	△	○	Example
34	55	2.2	4.3	0.56	0.00	0.0001	82	0.13	0.13	55	56	51	○	×	△	○	Example
35	55	2.3	4.4	0.60	0.03	0.0001	85	0.09	0.15	43	31	63	○	⊙	△	○	Example
36	55	2.3	4.3	0.59	0.09	0.0003	83	0.10	0.16	53	60	49	○	⊙	△	○	Example
37	55	2.2	4.3	0.60	0.11	0.0000	86	0.10	0.12	54	58	60	○	⊙	△	○	Example
38	55	2.2	4.6	0.55	0.10	0.0009	87	0.00	0.00	38	43	40	⊙	⊙	△	○	Example
39	55	2.2	4.6	0.56	0.10	0.0222	83	0.00	0.00	57	64	59	○	⊙	△	○	Example
40	55	2.2	4.6	0.59	0.10	0.0785	82	0.00	0.00	68	66	61	○	⊙	△	○	Example
41	55	2.2	4.6	0.57	0.10	0.1127	86	0.00	0.00	74	80	77	×	⊙	△	○	Comparative Example
42	55	2.2	5.9	0.57	0.10	0.0003	85	0.03	0.10	59	56	55	○	⊙	△	△	Example
43	55	2.2	6.4	0.55	0.00	0.0002	82	0.03	0.99	60	54	48	○	×	△	△	Example
44	55	2.9	2.0	0.60	0.00	0.0003	85	3.56	3.24	89	94	87	×	×	△	○	Comparative Example
45	55	2.9	3.2	0.61	0.10	0.0003	85	0.88	0.85	85	91	80	×	○	△	○	Comparative Example
46	55	2.9	5.5	0.60	0.11	0.0002	85	0.12	0.13	41	45	50	○	⊙	△	△	Example
47	55	3.1	4.5	0.62	0.10	0.0002	87	0.34	0.87	55	43	48	○	⊙	△	○	Example
48	55	3.6	4.4	0.63	0.09	0.0003	86	0.35	1.22	61	55	60	○	⊙	△	○	Example
49	55	3.9	3.6	0.61	0.10	0.0001	85	0.95	1.81	93	85	82	×	○	△	○	Comparative Example
50	55	4.0	5.8	0.60	0.11	0.0003	83	0.88	1.46	68	79	74	×	⊙	△	△	Comparative Example
51	55	4.1	4.4	0.58	0.09	0.0001	82	0.90	1.49	96	89	82	×	○	△	○	Comparative Example
52	55	2.9	9.7	0.61	0.09	0.0001	86	0.00	0.00	61	43	43	○	⊙	△	△	Example
53	55	1.5	4.4	0.55	0.10	0.0002	51	0.00	0.00	39	44	39	⊙	⊙	△	○	Example
54	55	1.5	4.4	0.55	0.10	0.0002	100	0.00	0.00	40	41	43	⊙	⊙	△	○	Example
55	55	1.5	4.4	0.55	0.10	0.0002	125	0.00	0.00	39	41	39	⊙	⊙	×	○	Example

[0167] As can be seen 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 **[0168]** [Example 2: Samples 1 to 134]

(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 varied 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 Co: 0.000 mass% to 0.120 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 104 and 117 to 134, 50 ± 5 g/m² per side in Samples 105
25 to 106, 100 ± 5 g/m² per side in Samples 107 to 108, $125 \text{ g/m}^2 \pm 5 \text{ g/m}^2$ per side in Samples 109 to 110, and 70 ± 5 g/m² per side in Samples 111 to 116.

[0169] (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 (resins, metallic compounds) contained in
35 each surface-treatment solution are as follows.

(Resins)

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

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

(Metallic compounds)

P compound: aluminum dihydrogen tripolyphosphate

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%).

[0170] [Table 2]

Chemical conversion treatment	Chemical conversion treatment liquid								Coating weight of chemical conversion layer (g/m ²)
	Resin (mass%)		Metallic compound (mass%)						
			Acrylic resin	P compound	Si compound	V compound	Mo compound	Zr compound	
	Urethane resin	SUPERFLEX 130	SUPERFLEX 126	VONCOAT EC-740EF	Aluminum dihydrogen triphosphate	Silica	Sodium metavanadate	Molybdic acid	
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

Table 2

[0171] (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.

5 **[0172]** (1) Coating (composition, coating weight, 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 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
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 Tables 3 and 4.

