

## DESCRIPTION

### TITLE

5 HOT-DIP Al-Zn-Si-Mg-Sr COATED STEEL SHEET, SURFACE-TREATED  
STEEL SHEET, AND PRE-PAINTED STEEL SHEET

### TECHNICAL FIELD

10 **[0001]** This disclosure relates to hot-dip Al-Zn-Si-Mg-Sr coated steel sheets, surface-treated steel sheets, and pre-painted steel sheets that stably exhibit excellent corrosion resistance.

### BACKGROUND

15 **[0002]** Hot-dip Al-Zn coated steel sheets, as typified by 55 % Al-Zn coated ones, are known to exhibit high corrosion resistance among hot-dip galvanized steel sheets because the sacrificial protection properties of Zn and the high corrosion resistance of Al can be obtained in a balanced manner. Because of their excellent corrosion resistance, hot-dip Al-Zn coated steel sheets are increasingly used mainly in the field of building materials such as roofs and walls, which are exposed to outdoor environments for a long period of time, and in the field of civil engineering and construction such as guardrails, wiring and piping, and sound proof walls. In particular, the demand for materials with superior corrosion resistance and maintenance-free materials has been increasing in recent years due to the growing demand for such materials under more severe operating environments, such as those exposed to acid rain caused by air pollution, snow-melting agents applied to prevent roads from freezing in snowy regions, and coastal areas development.

20 **[0003]** The coating layer of a hot-dip Al-Zn coated steel sheet, is composed of a dendrite-like solidified portion of Al supersaturated with Zn ( $\alpha$ -Al phase) and a Zn-Al eutectic structure existing in dendrite gaps (interdendrites), and is characterized by its multi-layered structure of  $\alpha$ -Al phase stacked in the thickness direction of the coating layer. It is also known that such characteristic coating structure makes the corrosion path from surfaces complicated and corrosion more difficult to propagate, with the result that a hot-dip Al-Zn coated steel sheet has better corrosion resistance than a hot-dip galvanized steel sheet with the same coating layer thickness.

35 **[0004]** Attempts are being made to further extend the service life of such hot-

dip Al-Zn coated steel sheets, and hot-dip Al-Zn-Si-Mg-Sr coated steel sheets with Mg added are now in practical use.

As such a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet, for example, JP 5020228 B (PTL 1) describes a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet having a coating layer containing an Al-Zn-Si alloy and including Mg, in which the Al-Zn-Si alloy contains 45 wt% to 60 wt% elemental aluminum, 37 wt% to 46 wt% elemental zinc, and 1.2 wt% to 2.3 wt% Si, and a concentration of Mg is 1 wt% to 5 wt%.

In addition, JP 5000039 B (PTL 2) describes a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet having a coating layer containing at least one of 2 % to 10 % Mg or 0.01 % to 10 % Ca to improve corrosion resistance and to enhance a protective action after exposure of a base steel sheet.

Further, JP 2002-12959 A (PTL 3) describes a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet with improved corrosion resistance in flat parts and ends, in which a coating layer is formed by forming a layer containing, in mass%, Mg: 1 % to 15 %, Si: 2 % to 15 %, and Zn: 11 % to 25 %, with the balance being Al and inevitable impurities, with intermetallic compounds such as  $Mg_2Si$  and  $MgZn_2$  phases present in the coating layer being controlled to a size of 10  $\mu m$  or less.

**[0005]** These hot-dip Al-Zn coated steel sheets are often used without pre-painting because of their aesthetic appearance with white metallic luster spangle patterns, and the requirements for appearance are becoming increasingly strict. Therefore, technologies have been developed to improve the appearance of hot-dip Al-Zn coated steel sheets.

For example, JP 3983932 B (PTL 4) describes a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet in which wrinkle-like unevenness defects are suppressed by adding 0.01 % to 10 % Sr to the coating layer.

In addition, JP 2011-514934 A (PTL 5) describes a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet in which speckled defects are suppressed by adding 500 ppm to 3000 ppm Sr to the coating layer. Technology to improve the view is described.

For example, JP 3983932 B (PTL 4) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which wrinkle-like unevenness defects are suppressed by adding 0.01 % to 10 % Sr to the coating layer.

Further, JP 2011-514934 A (PTL 5) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which speckled defects are suppressed by adding 500 ppm to 3000 ppm Sr to the coating layer.

In addition, WO 2020/179147 A (PTL 6) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which both surface appearance and corrosion resistance are ensured by adding 0.001 % to 1.0 % Sr to the coating layer.

5 Further, WO 2020/179148 A (PTL 7) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which both surface appearance and corrosion resistance are ensured at the flat part and the processed part by adding 0.001 % to 1.0 % Sr to the coating layer.

10 Still further, JP 2020-143370 A (PTL 8) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which both surface appearance and corrosion resistance are ensured by adding 0.01 % to 0.2 % Sr to the coating layer.

In addition, PTL 9: WO 2016/140370 A (PTL 9) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which corrosion resistance is improved by controlling the concentrations of Si and Mg in the coating layer at a specific ratio.

15 **[0006]** These hot-dip Al-Zn coated steel sheets have a problem that white rust occurs due to corrosion of the coating layer when used in a severe corrosion environment. Since this white rust causes deterioration in the appearance of steel sheets, development of coated steel sheets with an improved anti-white rust property is underway.

20 For example, JP 5751093 B (PTL 10) describes a hot-dip Al-Zn-Si-Mg coated steel sheet in which the mass ratio of Mg in the Si-Mg phase with respect to the total content of Mg in the coating layer is optimized for the purpose of improving the anti-white rust property in the processed part.

25 In addition, JP 2019-155872 A (PTL 11) describes a technology that improves the blackening resistance and the anti-white rust property by forming a chemical conversion layer containing urethane resin on the coating layer of a hot-dip Al-Zn-Si-Mg coated steel sheet.

30 **[0007]** Pre-painted steel sheets with a chemical conversion layer, a primer paint layer, a top coating layer, and the like formed on the surfaces of hot-dip Al-Zn coated steel sheets are subjected to various processing such as 90° bending and 180° bending by press forming, roll forming, or emboss forming, and are required to have long-term paint layer durability. In order to meet these requirements, as hot-dip Al-Zn coated steel sheets, there are pre-painted steel sheets in which a chemical conversion layer containing chromate and a primer paint layer also containing chromate-based anti-corrosion pigments are formed, 35 and a weather-resistant top coating layer such as a thermosetting polyester resin paint layer or a fluorine resin paint layer is formed thereon.

Recently, however, the use of chromate, an environmentally hazardous substance, has become a problem for these pre-painted steel sheets, and there is a strong desire to develop pre-painted steel sheets that can improve corrosion resistance and surface appearance even if they are chromate-free.

5 As a technology corresponding to these requirements, for example, JP 2005-169765 A (PTL 12) describes a surface-treated hot-dip coated steel material in which an aluminum-zinc alloy coating layer ( $\alpha$ ) that contains Al, Zn, Si, and Mg and is adjusted in terms of the content of these elements is coated on a surface of the steel material, and a layer ( $\beta$ ) is formed, as an upper layer, with  
10 at least one compound (A) selected from titanium compounds or zirconium compounds as a layer forming component, in which the mass ratio of the Si-Mg phase in the aluminum-zinc alloy coating layer ( $\alpha$ ) with respect to the total content of Mg in the coating layer is adjusted to 3 % or more.

## 15 CITATION LIST

### Patent Literature

[0008] PTL 1: JP 5020228 B  
PTL 2: JP 5000039 B  
PTL 3: JP 2002-12959 A  
20 PTL 4: JP 3983932 B  
PTL 5: JP 2011-514934 A  
PTL 6: WO 2020/179147 A  
PTL 7: WO 2020/179148 A  
PTL 8: JP 2020-143370 A  
25 PTL 9: WO 2016/140370 A  
PTL 10: JP 5751093 B  
PTL 11: JP 2019-155872 A  
PTL 12: JP 2005-169765 A

## 30 SUMMARY

### (Technical Problem)

[0009] However, the technology of containing Mg in the coating layer, as described in PTLs 1-3, does not always uniquely improve corrosion resistance. In the hot-dip Al-Zn-Si-Mg-Sr coated steel sheets described in PTLs 1-3,  
35 corrosion resistance is improved only by adding Mg to the coating components, but the characteristics of the metallic and intermetallic compound phases that

constitute the coating layer are not considered. Thus it is not possible to uniformly determine the superiority or inferiority of corrosion resistance. Therefore, even when hot-dip Al-Zn-Si-Mg-Sr coated steel sheets are manufactured using the same coating bath components, there are variations in corrosion resistance when corrosion tests are conducted, which is not necessarily superior to Al-Zn coated steel sheets with no Mg added.

Similarly, in the improvement of coating appearance, the addition of Sr to the coating layer alone does not necessarily eliminate wrinkle-like unevenness defects, and corrosion resistance and appearance may not be achieved at the same time in the hot-dip Al-Zn-Si-Mg-Sr coated steel sheets described in PTLs 4-8.

**[0010]** When steel sheets are coated in a hot-dip Al-Zn-Si bath with Mg added, it is known that  $Mg_2Si$ ,  $MgZn_2$ , and Si phases are precipitated in the coating layer in addition to the  $\alpha$ -Al phase. However, little was known about the influence of the amount of precipitation and proportions of each phase on corrosion resistance.

In the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet described in PTL 9, the concentrations of Si and Mg are controlled at a specific ratio to improve corrosion resistance by eliminating the precipitation of Si phase in the coating layer. However, it was not always possible to suppress the formation of Si phase, and even when the formation of Si phase in the coating layer could be suppressed, good corrosion resistance could not be obtained in some cases. Thus the technology described in PTL 9 was technically incomplete.

**[0011]** Further, no sufficient improvement in anti-white rust property could be achieved by any of the conventional technologies. Although the improvement of anti-white rust property in the processed part and the flat part after heating is described for the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet of PTL 10, the anti-white rust property in an unheated flat part was not considered, and provision of stable anti-white rust property was still an issue to be solved. In addition, with regard to the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet of PTL 11, it was not always possible to stably ensure high corrosion resistance and good anti-white rust property, and further improvement is desired.

**[0012]** Still further, as mentioned above, pre-painted steel sheets are required to have long-term coating layer durability after subsection to various processing such as 90° bending and 180° bending by press forming, roll forming, or emboss forming. However, with the technology of PTL 12,

corrosion resistance and surface appearance after processing were not necessarily stably ensured.

It goes without saying that the corrosion resistance of pre-painted steel sheets is affected by the corrosion resistance of the underlying coated steel sheets, and as for surface appearance, the difference in the height of irregularities in wrinkle defects is as large as several tens of micrometers. Thus, even if the surface is smoothed by the paint layer, such irregularities are not completely resolved, and it is not expected that the appearance as pre-painted steel sheets will improve. Further, there is a concern that corrosion resistance will be locally reduced because the paint layer will be thinner in a convex part. Therefore, it is important to improve the corrosion resistance and surface appearance of the underlying coated steel sheet in order to obtain a pre-painted sheet with excellent corrosion resistance and surface appearance.

**[0013]** It would thus be helpful to provide a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet that stably exhibits excellent corrosion resistance and good surface appearance.

It would also be helpful to provide a surface-treated steel sheet that stably exhibits excellent corrosion resistance and anti-white rust property.

It would also be helpful to provide a pre-painted sheet that stably exhibits excellent corrosion resistance and excellent corrosion resistance in processed parts.

(Solution to Problem)

**[0014]** As a result of our study to solve the above issues, it was found that the amount of precipitation of  $Mg_2Si$  phase,  $MgZn_2$  phase, and Si phase formed in the coating layer of a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet increases or decreases and their proportions change depending on the balance of each component in the coating layer and the conditions for forming the coating layer, and that in some cases no phase is deposited depending on the composition balance. It was also revealed that the corrosion resistance of a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet varies with the proportions of these phases, and that corrosion resistance is stably improved when there is less Si phase than  $Mg_2Si$  phase, in particular.

However, it is known that it is very difficult to distinguish between these  $Mg_2Si$  and Si phases even by observing secondary electron images or reflected electron images of the coating layer from the surface or cross-section using a

common method such as under a scanning electron microscope. Although it is possible to obtain microscopic information by observation using a transmission electron microscope (TEM) as a technique that enables more detailed analysis, it is not possible to determine the proportions of  $\text{Mg}_2\text{Si}$  and Si phases, which

5 affect macroscopic information such as corrosion resistance and appearance. Accordingly, the present inventors focused on the X-ray diffraction method, and found that the proportions of the phases can be quantitatively defined by using the intensity ratio of specific diffraction peaks for  $\text{Mg}_2\text{Si}$  and Si phases, and that if specific proportions of the  $\text{Mg}_2\text{Si}$  and Si phases are satisfied in the

10 coating layer, excellent corrosion resistance is stably obtained.

Still further, the present inventors also found that by controlling the concentration of Sr in the bath after controlling the proportions of  $\text{Mg}_2\text{Si}$  and Si phases in the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet, the generation of wrinkle-like unevenness defects is reliably suppressed and a coated steel sheet

15 with excellent surface appearance can be obtained.

**[0015]** The present inventors also studied the chemical conversion layer formed on the aforementioned coating layer and found that by forming the chemical conversion layer from a specific resin and a specific metal compound, the affinity of the chemical conversion layer with the coating layer and the

20 anti-rust effect can be enhanced and the anti-white rust property can be stably improved.

**[0016]** Further, the present inventors also studied the chemical conversion layer and the primer paint layer formed on the aforementioned coating layer, and found that by forming the chemical conversion layer from a specific resin

25 and a specific inorganic compound and forming the primer paint layer from a specific polyester resin and a specific inorganic compound, the barrier property and adhesion of the paint layer can be improved and excellent post-processing corrosion resistance can be achieved even in the case of chromate-free.

**[0017]** The present disclosure was completed based on these findings, and

30 primary features thereof are as described below.

1. A hot-dip Al-Zn-Si-Mg-Sr coated steel sheet comprising a coating layer, wherein the coating layer has a composition containing (consisting of) Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, Mg: 1.0 mass% to 10.0 mass%, and Sr: 0.01 mass% to 1.0 mass%, with the balance being Zn and

35 inevitable impurities, and diffraction intensities of Si and  $\text{Mg}_2\text{Si}$  in the coating layer as measured by an X-ray diffraction method satisfy the following relation

(1):

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

5 where Si(111) represents a diffraction intensity for a (111) plane of Si with an interplanar spacing  $d$  of 0.3135 nm, and Mg<sub>2</sub>Si(111) represents a diffraction intensity for a (111) plane of Mg<sub>2</sub>Si with an interplanar spacing  $d$  of 0.3668 nm.

**[0018]** 2. The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to aspect  
10 1, wherein the diffraction intensity of Si in the coating layer as measured by the X-ray diffraction method satisfies the following relation (2):

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

15 where Si(111) represents a diffraction intensity for the (111) plane of Si with an interplanar spacing  $d$  of 0.3135 nm.

**[0019]** 3. The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to aspect 1 or 2, wherein a content of Al in the coating layer is 50 mass% to 60 mass%.

**[0020]** 4. The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to any one  
20 of aspects 1 to 3, wherein a content of Si in the coating layer is 1.0 mass% to 3.0 mass%.

**[0021]** 5. The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to any one of aspects 1 to 4, wherein a content of Mg in the coating layer is 1.0 mass% to 5.0 mass%.

25 **[0022]** 6. A surface-treated steel sheet comprising the coating layer as recited in any one of aspects 1 to 5 and a chemical conversion layer formed on the coating layer, 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  
30 polyalkylene resin, an amino resin, and a fluororesin; and at least one metal 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.

35 **[0023]** 7. A pre-painted steel sheet comprising a paint layer formed either directly on the coating layer as recited in any one of aspects 1 to 5 or on a

chemical conversion layer on top of the coating layer, wherein the chemical conversion layer contains: a resin component containing (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%, in which a  
5 content ratio of (a) to (b), (a):(b), is in the range of 3:97 to 60:40 by mass; and an inorganic compound containing 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 paint layer has at least a primer paint layer, the primer paint layer containing: a polyester resin having a  
10 urethane bond; and an inorganic compound containing a vanadium compound, a phosphoric acid compound, and a magnesium oxide.

(Advantageous Effect)

**[0024]** The present disclosure provides a hot-dip Al-Zn-Si-Mg-Sr coated steel  
15 sheet that stably exhibits excellent corrosion resistance and good surface appearance.

The present disclosure also provides a surface-treated steel sheet that stably exhibits excellent corrosion resistance and anti-white rust property.

The present disclosure also provides a pre-painted steel sheet that stably  
20 exhibits excellent corrosion resistance and excellent corrosion resistance in processed parts.

## BRIEF DESCRIPTION OF THE DRAWING

**[0025]** FIG. 1 illustrates the flow of the cyclic corrosion test prescribed by the  
25 Japanese Automobile Standards Organization (JASO-CCT).