25 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
30 under the conditions of X-rays used: Cu-Kα (wavelength = 1.54178 Å), removal of Kβ 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
35 was taken to be diffraction intensity (cps), and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3135$ nm) of Si and the diffraction intensity of

(111) plane (interplanar spacing $d = 0.3668$ nm) of Mg_2Si were measured. The measurement results are shown in Tables 3 and 4.

[0173] (2) Evaluation of corrosion resistance

After shearing each sample of hot-dip coated steel sheet and surface-treated steel sheet to a size of $120 \text{ mm} \times 120 \text{ mm}$, 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 $100 \text{ mm} \times 100 \text{ mm}$ 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 Tables 3 and 4.

◎: The corrosion weight loss was 30 g/m^2 or less in all three samples.

○: The corrosion weight loss was 50 g/m^2 or less in all three samples.

×: The corrosion weight loss was more than 50 g/m^2 in one or more samples.

[0174] (3) White rust resistance

After shearing each sample of hot-dip coated steel sheet and surface-treated steel sheet to a size of $120 \text{ mm} \times 120 \text{ mm}$, 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 $100 \text{ mm} \times 100 \text{ mm}$ to obtain an evaluation sample.

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

◎: Flat parts had no white rust.

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

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

[0175] (4) Surface appearance

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.

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

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

[0176] (5) Workability

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® 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.

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

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

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

20 **[0177] (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 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.

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

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

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

[0178] [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)		Si(111)/Mg ₂ Si(111)	Si(111) (kps)	Corrosion weight loss (g/m ²)							Evaluation	
	Al	Si	Mg	Fe	Sr					Co	N1							N2
1	55	0.5	4.4	1.05	0.11	0.0003	85	0.00	0.00		97	98	95	×	×	Comparative Example		
2											A	80	83	75	×	Comparative Example		
3	55	1.0	4.4	0.68	0.11	0.0003	85	0.00	0.00			42	43	45	○	Comparative Example		
4											A	26	24	27	⊙	Example		
5	55	1.5	0.0	0.51	0.00	0.0001	82	No Mg ₂ Si	1.19			111	105	102	×	Comparative Example		
6											A	81	80	76	×	Comparative Example		
7	55	1.5	0.0	0.51	0.11	0.0001	85	No Mg ₂ Si	1.18			104	99	100	×	Comparative Example		
8											A	75	73	76	×	Comparative Example		
9	55	1.5	1.1	0.58	0.10	0.0001	84	No Mg ₂ Si	0.88			80	82	78	×	Comparative Example		
10											A	59	61	54	×	Comparative Example		
11	55	1.6	1.5	0.63	0.10	0.0003	82	0.85	0.75			75	77	66	×	Comparative Example		
12											A	53	56	55	×	Comparative Example		
13	54	1.5	1.9	0.39	0.00	0.0002	85	0.58	0.62			45	44	51	×	Comparative Example		
14											A	33	29	38	○	Example		
15	55	1.5	2.0	0.43	0.05	0.0002	84	0.55	0.62			46	48	50	○	Comparative Example		
16											A	31	36	35	○	Example		
17	55	1.5	1.9	0.62	0.11	0.0002	81	0.60	0.63			49	40	50	○	Comparative Example		
18											A	35	29	33	○	Example		
19	55	1.5	3.4	0.59	0.09	0.0002	85	0.00	0.00			45	43	45	○	Comparative Example		
20											A	29	25	24	⊙	Example		
21	5	0.0	0.5	0.39	0.00	0.0001	85	No Mg ₂ Si	0.00			251	246	210	×	Comparative Example		
22											A	131	125	116	×	Comparative Example		
23	15	0.3	3.0	0.42	0.00	0.0001	86	No Mg ₂ Si	0.00			216	241	198	×	Comparative Example		
24											A	118	129	134	×	Comparative Example		
25	32	1.5	4.5	0.58	0.10	0.0003	85	0.00	0.00			89	98	90	×	Comparative Example		
26											A	68	77	74	×	Comparative Example		
27	48	1.5	4.5	0.60	0.10	0.0003	84	0.00	0.00			42	44	43	○	Comparative Example		
28											A	23	20	27	⊙	Example		
29	50	1.5	4.5	0.59	0.01	0.0001	87	0.00	0.00			40	39	37	○	Comparative Example		
30											A	28	28	26	⊙	Example		
31	55	1.5	4.4	0.54	0.10	0.0002	86	0.00	0.00			40	37	36	○	Comparative Example		
32											A	24	23	23	⊙	Example		
33	55	1.5	4.4	0.55	0.10	0.0003	85	0.00	0.00			39	41	40	○	Comparative Example		
34											A	24	25	26	⊙	Example		
35	55	1.5	4.4	0.56	0.10	0.0003	86	0.00	0.00			42	37	41	○	Comparative Example		
36											A	28	29	29	⊙	Example		

Table 3(cont'd I)

No.	Coating						Chemical conversion treatment	Corrosion resistance				White rust resistance	Surface appearance	Workability	Bath stability	Remarks	
	Composition (mass%)					Coating weight (g/m ²)		Si(111)/Mg ₂ Si(111)	Si(111) (keps)	Corrosion weight loss (g/m ²)							
										Evaluation							
Al	Si	Mg	Fe	Sr	Co	N1	N2	N3									
37	55	1.5	4.5	0.54	0.11	0.0014	82	0.00	0.00	46	48	39	×	◎	△	○	Comparative Example
38										32	23	25	○				Example
39	55	1.5	4.5	0.49	0.11	0.0194	86	0.00	0.00	49	50	47	×	◎	△	○	Comparative Example
40										31	36	29	○				Example
41																	
42	55	1.5	4.5	0.54	0.11	0.0811	85	0.00	0.00	71	76	82	×	◎	△	○	Comparative Example
43										55	54	52	×	○			Comparative Example
44	60	1.5	4.5	0.63	0.10	0.0002	85	0.00	0.00	38	44	39	○	×	△	○	Comparative Example
45										22	23	24	◎	◎			Example
46	64	1.6	4.3	0.61	0.02	0.0002	83	0.00	0.00	44	43	44	○	×	△	○	Comparative Example
47										25	23	26	◎	◎			Example
48	68	1.5	4.5	0.60	0.10	0.0002	85	0.00	0.00	96	88	82	×	×	△	○	Comparative Example
49										66	77	65	×	○			Comparative Example
50	73	1.6	4.5	0.58	0.10	0.0002	86	0.00	0.00	99	94	92	×	×			Comparative Example
51										70	74	76	×	○	△	○	Comparative Example
52	55	1.5	5.9	0.63	0.09	0.0002	85	0.00	0.00	29	26	31	×	×			Comparative Example
53																	Comparative Example
54	55	2.3	0.0	0.57	0.00	0.0003	86	No Mg ₂ Si	4.21	23	21	25	◎	◎	△	△	Comparative Example
55										78	76	75	×	×	○	○	Comparative Example
56	55	2.3	0.0	0.60	0.09	0.0003	85	No Mg ₂ Si	3.98	104	113	104	×	×	○	○	Comparative Example
57										80	85	79	×	×	○	○	Comparative Example
58	55	2.3	0.9	0.58	0.11	0.0003	83	No Mg ₂ Si	3.13	111	98	96	×	×	△	○	Comparative Example
59										77	72	75	×	×			Comparative Example
60	55	2.2	2.0	0.55	0.10	0.0001	85		2.15	81	64	72	×	×	△	○	Comparative Example
61										43	45	51	×	×			Comparative Example
62	55	2.3	2.7	0.58	0.10	0.0001	87	1.67	1.23	68	89	79	×	×	△	○	Comparative Example
63										61	68	55	×	×	◎	◎	Comparative Example
64	55	2.2	3.1	0.55	0.10	0.0002	85	0.87	0.75	83	67	76	×	×	△	○	Comparative Example
65										54	57	51	×	×	△	○	Comparative Example
66	55	2.2	3.4	0.61	0.10	0.0001	85	0.12	0.30	62	59	60	×	×	◎	◎	Comparative Example
67										36	40	42	○	○			Example
68	55	2.2	4.3	0.56	0.00	0.0001	82	0.13	0.13	55	56	51	×	×	△	○	Comparative Example
69										35	41	38	○	○			Example
70	55	2.3	4.4	0.60	0.03	0.0001	85	0.09	0.15	43	31	63	×	×	△	○	Comparative Example
71										28	30	35	○	○			Example
72	55	2.3	4.3	0.59	0.09	0.0003	83	0.10	0.16	53	60	49	×	×	◎	◎	Comparative Example
										39	41	38	○	○			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)	Si(111)/Mg ₂ Si(111)		Si(111) (keps)	Corrosion weight loss (g/m ²)								
Al	Si	Mg	Fe			Sr		Co	N1	N2	N3	Evaluation				
73	55	2.2	4.3	0.60	0.11	0.0000	86	0.10	0.12	-	54	58	60	×	×	Comparative Example
74	55	2.2	4.6	0.55	0.10	0.0009	87	0.00	0.00	A	38	40	42	○	○	Comparative Example