## DETAILED DESCRIPTION

**[0026]** (Hot-dip Al-Zn-Si-Mg-Sr Coated Steel Sheet)

The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet disclosed herein comprises a  
30 coating layer on its surface. The coating layer has a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, Mg: 1.0 mass% to 10.0 mass%, and Sr: 0.01 mass% to 1.0 mass%, with the balance being Zn and inevitable impurities.

**[0027]** From the viewpoint of balancing the corrosion resistance with actual  
35 operation requirements, the content of Al in the coating layer is 45 mass% to 65 mass%. It is preferably 50 mass% or more. It is preferably 60 mass% or less.

This is because if the content of Al in the coating layer is at least 45 mass%, dendrite solidification of Al occurs and a coating layer structure mainly composed of a microstructure with dendrite solidification of  $\alpha$ -Al phase can be obtained. Such microstructures with dendrite solidification layered in the thickness direction of the coating layer make the corrosion path complicated and improves the corrosion resistance of the coating layer itself. The more dendrite portions of  $\alpha$ -Al phase are stacked, the more complicated the corrosion path becomes, and the harder it is for corrosion to reach the base steel sheet, resulting in improved corrosion resistance. Therefore, the content of Al is preferably 50 mass% or more. On the other hand, if the content of Al in the coating layer exceeds 65 mass%, the microstructure changes to one in which most of Zn is solidly dissolved in  $\alpha$ -Al, the dissolution reaction of the  $\alpha$ -Al phase cannot be suppressed, and the corrosion resistance of the Al-Zn-Si-Mg-Sr coating deteriorates. For this reason, the content of Al in the coating layer should be 65 mass% or less, and is preferably 60 mass% or less.

**[0028]** Si in the coating layer is mainly added to inhibit the growth of Fe-Al and/or Fe-Al-Si interfacial alloy layer that form at the interface with the base steel sheet and to prevent deterioration of the adhesion between the coating layer and the steel sheet. In fact, when a steel sheet is dipped in an Al-Zn coating bath containing Si, Fe on the steel sheet surface reacts with Al and Si in the bath to form an alloy, and an Fe-Al and/or Fe-Al-Si intermetallic compound layer forms at the interface between the base steel sheet and the coating layer. At this point, the Fe-Al-Si alloy grows more slowly than the Fe-Al alloy, and hence the higher the proportion of Fe-Al-Si alloy, the more the overall growth of the interfacial alloy layer is suppressed. Therefore, the content of Si in the coating layer should be 1.0 mass% or more. On the other hand, if the content of Si in the coating layer exceeds 4.0 mass%, not only does the aforementioned effect of inhibiting the growth of the interfacial alloy layer become saturated, but corrosion is also accelerated due to the presence of excess Si phase in the coating layer. Therefore, the content of Si is 4.0 % or less. Further, the content of Si in the coating layer is preferably 3.0 mass% or less from the viewpoint of suppressing the existence of excess Si phase. In relation to the content of Mg described below, from the viewpoint of easily satisfying the relational equation (1) described below, the content of Si is preferably 1.0 mass% or more. It is preferably 3.0 mass% or less.

**[0029]** The coating layer contains 1.0 % to 10.0 % of Mg. The presence of Mg

in the coating layer allows the above-mentioned Si to exist in the form of an intermetallic compound of  $\text{Mg}_2\text{Si}$  phase, thereby inhibiting the acceleration of corrosion.

When Mg is contained in the coating layer, an intermetallic compound,  $\text{MgZn}_2$  phase, is also formed in the coating layer, which has the effect of further improving corrosion resistance. If the content of Mg in the coating layer is less than 1.0 mass%, sufficient corrosion resistance cannot be ensured because Mg is used for solid dissolution in  $\alpha\text{-Al}$  phase, which is the main phase, rather than for formation of intermetallic compounds ( $\text{Mg}_2\text{Si}$ ,  $\text{MgZn}_2$ ). On the other hand, if the content of Mg in the coating layer increases, the effect of improving corrosion resistance will be saturated, and workability will decrease due to the weakening of  $\alpha\text{-Al}$  phase. Therefore, the content of Mg is 10.0 % or less. Further, it is preferable that the content of Mg in the coating layer be 5.0 mass% or less from the viewpoint of suppressing dross generation during coating formation and facilitating control of the coating bath. From the viewpoint of easily satisfying the relational equation (1) below in relation to the content of Si, it is preferable to set the content of Mg to 3.0 mass%, and from the viewpoint of compatibility with dross suppression, it is more preferable to set the content of Mg to 3.0 mass% or more and to 5.0 mass% or less.

**[0030]** In the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet, diffraction intensities of Si and  $\text{Mg}_2\text{Si}$  in the coating layer as measured by an X-ray diffraction method should satisfy the following relation (1):

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

where  $\text{Si}(111)$  represents a diffraction intensity of a (111) plane of Si with an interplanar spacing  $d$  of 0.3135 nm, and  $\text{Mg}_2\text{Si}(111)$  represents a diffraction intensity of a (111) plane of  $\text{Mg}_2\text{Si}$  with an interplanar spacing  $d$  of 0.3668 nm.

**[0031]** As mentioned above, in the present disclosure, it is important to control the proportions of  $\text{Mg}_2\text{Si}$  and Si phases, which are formed in the coating layer by the inclusion of Mg and Si, to a specific ratio. Although the effects of these factors on corrosion resistance are still under investigation and have many unknowns, the following mechanisms can be inferred.

**[0032]** When a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet is exposed to a corrosion environment, the aforementioned intermetallic compounds dissolve preferentially over  $\alpha\text{-Al}$  phase, resulting in a Mg-rich environment near the

corrosion products formed. It is presumed that in such a Mg-rich environment, the corrosion products formed are less likely to be decomposed, and as a result, the protective action effect of the coating layer is enhanced. In addition, since this effect of improving the protective action effect of the coating layer is more surely expressed when Si in the coating layer exists as Mg<sub>2</sub>Si phase rather than Si phase, it is considered effective to reduce the proportion of the Si phase relative to the Mg<sub>2</sub>Si phase.

**[0033]** The proportions of Mg<sub>2</sub>Si and Si in the coating layer should satisfy the relation (1) of  $\text{Si}(111)/\text{Mg}_2\text{Si}(111) \leq 0.8$ , using the diffraction peak intensities obtained by an X-ray diffraction method. However, if the proportions of Mg<sub>2</sub>Si and Si in the coating layer do not satisfy the relation (1), that is if  $\text{Si}(111)/\text{Mg}_2\text{Si}(111) > 0.8$ , the amount of Si phase present in the coating layer will increase, and the aforementioned Mg-rich environment cannot be obtained near the corrosion products, making it difficult to obtain the effect of improving the protective action of the coating layer. From the same perspective, the ratio of Si to Mg<sub>2</sub>Si,  $\text{Si}(111)/\text{Mg}_2\text{Si}(111)$ , is preferably 0.5 or less, more preferably 0.3 or less, and particularly preferably 0.2 or less.

Regarding the proportions of Mg<sub>2</sub>Si and Si in the coating layer, even in the case where the composition of the coating layer satisfies the ranges specified in the present disclosure (i.e., Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, Mg: 1.0 mass% to 10.0 mass%, and Sr: 0.01 mass% to 1.0 mass%, with the balance being Zn and inevitable impurities), the effect of improving the protective action of the coating layer according to the present disclosure cannot be sufficiently obtained if Mg<sub>2</sub>Si and Si do not satisfy the relation (1).

**[0034]** In the relation (1), Si(111) represents a diffraction intensity of the (111) plane of Si with an interplanar spacing  $d$  of 0.3135 nm and Mg<sub>2</sub>Si(111) represents a diffraction intensity of the (111) plane of Mg<sub>2</sub>Si with an interplanar spacing  $d$  of 0.3668 nm.

The method of measuring Si(111) and Mg<sub>2</sub>Si(111) by X-ray diffraction may include mechanically scraping off a part of the coating layer and performing X-ray diffraction on the shaved part in powder form (i.e., powder X-ray diffraction measurement method). For the measurement of diffraction intensities, the diffraction peak intensity of Si corresponding to an interplanar spacing  $d$  of 0.3135 nm and the diffraction peak intensity of Mg<sub>2</sub>Si corresponding to an interplanar spacing  $d$  of 0.3668 nm can be measured and the ratio of these can be calculated to obtain  $\text{Si}(111)/\text{Mg}_2\text{Si}(111)$ .