75	55	2.2	4.6	0.55	0.10	0.0009	87	0.00	0.00	-	38	43	40	○	×	Comparative Example
76	55	2.2	4.6	0.56	0.10	0.0222	83	0.00	0.00	A	28	27	23	⊙	⊙	Comparative Example
77	55	2.2	4.6	0.56	0.10	0.0222	83	0.00	0.00	-	57	64	59	×	×	Comparative Example
78	55	2.2	4.6	0.59	0.10	0.0785	82	0.00	0.00	A	44	37	41	○	○	Comparative Example
79	55	2.2	4.6	0.59	0.10	0.0785	82	0.00	0.00	-	68	66	61	×	×	Comparative Example
80	55	2.2	4.6	0.57	0.10	0.1127	86	0.00	0.00	A	48	44	45	○	○	Comparative Example
81	55	2.2	4.6	0.57	0.10	0.1127	86	0.00	0.00	-	74	80	77	×	×	Comparative Example
82	55	2.2	5.9	0.57	0.10	0.0003	85	0.03	0.10	A	52	55	59	×	×	Comparative Example
83	55	2.2	5.9	0.57	0.10	0.0003	85	0.03	0.10	-	59	56	55	×	×	Comparative Example
84	55	2.2	6.4	0.55	0.00	0.0002	82	0.03	0.99	A	42	40	39	○	○	Comparative Example
85	55	2.2	6.4	0.55	0.00	0.0002	82	0.03	0.99	-	60	54	48	×	×	Comparative Example
86	55	2.9	2.0	0.60	0.00	0.0003	85	3.56	3.24	A	38	40	35	○	○	Comparative Example
87	55	2.9	2.0	0.60	0.00	0.0003	85	3.56	3.24	-	89	94	87	×	×	Comparative Example
88	55	2.9	3.2	0.61	0.10	0.0003	85	0.88	0.85	A	74	72	66	×	×	Comparative Example
89	55	2.9	3.2	0.61	0.10	0.0003	85	0.88	0.85	-	85	91	80	×	×	Comparative Example
90	55	2.9	5.5	0.60	0.11	0.0002	85	0.12	0.13	A	73	65	71	×	×	Comparative Example
91	55	3.1	4.5	0.62	0.10	0.0002	87	0.34	0.87	-	41	45	50	○	○	Comparative Example
92	55	3.1	4.5	0.62	0.10	0.0002	87	0.34	0.87	A	28	31	27	○	×	Comparative Example
93	55	3.6	4.4	0.63	0.09	0.0003	86	0.35	1.22	-	55	43	48	×	×	Comparative Example
94	55	3.6	4.4	0.63	0.09	0.0003	86	0.35	1.22	A	42	40	33	○	○	Comparative Example
95	55	3.6	4.4	0.63	0.09	0.0003	86	0.35	1.22	-	61	55	60	×	×	Comparative Example
96	55	3.9	3.6	0.61	0.10	0.0001	85	0.95	1.81	A	44	39	45	○	○	Comparative Example
97	55	3.9	3.6	0.61	0.10	0.0001	85	0.95	1.81	-	93	85	82	×	×	Comparative Example
98	55	4.0	5.8	0.60	0.11	0.0003	83	0.88	1.46	A	73	73	65	×	×	Comparative Example
99	55	4.1	4.4	0.58	0.09	0.0001	82	0.90	1.49	-	68	79	74	×	×	Comparative Example
100	55	4.1	4.4	0.58	0.09	0.0001	82	0.90	1.49	A	57	53	51	×	×	Comparative Example
101	55	2.9	9.7	0.61	0.09	0.0001	86	0.00	0.00	-	96	89	82	×	×	Comparative Example
102	55	2.9	9.7	0.61	0.09	0.0001	86	0.00	0.00	A	71	76	69	×	×	Comparative Example
103	55	1.5	4.4	0.55	0.10	0.0002	51	0.00	0.00	-	61	43	43	×	×	Comparative Example
104	55	1.5	4.4	0.55	0.10	0.0002	51	0.00	0.00	A	39	37	33	○	○	Comparative Example
105	55	1.5	4.4	0.55	0.10	0.0002	100	0.00	0.00	-	39	44	39	○	×	Comparative Example
106	55	1.5	4.4	0.55	0.10	0.0002	100	0.00	0.00	A	21	26	25	⊙	⊙	Comparative Example
107	55	1.5	4.4	0.55	0.10	0.0002	125	0.00	0.00	-	40	41	43	○	×	Comparative Example
108	55	1.5	4.4	0.55	0.10	0.0002	125	0.00	0.00	A	26	24	27	⊙	⊙	Comparative Example
109	55	1.5	4.4	0.55	0.10	0.0002	125	0.00	0.00	-	39	41	39	○	×	Comparative Example
110	55	1.5	4.4	0.55	0.10	0.0002	125	0.00	0.00	A	28	29	25	⊙	○	Comparative Example

[0179] [Table 4]

Table 4																
No.	Coating						Chemical conversion treatment	Corrosion resistance			White rust resistance	Surface appearance	Workability	Bath stability	Remarks	
	Composition (mass%)							Coating weight (g/m ²)	Si(111)/Mg ₂ Si(111)	Si(111) (kcps)						
Al	Si	Mg	Fe	Sr	Co	N1	N2	N3	Corrosion weight loss (g/m ²)	Evaluation						
111							A	33	39	35	○				Example	
112							B	32	37	33	○				Example	
113							C	35	36	38	○				Example	
114	55	1.7	1.9	0.42	0.03	0.0002		39	34	33	○		◎	△	○	Example
115							E	40	39	41	○	×			Comparative Example	
116							F	47	43	44	○	×			Comparative Example	
117							A	30	35	36	○	○			Example	
118							B	34	35	37	○	○			Example	
119							C	31	38	33	○	○			Example	
120	55	1.6	2.0	0.45	0.00	0.0001		34	36	35	○	○		×	△	○
121							E	38	43	44	○	×			Comparative Example	
122							F	42	43	39	○	×			Comparative Example	
123							A	24	25	26	◎	◎			Example	
124							B	22	23	26	◎	◎			Example	
125	55	1.5	4.4	0.55	0.10	0.0001		28	24	25	◎	◎		△	○	Example
126							D	21	28	25	◎	◎			Example	
127							E	28	27	29	◎	◎			Example	
128							F	35	30	33	○	○			Example	
129							A	39	41	38	○	○			Example	
130							B	37	36	33	○	○			Example	
131	55	2.3	4.3	0.59	0.09	0.0001		39	38	36	○	○		△	○	Example
132							D	36	35	32	○	○			Example	
133							E	39	40	37	○	○			Example	
134							F	46	42	48	○	○			Example	

Table 4

[0180] As can be seen 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 seen from the results in Table 4, each sample subjected to chemical conversion treatments A to D was particularly excellent in white rust resistance.

[0181] [Example 3: Samples 1 to 55]

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 1 to 55 of hot-dip coated steel sheets under the conditions shown in Table 6.

15 The composition of the molten bath used in the hot-dip coated steel sheet production was varied 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 Co: 0.000 mass% to 0.120 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 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. Moreover, 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
25 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 52, 50 ± 5 g/m² per side in Sample 53, 100 ± 5 g/m² per side in Sample 54, and 125 ± 5 g/m² per side in Sample 55.

30 **[0182]** (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 (peak sheet 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 components, inorganic compounds) 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
5 having a bisphenol skeleton (YUKARESIN RE-1050 produced by Yoshimura Oil Chemical Co., Ltd.) at a content mass ratio (a):(b) = 50:50

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

(Inorganic compounds)

10 Vanadium compound: organic vanadium compound chelated with acetylacetone

Zirconium compound: ammonium zirconium carbonate

Fluorine compound: ammonium fluoride

[0183] (3) A primer paint was then applied onto the chemical conversion layer
15 formed as described above with a bar coater, and baked under the conditions of a steel sheet peak sheet temperature of 230 °C and a baking time of 35 sec to form a primer painting layer having the chemical composition shown in Table 5. A top coat paint composition was then applied onto the primer painting layer formed as described above with a bar coater, and baked under the
20 conditions of a steel sheet peak sheet 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 thickness shown in Table 5. Each sample of prepainted steel sheet was thus produced.

The primer paint was obtained by mixing the components and then
25 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 layer.