The amount of the coating layer required for powder X-ray diffraction measurement (i.e., the amount of the coating layer to be scraped off may be at least 0.1 g, preferably at least 0.3 g, from the viewpoint of measuring Si(111) and Mg<sub>2</sub>Si(111) with high accuracy. Although steel sheet components other than the coating layer may be included in the powder when the coating layer is scraped off, these intermetallic compound phases are included only in the coating layer and do not affect the peak intensities. Further, the reason why X-ray diffraction is performed on the coating layer in powder form is because it is difficult to calculate the proportions of phases correctly due to the influence of the face orientation of the microstructure with solidification of the coating layer when X-ray diffraction is performed on the coating layer formed on the coated steel sheet.

**[0035]** Further, in the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet disclosed herein, from the viewpoint of more stably improving the corrosion resistance, it is preferable that the diffraction intensity of Si in the coating layer as measured by the X-ray diffraction method satisfy the following relation (2):

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

where Si(111) represents a diffraction intensity for the (111) plane of Si with an interplanar spacing  $d$  of 0.3135 nm.

In general, it is known that in the dissolution reaction of Al alloys in aqueous solution, the presence of the Si phase as a cathodic site promotes the dissolution of the surrounding  $\alpha$ -Al phase. Accordingly, the most excellent way to stabilize the corrosion resistance is to make the layer free from Si phase (i.e., to make the Si(111) diffraction peak intensity zero) as presented in the relation (2).

The method of measuring the diffraction peak intensity of the (111) plane of Si by X-ray diffraction is as described above.

**[0036]** There is no particular limitation on how to satisfy the above-mentioned relations (1) and (2). For example, in order to satisfy the relations (1) and (2), the proportions of Mg<sub>2</sub>Si and Si (diffraction intensities of Mg<sub>2</sub>Si(111) and Si(111)) can be controlled by adjusting the balance between the content of Si, the content of Mg, and the content of Al in the coating layer. As to the balance between the content of Si, the content of Mg, and the content of Al in the coating layer, it does not necessarily follow that the relations (1) and (2) can

be satisfied by simply setting a certain content ratio. In fact, for example, the content ratio of Mg and Al should be changed depending on the content in mass % of Si.

In addition to adjusting the balance between the content of Si, the content of Mg, and the content of Al in the coating layer, by adjusting the conditions during coating layer formation (e.g., cooling conditions after the formation of coating), the diffraction intensities of  $\text{Mg}_2\text{Si}(111)$  and  $\text{Si}(111)$  can be controlled to satisfy the relations (1) and (2).

**[0037]** In the hot-dip Al-Zn-Si-Mg-Sr steel sheet disclosed herein, the coating layer contains 0.01 mass% to 1.0 mass% of Sr. The coating layer containing Sr can more reliably suppress the occurrence of surface defects such as wrinkle-like unevenness defects and achieve good surface appearance.

The wrinkle-like defects are defects of wrinkle-like irregularities formed on the surface of the coating layer, which are observed as whitish streaks on the surface of the coating layer. Such wrinkle-like defects are more likely to occur when more Mg is added to the coating layer. Therefore, in the hot-dip coated steel sheet, by including Sr in the coating layer, Sr can be oxidized preferentially over Mg in the surface layer of the coating layer, and the oxidation reaction of Mg can be suppressed, thereby reducing the occurrence of wrinkle-like defects.

**[0038]** The coating layer contains 0.01 mass% to 1.0 mass% of Sr for the following reason. If the content of Sr in the coating layer is less than 0.01 mass%, the appearance improving effect cannot be obtained. If the content of Sr in the coating layer is more than 1.0 mass%, Sr is excessively incorporated into the interfacial alloy layer, which adversely affects coating and other properties. From the same perspective, the content of Sr in the coating layer is preferably 0.05 mass% or more. It is preferably 0.5 mass% or less. It is more preferably 0.1 mass% or more. It is more preferably 0.4 mass% or less.

In the hot-dip Al-Zn-Si-Mg-Sr steel sheet disclosed herein, the proportions of Si and  $\text{Mg}_2\text{Si}$  present in the coating layer satisfy the relation (1) and that the coating layer contains 0.01 mass% to 1.0 mass% of Sr. This allows the above-mentioned effect of Sr to improve surface appearance to be obtained more reliably. Although the cause of this is not clear, it is presumed to be because when the amount of Si in the coating layer increases, oxidation of the surface layer of the coating is difficult to suppress in the first place, and this affects the surface appearance improving effect obtained by the addition of Sr.

**[0039]** The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet contains Zn and inevitable impurities.

Among these, the inevitable impurities contain Fe. Fe is unavoidably contained in the coating layer as a result of its unavoidable inclusion by leaching of the steel sheet or bath equipment into the coating bath and its supply by diffusion from the base steel sheet during the formation of the interfacial alloy layer. The content of Fe in the coating layer is usually around 0.3 mass% to 2.0 mass%. Other inevitable impurities include, for example, Cr, Ni, and Cu. The total content of the inevitable impurities is not particularly limited, yet is preferably 5.0 mass% or less in total, since excessive content may affect various properties of the coated steel sheet.

**[0040]** From the viewpoint of achieving the effect of improving the stability of corrosion products and delaying the progress of corrosion, as is the case with Mg, it is also preferable that the coating layer further contain at least one selected from the group consisting of Cr, Mn, V, Mo, Ti, Ca, Ni, Co, Sb, and B. The total content of these components is preferably 0.01 mass% or more. The total content of these components is preferably 10 mass% or less. The reason why the total content of these components is set in the range of 0.01 mass% to 10 mass% is that a sufficient corrosion retardation effect can be obtained and the effect is not saturated.

**[0041]** From the viewpoint of satisfying various properties, the coating weight of the coating layer is preferably 45 g/m<sup>2</sup> or more per surface. The coating weight of the coating layer is preferably 120 g/m<sup>2</sup> or less per surface. When the coating weight of the coating layer is 45 g/m<sup>2</sup> or more, sufficient corrosion resistance can be obtained for applications requiring long-term corrosion resistance such as in building materials, and when the coating weight of the coating layer is 120 g/m<sup>2</sup> or less, excellent corrosion resistance can be achieved while suppressing the occurrence of defects such as coating cracks during processing. From the same perspective, the coating weight of the coating layer is more preferably 45 g/m<sup>2</sup> or more. The coating weight of the coating layer is more preferably 100 g/m<sup>2</sup> or less.

**[0042]** The coating weight of the coating layer can be derived, for example, by dissolving and exfoliating a specific area of the coating layer with a mixture of hydrochloric acid and hexamethylenetetramine as prescribed in JIS H 0401:2013, and calculating the difference in weight of the steel sheet before and after the exfoliation. To determine the coating weight per surface using

this method, the non-target surface may be sealed with tape so that the coated surface is not exposed thereon before the aforementioned dissolution.

5     **[0043]** The chemical composition of the coating layer can be confirmed, for example, by immersing the coating layer in hydrochloric acid or the like to dissolve it, and then analyzing the solution by a certain method such as ICP atomic emission spectrometry or atomic absorption spectrometry. This method is described for illustration purposes only and by no means a limitation of the disclosure. Any method that can accurately quantify the chemical composition of the coating layer may be used.

10    **[0044]** The composition of the coating layer of the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet obtained according to the present disclosure is, as a whole, almost equivalent to the composition of the coating bath. Therefore, the composition of the coating layer can be accurately controlled by controlling the composition of the coating bath.

15    **[0045]** As for the base steel sheet that constitutes the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet, there is no particular limitation, and a cold-rolled steel sheet or a hot-rolled steel sheet, for example, may be used as appropriate depending on the required performance and standards.

20    **[0046]** Further, the method of obtaining the base steel sheet is not limited. For example, in the case of a hot-rolled steel sheet, the one that has undergone hot rolling and pickling can be used, and in the case of a cold-rolled steel sheet, the one that has been additionally subjected to cold rolling can be used. In addition, recrystallization annealing, for example, can be performed prior to hot dip coating as appropriate for the required properties of the steel sheet.

25    **[0047]** There is no particular limitation on the method of producing the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet. For example, the method may include cleaning, heating, and dipping the base steel sheet in the coating bath in a continuous galvanizing line (CGL). In the heating of the steel sheet, it is effective to perform recrystallization annealing in order to control the microstructure of the base steel sheet itself, and to perform heating in a  
30    reducing atmosphere such as a nitrogen-hydrogen atmosphere in order to prevent oxidation of the steel sheet and to reduce a small amount of oxide film existing on the surface.

35    **[0048]** As for the coating bath used in the production of the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet, as mentioned above, the composition of the coating layer as a whole is almost equivalent to the composition of the coating bath.