(Resin components)

Resin α : urethane-modified polyester resin (obtained by reacting 455
30 parts by mass of polyester resin and 45 parts by mass of isophorone diisocyanate; resin acid value: 3, number average molecular weight: 5,600, and hydroxyl value: 36) cured 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
35 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

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 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 Kansai Paint Co., Ltd.).

(Inorganic compounds)

Vanadium compound: magnesium vanadate

Phosphate compound: calcium phosphate

Magnesium oxide compound: magnesium oxide

For the resins 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.)

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

[0184] [Table 5]

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%)			
						Type	Content (mass%)							
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

[0185] (Evaluation)

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

[0186] (1) Coating (composition, coating weight, X-ray diffraction intensity)

5 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
10 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 was performed on the filtrate to quantify the components other than insoluble
15 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.
20 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.

In addition, after shearing each sample to a size of 100 mm × 100 mm,
25 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-Kα (wavelength = 1.54178 Å),
30 removal of Kβ 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)
35 plane (interplanar spacing $d = 0.3135$ nm) of Si and the diffraction intensity of (111) plane (interplanar spacing $d = 0.3668$ nm) of Mg₂Si were measured. The

measurement results are shown in Table 6.

[0187] (2) Evaluation of corrosion resistance

After shearing each sample of prepainted 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 cycles when red rust occurred in each of the three samples ≥ 600 cycles.

○: 600 cycles > the number of cycles when red rust occurred in each of the three samples ≥ 500 cycles.

×: The number of cycles when red rust occurred in at least one sample < 500 cycles.

[0188] (3) Appearance after painting

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

The observation results were evaluated based on the following criteria. The evaluation results are shown in Table 6.

◎: No wrinkle-like defects were observed.

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

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

[0189] (4) Workability after painting

After shearing each sample of prepainted 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 workability was evaluated based on the following criteria. The evaluation results are shown in Table 6.

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

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

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

10 **[0190]** (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 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.