Therefore, a coating bath containing 45 mass% to 65 mass% of Al, 1.0 mass% to 4.0 mass% of Si, 1.0 mass% to 10.0 mass% of Mg, and 0.01 mass% to 1.0 mass% of Sr, with the balance being Zn, Fe, and inevitable impurities can be used.

5    **[0049]** Further, the bath temperature of the coating bath is not limited, yet is preferably (melting point + 20 °C) or higher. It is preferably 650 °C or lower. The lower limit of the bath temperature is set at the temperature of (melting point + 20 °C) because the bath temperature should be equal to or higher than the solidifying point in order to carry out hot-dip coating treatment, and setting  
10 the lower limit at the temperature of (melting point + 20 °C) reliably prevents the components of the coating bath from being solidified due to localized drop of the bath temperature of the coating bath. On the other hand, the upper limit of the bath temperature is set at 650 °C because a bath temperature exceeding 650 °C may make rapid cooling of the coating layer difficult, thereby  
15 increasing the thickness of the interfacial alloy layer formed between the coating layer and the steel sheet.

**[0050]** Further, the temperature of the base steel sheet entering the coating bath (entering sheet temperature) is not particularly limited, yet from the viewpoint of securing proper coating characteristics in the continuous hot-dip  
20 coating operation and preventing the change of the bath temperature, it is preferable to control the temperature within  $\pm 20$  °C in relation to the temperature of the coating bath.

**[0051]** Further, the dipping time of the steel sheet in the coating bath is 0.5 seconds or more. This is because if the dipping time is less than 0.5 seconds,  
25 there is a possibility that a sufficient coating layer cannot be formed on the surface of the base steel sheet. Although no limit is placed on the upper limit of the dipping time, it is preferable to set the dipping time to 8 seconds or less, since a longer dipping time may result in a thicker interfacial alloy layer formed between the coating layer and the steel sheet.

30 **[0052]** Still further, during the cooling process after the coating, the sheet temperature is preferably cooled from 520 °C to 500 °C for at least 3 seconds. The precipitation start temperatures of single Si phase and Mg<sub>2</sub>Si in the coating layer are 500 °C to 490 °C for single Si phase and 520 °C to 500 °C for Mg<sub>2</sub>Si. This is because increasing the holding time in the temperature range of 520 °C  
35 to 500 °C, where only Mg<sub>2</sub>Si precipitates, promotes the precipitation of Mg<sub>2</sub>Si and suppresses the precipitation of single Si phase, thus making it easier to

satisfy the aforementioned relation (1).

**[0053]** In the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet, a paint layer can be formed either directly on the coating layer or on an intermediate layer on top of the coating layer, depending on the required performance.

5 **[0054]** The method of forming the paint layer is not particularly limited, and can be selected as appropriate depending on the required performance. For example, roll coater coating, curtain flow coating, spray coating, or other formation methods can be used. The paint layer can be formed by applying a paint containing an organic resin, and then heating and drying the applied paint  
10 by means of hot air drying, infrared heating, induction heating, or the like.

**[0055]** The intermediate layer is also not limited as long as it is formed between the coating layer and the paint layer of the hot-dip coated steel sheet.

**[0056]** (Surface-treated Steel Sheet)

The surface-treated steel sheet disclosed herein comprises: a coating layer on  
15 a surface thereof; and a chemical conversion layer formed on the coating layer. The configuration of the coating layer is the same as that of the coating layer of the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to the present disclosure as described above.

**[0057]** In the surface-treated steel sheet disclosed herein, a chemical  
20 conversion layer is formed on the coating layer.

Although it suffices for the chemical conversion layer to be formed on at least one surface of the surface-treated steel sheet, the chemical conversion layer may be formed on both surfaces of the surface-treated steel sheet depending on the application and required performance.

25 **[0058]** In the surface-treated steel sheet disclosed herein, 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 metal compound selected from the group  
30 consisting of a P compound, a Si compound, a Co compound, a Ni compound, a Zn compound, an Al compound, a Mg compound, a V compound, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

By forming the chemical conversion layer on the coating layer, it is possible to enhance the anti-rust and barrier effects of the chemical conversion layer, in  
35 addition to increasing its affinity with the coating layer and enabling the uniform formation of the chemical conversion layer on the coating layer. This

setup stably ensures proper corrosion resistance and anti-white rust property of the surface-treated steel sheet.

**[0059]** The resin that constitutes the chemical conversion layer may be at least one 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 from the viewpoint of improving corrosion resistance. From the same perspective, it is preferable that the resin contain at least one of an urethane resin or an acrylic resin. Examples of the resin constituting the chemical conversion layer also include addition polymerization products of the resins listed above.

**[0060]** Examples of the epoxy resin include: glycidyl-etherified products of bisphenol-A, bisphenol-F, or novolac epoxy resins; glycidyl-etherified products obtained by adding propylene oxide, ethylene oxide, or polyalkylene glycol to bisphenol-A epoxy resins; fatty epoxy resins; alicyclic epoxy resins; and polyether epoxy resins.

**[0061]** Examples of the urethane resin include oil-modified polyurethane resins, alkyd polyurethane resins, polyester polyurethane resins, polyether polyurethane resins, and polycarbonate polyurethane resins.

**[0062]** Examples of the acrylic resin include polyacrylic acid and copolymers thereof, polyacrylic acid esters and copolymers thereof, polymethacrylic acid and copolymers thereof, polymethacrylic acid esters and copolymers thereof, urethane-acrylic acid copolymers (or urethane-modified acrylic resins), and styrene-acrylic acid copolymers, and moreover, products obtained by modifying these resins with other resins such as alkyd resins, epoxy resins, or phenolic resins.

**[0063]** Examples of the acrylic silicon resin include products obtained by adding a curing agent to resins with hydrolysable alkoxysilyl groups on the side chains or ends of acrylic copolymers as the main agent. When the acrylic silicon resin is used, excellent weather resistance can be obtained in addition to excellent corrosion resistance.

**[0064]** Examples of the alkyd resin include oil-modified alkyd resins, rosin-modified alkyd resins, phenol-modified alkyd resins, styrenated alkyd resins, silicon-modified alkyd resins, acrylic-modified alkyd resins, oil-free alkyd resins, and high-molecular-weight oil-free alkyd resins.

**[0065]** Examples of the polyester resin include polycondensates synthesized by dehydration-condensation of polyvalent carboxylic acids and polyalcohols

to form ester bonds. Examples of the polyvalent carboxylic acids include terephthalic acid and 2,6-naphthalene dicarboxylic acid. Examples of the polyalcohols include ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,4-cyclohexanedimethanol. Specifically, the polyesters include polyethylene  
5 terephthalate, polytrimethylene terephthalate, polyethylene naphthalate, and polybutylene naphthalate. In addition, acrylic-modified products of these polyester resins can also be used.

**[0066]** Examples of the polyalkylene resins include: ethylene copolymers such as ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers,  
10 and carboxyl-modified polyolefin resins; ethylene-unsaturated carboxylic acid copolymers; and ethylene ionomers. In addition, products obtained by modifying these resins with other resins such as alkyd resins, epoxy resins, or phenolic resins can also be used.

**[0067]** Examples of the amino resin include thermosetting resins formed by  
15 the reaction of an amine or amide compound with an aldehyde, including melamine resins, guanamine resins, and thiourea resins. Among these preferred are melamine resins in terms of, for example, corrosion resistance, weather resistance, and adhesion. Examples of the melamine resin include, but are not limited to, butylated melamine resins, methylated melamine resins, and  
20 waterborne melamine resins.

**[0068]** Examples of the fluororesin include fluoroolefin polymers and copolymers of fluoroolefins and alkyl vinyl ethers, cycloalkyl vinyl ethers, carboxylic acid-modified vinyl esters, hydroxyalkyl allyl ethers, tetrafluoropropyl vinyl ethers, and the like. When these fluororesins are used,  
25 not only excellent corrosion resistance, but also excellent weather resistance and hydrophobicity can be obtained.

**[0069]** Further, it is especially preferable to use a curing agent with the aim of improving corrosion resistance and workability. As the curing agent, urea resins (such as butylated urea resins), melamine resins (such as butylated  
30 melamine resins or butyl ether melamine resins), butylated urea-melamine resins, amino resins such as benzoguanamine resins, block isocyanates, oxazoline compounds, or phenol resins can be used as appropriate.

**[0070]** As for the metal compound that constitutes the chemical conversion layer, at least one selected from the group consisting of a P compound, a Si  
35 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 perspective, it is preferable that the metal compound contain at least one of a P compound, a Si compound, or a V compound.

5 [0071] The P compound can be included in the chemical conversion layer to improve corrosion resistance and perspiration resistance. The P compound is a P-containing compound that can contain, for example, at least one selected from the group consisting of inorganic phosphoric acid, organic phosphoric acid, and their salts.

10 [0072] As the inorganic phosphoric acid, organic phosphoric acid, and their salts, any compounds can be used without any particular limitation. For example, as the inorganic phosphoric acid, it is preferable to use at least one selected from the group consisting of phosphoric acid, primary phosphate, secondary phosphate, tertiary phosphate, pyrophosphoric acid, pyrophosphate, tripolyphosphoric acid, tripolyphosphate, phosphorous acid, phosphite, hypophosphorous acid, and hypophosphite. As the organic phosphoric acid, it is preferable to use phosphonic acid (phosphonic acid compound). As the phosphonic acid, it is preferable to use at least one selected from the group consisting of nitrilotrismethylenephosphonic acid, phosphonobutane tricarboxylic acid, methyl diphosphonic acid, methylene phosphonic acid, and ethylidene diphosphonic acid.

When the P compound is a salt, the salt is preferably a salt of group 1-13 elements in the periodic table, more preferably a metal salt, and preferably at least one selected from the group consisting of alkali metal salts and alkaline earth metal salts.

25 [0073] When a chemical conversion treatment liquid containing the P compound is applied to the hot dip Al-Zn-Si-Mg coated steel sheet, the P compound causes the surface of the coating layer to be etched, thereby forming, on the coating layer side of the chemical conversion layer, an enriched layer in which the constituent elements of the coating layer, Al, Zn, Si and Mg, are incorporated. The formation of the enriched layer increases the bonding force between the chemical conversion layer and the surface of the coating layer, improving the adhesion of the chemical conversion layer.

35 The concentration of the P compound in the chemical conversion treatment liquid may be, but is not limited to, 0.25 mass% to 5 mass%. If the concentration of the P compound is less than 0.25 mass%, the etching effect is insufficient and adhesion to the coating interface is reduced, resulting not only

in reduced corrosion resistance in the flat parts but also in reduced corrosion resistance and perspiration resistance in defective parts, cut edges, and those parts of the coating or coating layer damaged by processing or the like. From the same perspective, the concentration of the P compounds is preferably 0.35 mass% or more, and more preferably 0.50 % or more. On the other hand, if the concentration of the P compound exceeds 5 mass%, not only will the life of the chemical conversion treatment liquid be shortened, but the appearance after the formation of the coating layer is likely to become uneven, and the amount of P leaching out from the chemical conversion layer may increase, resulting in a decrease in blackening resistance. From the same perspective, the concentration of the P compounds is preferably 3.5 mass% or less, and more preferably 2.5 mass% or less. For the content of the P compound in the chemical conversion layer, for example, by applying and drying a chemical conversion treatment liquid with the concentration of the P compound ranging from 0.25 mass% to 5 mass%, the coating weight of P in the chemical conversion layer after drying can be 5 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>.

**[0074]** The Si compound is a component that, together with the resin, forms the backbone of the chemical conversion layer, and enhances affinity with the coating layer and allows the chemical conversion layer to be formed uniformly. The Si compound is a Si-containing compound that preferably contains at least one selected from the group consisting of, for example, silica, trialkoxysilane, tetraalkoxysilane, and silane coupling agents.

**[0075]** The silica may be any silica without any particular limitation. For example, at least one of wet silica or dry silica can be used as the silica. As colloidal silica, which is a type of the wet silica, for example, SNOWTEX O, C, N, S, 20, OS, OXS, NS, etc., manufactured by Nissan Chemical Corporation, can be suitably used. As the dry silica, for example, AEROSIL 50, 130, 200, 300, 380, etc., manufactured by NIPPON AEROSIL Co., Ltd., can be suitably used.

**[0076]** The trialkoxysilane may be any trialkoxysilane without any particular limitation. For example, preferred are trialkoxysilanes represented by the general formula:  $R_1Si(OR_2)_3$  (where  $R_1$  is hydrogen or an alkyl group having 1-5 carbon atoms, and  $R_2$  is the same or different alkyl group having 1-5 carbon atoms). Such trialkoxysilanes include, for example, trimethoxysilane, triethoxysilane, and methyltriethoxysilane.

**[0077]** The tetraalkoxysilane may be any tetraalkoxysilane without any

particular limitation. For example, preferred are tetraalkoxysilanes represented by the general formula:  $\text{Si}(\text{OR})_4$  (where R is the same or different alkyl group having 1-5 carbon atoms). Such tetraalkoxysilanes include, for example, tetramethoxysilane, tetraethoxysilane, and tetrapropoxysilane.

5 **[0078]** The silane coupling agent may be any silane coupling agent without any particular limitation. Examples of the silane coupling agent include  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -aminopropylmethyldiethoxysilane,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -methacryloxypropyltriethoxysilane,  $\gamma$ -mercaptopropylmethyldimethoxysilane, and  $\gamma$ -mercaptopropyltrimethoxysilane, vinyltriethoxysilane, and  $\gamma$ -isocyanate propyltriethoxysilane.

**[0079]** By including the Si compound in the chemical conversion layer, the Si  
15 compound will dehydrate and condense to form an amorphous chemical conversion layer having a siloxane bond with a high barrier effect to shield against corrosion factors. In addition, the chemical conversion layer with higher barrier properties is formed by bonding with the aforementioned resins. Further, in a corrosion environment, dense and stable corrosion products are  
20 formed in defective parts or those parts of the coating or coating layer damaged by processing, thereby providing the combined effect with the coating layer to suppress corrosion of the base steel sheet. From the viewpoint of being highly effective in forming stable corrosion products, it is preferable to use at least one of colloidal silica or dry silica as the Si compound.

25 **[0080]** The concentration of the Si compound in the chemical conversion treatment liquid to form 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, a barrier effect by siloxane bonding can be obtained, resulting in improved corrosion resistance and perspiration  
30 resistance in defective parts, cut edges, and those parts damaged by processing or the like, in addition to improved corrosion resistance in flat parts. If the concentration of the Si compound is 9.5 mass% or less, the life of the chemical conversion treatment liquid can be extended. By applying and drying a chemical conversion treatment liquid with the concentration of the Si  
35 compound ranging from 0.2 mass% to 9.5 mass%, the coating weight of Si in the chemical conversion layer after drying can be 2 mg/m<sup>2</sup> to 95 mg/m<sup>2</sup>.

**[0081]** The Co and Ni compounds can be included in the chemical conversion layer to improve blackening resistance. This may be due to the fact that Co and Ni have the effect of delaying the leaching of water-soluble components out from the coating layer in a corrosion environment. In addition, Co and Ni are  
5 elements that are less susceptible to oxidation than Al, Zn, Si, and Mg. Therefore, by enriching (forming an enriched layer of) at least one of the Co compound or the Ni compound at the interface between the chemical conversion layer and the coating layer, the enriched layer becomes a barrier against corrosion, resulting in improved blackening resistance.

10 **[0082]** By using a chemical conversion treatment liquid containing the Co compound, Co can be included in the chemical conversion layer and incorporated into the enriched layer. It is preferable to use a cobalt salt as the Co compound. As the cobalt salt, it is more preferable to use at least one of cobalt sulfate, cobalt carbonate, or cobalt chloride.

15 By using a chemical conversion treatment liquid containing the Ni compound, Ni can be included in the chemical conversion layer and incorporated into the enriched layer. It is preferable to use a nickel salt as the Ni compound. As the nickel salt, it is more preferable to use at least one of nickel sulfate, nickel carbonate, or nickel chloride.

20 **[0083]** The concentration of the Co and/or Ni compounds in the chemical conversion treatment liquid is not particularly limited, yet can be 0.25 mass% to 5 mass% in total. If the concentration of the Co and/or Ni compounds is less than 0.25 mass%, the interfacial enriched layer will be non-uniform, and not only will the corrosion resistance in flat parts be reduced, but also the corrosion  
25 resistance in defective parts, cut edges, and those parts of the coating or coating layer damaged by processing or the like may be reduced. From the same perspective, the concentration is preferably 0.5 mass% or more, and more preferably 0.75 mass% or more. On the other hand, if the concentration of the Co and/or Ni compounds exceeds 5 mass%, the appearance after the formation  
30 of the coating layer is likely to become non-uniform and corrosion resistance may decrease. From the same perspective, the concentration is preferably 4.0 mass% or less, and more preferably 3.0 mass% or less. By applying and drying a chemical conversion treatment liquid with a total concentration of the Co and/or Ni compounds ranging from 0.25 mass% to 5 mass%, the total coating  
35 weight of Co and Ni in the chemical conversion layer after drying can be 5 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>.