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

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

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

[0191] [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)	Si(111)/Mg ₂ Si(111)	Si(111) (kcps)	Red rust occurrence time (cycle)		Evaluation							
Al	Si	Mg	Fe	Sr	Co				N1	N2	N3									
1	55	0.5	4.4	1.01	0.11	0.0003	86	0.00	0.00	T1	400	360	340	×	◎	×	○	Comparative Example		
2	55	1.0	4.4	0.65	0.11	0.0003	83	0.00	0.00	T1	620	640	640	◎	◎	△	○	Example		
3	55	1.5	0.0	0.49	0.00	0.0001	84	No Mg ₂ Si	1.25	T1	320	300	320	×	◎	○	○	Comparative Example		
4	55	1.5	0.0	0.48	0.11	0.0001	82	No Mg ₂ Si	1.24	T1	280	320	320	×	◎	○	○	Comparative Example		
5	55	1.5	1.1	0.55	0.10	0.0001	85	No Mg ₂ Si	0.92	T1	420	460	460	×	◎	△	○	Comparative Example		
6	55	1.6	1.5	0.58	0.10	0.0003	86	0.85	0.76	T1	460	480	460	×	◎	△	○	Comparative Example		
7	54	1.5	1.9	0.36	0.00	0.0002	83	0.58	0.65	T1	540	520	560	○	×	△	○	Example		
8	55	1.5	2.0	0.41	0.05	0.0002	82	0.55	0.61	T1	560	580	580	○	◎	△	○	Example		
9										T1	620	580	620	○	◎	△	○	Example		
										T2	580	600	560	○	◎	△		Example		
										T3	420	360	400	×	◎	△		Comparative Example		
										T4	380	400	360	×	◎	△		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	0.0002	84	0.00	0.00	T1	660	680	680	◎	◎	△	○	Example		
11	5	0.0	0.5	0.39	0.00	0.0001	85	No Mg ₂ Si	0.00	T1	360	400	340	×	◎	△	○	Comparative Example		
12	15	0.3	3.0	0.42	0.00	0.0001	86	No Mg ₂ Si	0.00	T1	360	320	380	×	◎	△	○	Comparative Example		
13	32	1.5	4.5	0.55	0.10	0.0003	86	0.00	0.00	T1	380	400	360	×	◎	△	○	Comparative Example		
14	48	1.5	4.5	0.58	0.10	0.0003	85	0.00	0.00	T1	720	680	680	◎	◎	△	○	Example		
15	50	1.5	4.5	0.56	0.01	0.0001	87	0.00	0.00	T1	700	680	680	◎	◎	△	○	Example		
16	55	1.5	4.4	0.54	0.10	0.0002	86	0.00	0.00	T1	680	660	680	◎	◎	△	○	Example		
17	55	1.5	4.4	0.52	0.10	0.0003	84	0.00	0.00	T1	720	640	660	◎	◎	△	○	Example		
18	55	1.5	4.4	0.56	0.10	0.0003	84	0.00	0.00	T1	640	700	660	◎	◎	△	○	Example		
19	55	1.5	4.5	0.54	0.11	0.0014	82	0.00	0.00	T1	660	660	680	◎	◎	△	○	Example		
20	55	1.5	4.5	0.49	0.11	0.0194	86	0.00	0.00	T1	580	660	640	○	◎	△	○	Example		
21	55	1.5	4.5	0.54	0.11	0.0811	85	0.00	0.00	T1	640	640	560	○	◎	△	○	Example		
22	60	1.5	4.5	0.59	0.10	0.0002	83	0.00	0.00	T1	440	520	420	×	◎	△	○	Comparative Example		
23	64	1.6	4.3	0.58	0.02	0.0002	86	0.00	0.00	T1	680	660	680	◎	◎	△	○	Example		
24	68	1.5	4.5	0.60	0.10	0.0002	85	0.00	0.00	T1	660	700	660	◎	◎	△	○	Example		
25	73	1.6	4.5	0.55	0.10	0.0002	88	0.00	0.00	T1	360	460	400	×	◎	△	○	Comparative Example		
26	55	1.5	5.9	0.61	0.09	0.0002	84	0.00	0.00	T1	380	360	400	×	◎	△	○	Comparative Example		
27	55	2.3	0.0	0.54	0.00	0.0003	83	No Mg ₂ Si	4.36	T1	680	680	700	◎	◎	△	△	Example		
28	55	2.3	0.0	0.56	0.09	0.0003	86	No Mg ₂ Si	4.22	T1	300	280	340	×	◎	○	○	Comparative 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)	Si(111)/Mg ₂ Si(111)	Si(111) (kcps)	Red rust occurrence time (cycle)	Evaluation								
	Al	Si	Mg	Fe	Sr							Co						
												N1	N2	N3				
29	55	2.3	0.9	0.52	0.11	0.0003	85	No Mg ₂ Si	3.46	T1	420	380	400	×	◎	△	○	Comparative Example
30	55	2.2	2.0	0.52	0.10	0.0001	84	3.26	2.28	T1	460	500	480	×	◎	△	○	Comparative Example
31	55	2.3	2.7	0.58	0.10	0.0001	87	1.67	1.23	T1	460	480	460	×	◎	△	○	Comparative Example
32	55	2.2	3.1	0.55	0.10	0.0002	85	0.87	0.75	T1	500	480	440	×	◎	△	○	Comparative Example
33	55	2.2	3.4	0.58	0.10	0.0001	87	0.12	0.35	T1	520	560	500	○	◎	△	○	Example
34	55	2.2	4.3	0.52	0.00	0.0001	86	0.13	0.20	T1	520	540	580	○	×	△	○	Example
35	55	2.3	4.4	0.59	0.03	0.0001	84	0.09	0.18	T1	560	600	560	○	◎	△	○	Example
										T2	540	560	580	○	◎	△		
36	55	2.3	4.3	0.56	0.09	0.0003	85	0.10	0.21	T1	620	560	600	○	◎	△	○	Example
37	55	2.2	4.3	0.57	0.11	0.0000	87	0.10	0.15	T1	580	580	600	○	◎	△	○	Example
38	55	2.2	4.6	0.55	0.10	0.0009	87	0.00	0.00	T1	700	640	660	◎	◎	△	○	Example
39	55	2.2	4.6	0.56	0.10	0.0222	83	0.00	0.00	T1	580	560	540	○	◎	△	○	Example
40	55	2.2	4.6	0.59	0.10	0.0785	82	0.00	0.00	T1	520	520	560	○	◎	△	○	Example
41	55	2.2	4.6	0.57	0.10	0.1127	86	0.00	0.00	T1	460	420	440	×	◎	△	○	Comparative Example
42	55	2.2	5.9	0.55	0.10	0.0003	84	0.03	0.12	T1	580	560	580	○	◎	△	△	Example
43	55	2.2	6.4	0.53	0.00	0.0002	83	0.03	1.05	T1	560	540	580	○	×	△	△	Example
44	55	2.9	1.9	0.61	0.00	0.0003	85	3.56	3.24	T1	440	380	420	×	×	△	○	Comparative Example
45	55	2.9	3.3	0.60	0.10	0.0003	85	0.88	0.85	T1	400	440	380	×	○	△	○	Comparative Example
46	55	2.9	5.5	0.60	0.11	0.0002	85	0.12	0.13	T1	540	600	600	○	◎	△	△	Example
47	55	3.1	4.5	0.54	0.10	0.0002	85	0.34	0.98	T1	600	580	600	○	◎	△	○	Example
48	55	3.6	4.4	0.57	0.09	0.0003	87	0.35	1.24	T1	520	560	540	○	◎	△	○	Example
49	55	4.0	3.7	0.60	0.10	0.0001	85	0.95	1.81	T1	420	420	380	×	○	△	○	Comparative Example
50	55	4.0	5.8	0.60	0.11	0.0003	83	0.88	1.46	T1	480	540	520	×	◎	△	△	Comparative Example
51	55	4.1	4.4	0.58	0.09	0.0001	82	0.90	1.49	T1	360	380	360	×	○	△	○	Comparative Example
52	55	2.9	9.7	0.57	0.09	0.0001	88	0.00	0.00	T1	500	560	520	○	◎	△	△	Example
53	55	1.5	4.4	0.50	0.10	0.0002	52	0.00	0.00	T1	640	620	600	◎	◎	△	○	Example
54	55	1.5	4.4	0.52	0.10	0.0002	98	0.00	0.00	T1	660	660	640	◎	◎	△	○	Example
55	55	1.5	4.4	0.54	0.10	0.0002	128	0.00	0.00	T1	720	720	700	◎	◎	×	○	Example