**[0084]** As for the Al compound, the Zn compound, and the Mg compound, by including them in the chemical conversion treatment liquid, an enriched layer containing at least one of Al, Zn, or Mg can be formed on the coating layer side of the chemical conversion layer. The enriched layer formed can improve corrosion resistance.

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

**[0085]** Examples of the Al compound include at least one selected from the group consisting of aluminum sulfate, aluminum carbonate, aluminum chloride, aluminum oxide, and aluminum hydroxide.

Examples of the Zn compound include at least one selected from the group consisting of zinc sulfate, zinc carbonate, zinc chloride, zinc oxide, and zinc hydroxide.

Examples of the Mg compound include at least one selected from the group consisting of magnesium sulfate, magnesium carbonate, magnesium chloride, magnesium oxide, and magnesium hydroxide.

**[0086]** The total concentration of the Al, Zn, and/or Mg compounds in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.25 mass% or more. The total concentration is preferably 5 mass% or less. If the total concentration is 0.25 mass% or more, the aforementioned enriched layer can be formed more effectively, resulting in further improvement of corrosion resistance. In addition, if the total concentration is 5 mass% or less, the appearance of the chemical conversion layer becomes more uniform and the corrosion resistance is further improved in flat parts, defective parts, and those parts of the coating or coating layer damaged by processing or the like.

**[0087]** The V compound can be included in the chemical conversion layer to allow V to leach out moderately under a corrosion environment and combine with zinc ions and other coating components that also leach out under a corrosion environment to form a dense protective layer. The protective layer thus formed can further enhance corrosion resistance against such corrosion that propagates not only in flat parts of the steel sheet, but also in defective parts, those parts of the coating layer damaged by processing, cut edges to flat parts, and so on.

**[0088]** The V compound is a V-containing compound including, for example,

at least one selected from the group consisting of sodium metavanadate, vanadyl sulfate, and vanadium acetylacetonate.

**[0089]** The concentration of the V compound in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.05 mass% or more. The concentration of the V compound is preferably 4 mass% or less. If the concentration of the V compound is 0.05 mass% or more, the V compound is more likely to leach out in a corrosion environment to form a protective layer, improving corrosion resistance in defective parts, cut edges, and those parts of the coating layer damaged by processing. On the other hand, if the concentration of the V compound exceeds 4 mass%, the appearance of the chemical conversion layer tends to be non-uniform and blackening resistance also decreases.

**[0090]** The Mo compound can be included in the chemical conversion layer to increase the blackening resistance of the surface-treated steel sheet. The Mo compound is a Mo-containing compound that can be obtained by adding one or both of molybdic acid and molybdate to the chemical conversion treatment liquid.

Examples of the molybdate include, for example, at least one selected from the group consisting of sodium molybdate, potassium molybdate, magnesium molybdate, and zinc molybdate.

**[0091]** The concentration of the Mo compound in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.01 mass% or more. The concentration of the Mo compound is preferably 3 mass% or less. If the concentration of the Mo compound is 0.01 mass% or more, the formation of oxygen-deficient zinc oxide can be further suppressed, making it possible to further improve blackening resistance. In addition, if the concentration of the Mo compound is 3 mass% or less, the life of the chemical conversion treatment liquid can be further extended and corrosion resistance can be further improved.

**[0092]** The Zr and Ti compounds can be included in the chemical conversion layer to prevent the chemical conversion layer from becoming porous and to densify the layer. As a result, corrosion factors are less likely to penetrate the chemical conversion layer, thereby enhancing corrosion resistance.

**[0093]** The Zr compound is a Zr-containing compound. As the Zr compound, for example, at least one selected from the group consisting of zirconyl acetate, zirconyl sulfate, zirconyl potassium carbonate, zirconyl sodium carbonate, and

zirconyl ammonium carbonate can be used. Among these, organotitanium chelate compounds are suitable because they densify the resulting layer and provide even better corrosion resistance when the chemical conversion treatment liquid is dried to form the layer.

5   **[0094]** The Ti compound is a Ti-containing compound. As the Ti compound, for example, at least one selected from the group consisting of titanium sulfate, titanium chloride, titanium hydroxide, titanium acetylacetonato, titanium octyleneglycolate, and titanium ethylacetoacetate can be used.

10   **[0095]** The total concentration of the Zr and/or Ti compounds in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.2 mass% or more. The total concentration is preferably 20 mass% or less. If the total concentration of the Zr and/or Ti compounds is 0.2 mass% or more, the effect of suppressing permeation of corrosion factors is enhanced, and the corrosion resistance can be further improved not only in flat parts but also in  
15   defective parts, cut edges, and those parts of the coating layer damaged by processing. In addition, if the total concentration of the Zr and/or Ti compounds is 20 mass% or less, the life of the chemical conversion treatment liquid can be further extended.

20   **[0096]** The Ca compound has the effect of reducing the corrosion rate when included in the chemical conversion layer.

25   **[0097]** The Ca compound is a Ca-containing compound. Examples of the Ca compound include Ca oxides, Ca nitrates, Ca sulfates, and Ca-containing intermetallic compounds. More specifically, examples of the Ca compound include CaO, CaCO<sub>3</sub>, Ca(OH)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and CaSO<sub>4</sub>·2H<sub>2</sub>O. The content of the Ca compound in the chemical conversion layer is not particularly limited.

30   **[0098]** The chemical conversion layer may contain various known components normally used in the field of paints, if necessary. For example, such components include: surface adjustment agents such as leveling agents and defoamers; additives such as dispersants, anti-settling agents, UV absorbers, light stabilizers, silane coupling agents, and titanate coupling agents; pigments such as colored pigments, body pigments, and optical brightening agents; curing catalysts; organic solvents; and lubricants.

35   **[0099]** In the surface-treated steel sheet disclosed herein, it is preferable that the chemical conversion layer do not contain harmful components such as hexavalent chromium, trivalent chromium, and fluorine. This is because the chemical conversion treatment liquid used to form the chemical conversion

layer does not contain these harmful components, making it safer and less harmful to the environment.

**[0100]** The coating weight of the chemical conversion layer is not limited. For example, from the viewpoint of preventing exfoliation of the chemical conversion layer while ensuring more reliable corrosion resistance, the coating weight of the chemical conversion layer is preferably 0.1 g/m<sup>2</sup> or more, and more preferably 0.5 g/m<sup>2</sup> or more. The coating weight of the chemical conversion layer is preferably 3.0 g/m<sup>2</sup> or less, and more preferably 2.5 g/m<sup>2</sup> or less. By setting the coating weight of the chemical conversion layer to 0.1 g/m<sup>2</sup> or more, corrosion resistance can be ensured more reliably, and by setting the coating weight of the chemical conversion layer to 3.0 g/m<sup>2</sup> or less, cracking and exfoliation 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 measuring the proportions of elements whose content in the layer is known beforehand by X-ray fluorescence analysis of the layer.

**[0101]** The method of forming the chemical conversion layer is not particularly limited, and can be selected according to the required performance, manufacturing facilities, and so on. For example, the chemical conversion layer can be formed by continuously applying the chemical conversion treatment liquid on the coating layer using a roll coater, etc., followed by drying at a peak metal temperature (PMT) of about 60 °C to about 200 °C using hot blast, induction heating, or the like. In addition to a roll coater, other known means such as airless spray, electrostatic spray, curtain flow coater, or the like can be employed as appropriate for the application of the chemical conversion treatment liquid. Further, the chemical conversion layer may be in the form of either monolayer or multilayer, as long as it contains the aforementioned resins and metal compounds, and is not limited to any particular type.

**[0102]** In the surface-treated steel sheet disclosed herein, a paint layer may be formed on the chemical conversion layer, if necessary.

**[0103]** (Pre-painted Steel Sheet)

The pre-painted steel sheet disclosed herein is a pre-painted steel sheet in which a paint layer is formed either directly on the coating layer or on a chemical conversion layer on top of the coating layer.

The configuration of the coating layer is the same as that of the coating layer of the hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to the present

disclosure as described above.

**[0104]** In the pre-painted steel sheet disclosed herein, a chemical conversion layer can be formed on the coating layer.

Although it suffices for the chemical conversion layer to be formed on at least one surface of the pre-painted steel sheet, the chemical conversion layer may be formed on both surfaces of the pre-painted steel sheet depending on the application and required performance.

**[0105]** In the pre-painted steel sheet disclosed herein, the chemical conversion layer contains: a resin component containing (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%, in which a content ratio of (a) to (b), (a):(b), is in the range of 3:97 to 60:40 by mass; and an inorganic compound containing 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.