[0192] As can be seen 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

[0193] It is thus possible to provide a hot-dip Al-Zn-Si-Mg coated steel sheet having consistently 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 Co content in the inevitable impurities is 0.080 mass% or less
with respect to a total mass of the coating, and

respective diffraction intensities of Si and Mg₂Si in the coating by an
10 X-ray diffraction method satisfy the following relationship (1):

$$\text{Si (111)}/\text{Mg}_2\text{Si (111)} \leq 0.8 \quad \dots (1)$$

where Si (111) is a diffraction intensity of (111) plane of Si with
interplanar spacing $d = 0.3135$ nm, and Mg₂Si (111) is a diffraction intensity
of (111) plane of Mg₂Si with interplanar spacing $d = 0.3668$ nm.

15

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

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

20 where Si (111) is the diffraction intensity of (111) plane of Si with
interplanar spacing $d = 0.3135$ nm.

[Claim 3] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
1 or 2, wherein the coating further contains Sr: 0.01 mass% to 1.0 mass%.

25

[Claim 4] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
1 or 2, wherein Al content in the coating is 50 mass% to 60 mass%.

[Claim 5] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
30 1 or 2, wherein Si content in the coating is 1.0 mass% to 3.0 mass%.

[Claim 6] The hot-dip Al-Zn-Si-Mg coated steel sheet according to claim
1 or 2, wherein Mg content in the coating is 1.0 mass% to 5.0 mass%.

35 [Claim 7] 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,

5 wherein Co content in the inevitable impurities in the molten bath is controlled to be 0.080 mass% or less with respect to a total mass of the molten bath.

[Claim 8] The production method for a hot-dip Al-Zn-Si-Mg coated steel
10 sheet according to claim 7, wherein the molten bath further contains Sr: 0.01 mass% to 1.0 mass%.

[Claim 9] A surface-treated steel sheet comprising:
the coating according to claim 1 or 2; and
15 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
20 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.

25 [Claim 10] 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 7 or 8; and a chemical conversion layer formed on the coating,

wherein the chemical conversion layer contains: at least one resin
30 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
35 compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

[Claim 11] A prepainted steel sheet comprising:

the coating according to claim 1 or 2; and

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

wherein the chemical conversion layer contains: resin components that include (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
10 60:40 in mass ratio; and inorganic compounds that include 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 inorganic compounds including
15 a vanadium compound, a phosphate compound, and magnesium oxide.

[Claim 12] A production method for a prepainted 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 7 or 8; and a painting layer formed on the coating
20 directly or with a chemical conversion layer therebetween,

wherein the chemical conversion layer contains: resin components that include (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
25 60:40 in mass ratio; and inorganic compounds that include 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 inorganic compounds including
30 a vanadium compound, a phosphate compound, and magnesium oxide.