By forming the chemical conversion layer on the coating layer, the strength and adhesion of the chemical conversion layer can be improved, while corrosion resistance can also be enhanced.

**[0106]** The resin component constituting the chemical conversion layer contains (a) the anionic polyurethane resin having an ester bond and the epoxy resin (b) having a bisphenol skeleton.

**[0107]** Examples of the anionic polyurethane resin (a) having an ester bond include resins obtained by copolymerizing dimethylolalkyl acid with a reaction product of polyester polyol and diisocyanate or polyisocyanate having two or more isocyanate groups. The anionic polyurethane resin (a) having an ester bond can be dispersed in water or other liquids using a known method to obtain a chemical conversion treatment liquid.

**[0108]** Examples of the polyester polyol include: polyesters obtained by dehydration-condensation reactions from glycol components and acid components such as ester-forming derivatives of hydroxyl carboxylic acids; polyesters obtained by ring-opening polymerization reactions of cyclic ester compounds such as  $\epsilon$ -caprolactone; and copolymerized polyesters of these compounds.

Examples of the polyisocyanate include aromatic polyisocyanates, aliphatic polyisocyanates, and alicyclic polyisocyanates. Examples of the aromatic polyisocyanate include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate,

m-xylene diisocyanate, diphenylmethane diisocyanate, 2,4-diphenylmethane diisocyanate, 2,2-diphenylmethane diisocyanate, triphenylmethane triisocyanate, polymethylene polyphenyl polyisocyanate, naphthalene diisocyanate, and their derivatives (e.g., prepolymers obtained by reaction with polyols, modified polyisocyanates such as carbodiimide compounds of diphenylmethane diisocyanate).

**[0109]** When synthesizing urethane by reacting the polyester polyol with the diisocyanate or polyisocyanate, for example, the anionic polyurethane resin (a) having an ester bond can be obtained by copolymerizing dimethylolalkyl acid and self-emulsifying the product to make it water soluble (water dispersible). In this case, examples of the dimethylolalkyl acid include dimethylolalkyl acids having 2-6 carbon atoms, more specifically, dimethylolethane acid, dimethylolpropanoic acid, dimethylolbutanoic acid, dimethylolheptanoic acid, and dimethylolhexanoic acid.

**[0110]** The epoxy resin (b) having a bisphenol skeleton may be any known epoxy resin. Examples thereof include bisphenol-A epoxy resins, bisphenol-F epoxy resins, bisphenol-AD epoxy resins, and bisphenol-S epoxy resins. 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 it is preferable that the component [A] contain a bisphenol-A epoxy resin or a bisphenol-F epoxy resin; among these more preferred is a bisphenol-A epoxy resin. The epoxy resin (b) having a bisphenol skeleton can be dispersed in water or other liquids using a known method to obtain a chemical conversion treatment liquid.

**[0111]** The resin component acts as a binder of the conversion chemical conversion layer. The anionic polyurethane resin (a) having an ester bond, which constitutes the binder, can achieve the effect of making the chemical conversion layer less likely to be fractured (exfoliated) when subjected to processing because of its flexibility. The epoxy resin (b) having a bisphenol skeleton can achieve the effect of improving the adhesion with the zinc or zinc alloy coated steel sheet as the base steel sheet and with the upper primer paint layer.

The resin component is contained in a total of 30 mass% to 50 mass% in the chemical conversion layer. If the content of the resin component is less than 30 mass%, the binder effect of the chemical conversion layer is reduced, and if the content exceeds 50 mass%, the function of the inorganic components

described below, such as inhibitor action, is reduced. From the same viewpoint, the content of the resin component in the chemical conversion layer is preferably 35 mass% or more. It is preferably 45 mass% or less.

5     **[0112]** Further, in the resin component, it is necessary that the content ratio of the anionic polyurethane resin (a) having an ester bond to the epoxy resin (b) having a bisphenol skeleton, (a):(b), be in the range of 3:97 to 60:40 by mass. If the ratio of (a):(b) is outside this range, sufficient corrosion resistance cannot be obtained due to a decrease in flexibility and adhesion as a chemical conversion layer. From the same perspective, the ratio of (a):(b) is preferably  
10    in the range of 10:90 to 55:45.

**[0113]** The resin component may include resins other than the anionic polyurethane resin (a) having an ester bond and the epoxy resin (b) having a bisphenol skeleton (i.e., other resin components), depending on the required performance. The other resin components include, but are not limited to, for  
15    example, at least one or a combination of two or more of acrylic resins, acrylic silicon resins, alkyd resins, polyester resins, polyalkylene resins, amino resins, and fluororesins.

      When the resin component contains the other resins, the total content of the anionic polyurethane resin (a) having an ester bond and the epoxy resin (b)  
20    having a bisphenol skeleton is preferably 50 mass% or more, and more preferably 75 mass% or more. This is to ensure that the flexibility and adhesion as the chemical conversion layer is obtained more reliably.

**[0114]** 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  
25    zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound.

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

**[0115]** The vanadium compound is added to the chemical conversion treatment liquid to act as an anti-rust agent (inhibitor). The inclusion of the vanadium  
30    compound in the chemical conversion layer allows the vanadium compound to leach out moderately under a corrosion environment and combine with zinc ions and other coating components that also leach out under a corrosion environment to form a dense protective layer. The protective layer thus formed can further enhance corrosion resistance against such corrosion that propagates  
35    not only in flat parts of the steel sheet, but also in defective parts, those parts of the coating layer damaged by processing, cut edges to flat parts, and so on.

Examples of the vanadium compound include vanadium pentoxide, metavanadate, ammonium metavanadate, vanadium oxytrichloride, vanadium trioxide, vanadium dioxide, magnesium vanadate, vanadyl acetylacetonate, and vanadium acetylacetonate. Among these, in particular, it is desirable to use  
5 tetraivalent vanadium compounds or tetraivalent vanadium compounds obtained by reduction or oxidation.

**[0116]** The content of the vanadium compound in the chemical conversion layer is 2 mass% to 10 mass%. The reason is as follows. If the content of the vanadium compound in the chemical conversion layer is less than 2 mass%, the  
10 inhibitor effect is not sufficient, resulting in a decrease in corrosion resistance. If the content of the vanadium compound exceeds 10 mass%, the moisture resistance of the chemical conversion layer will decrease.

**[0117]** The zirconium compound is contained in the chemical conversion layer and is expected to improve the strength and corrosion resistance as the  
15 chemical conversion layer by reacting with the coating metal and coexisting with the resin components. Further, the zirconium compound itself is expected to have a barrier effect since it contributes to the formation of a dense chemical conversion layer and exhibits good covering properties.

Examples of the zirconium compound include neutralized salts of zirconium sulfate, zirconium carbonate, zirconium nitrate, zirconium lactate, zirconium  
20 acetate, and zirconium chloride.

**[0118]** The content of the zirconium compound in the chemical conversion layer is 40 mass% to 60 mass%. The reason is as follows. If the content of the zirconium compound in the chemical conversion layer is less than 40 mass%,  
25 the strength and corrosion resistance as the chemical conversion layer will decrease. If the content of the zirconium compound exceeds 60 mass%, the chemical conversion layer will become brittle, resulting in fracture and exfoliation of the chemical conversion layer under severe processing conditions.

**[0119]** The fluorine compound is contained in the chemical conversion layer and acts as an agent to impart adhesion with the coating layer. As a result, the corrosion resistance of the chemical conversion layer can be increased.

As the fluorine compound, fluoride salts such as ammonium salts, sodium salts, and potassium salts, or fluorine compounds such as ferrous fluorides and ferric  
35 fluorides can be used. Among these, fluoride salts such as ammonium fluoride, sodium fluoride, and potassium fluoride are preferred.

**[0120]** The content of the fluorine compound in the chemical conversion layer is 0.5 mass% to 5 mass%. The reason is as follows. If the content of the fluorine compound in the chemical conversion layer is less than 0.5 mass%, sufficient adhesion cannot be obtained in the processed parts. If the content of the fluorine compound exceeds 5 mass%, the moisture resistance of the chemical conversion layer is reduced.

**[0121]** The coating weight of the chemical conversion layer is not limited. For example, from the viewpoint of improving the adhesion of the chemical conversion layer while more reliably ensuring corrosion resistance, the coating weight of the chemical conversion layer is preferably 0.025 g/m<sup>2</sup> or more. It is preferably 0.5 g/m<sup>2</sup> or less. By setting the coating weight of the chemical conversion layer to 0.025 g/m<sup>2</sup> or more, corrosion resistance can be ensured more reliably, and by setting the coating weight of the chemical conversion layer to 0.5 g/m<sup>2</sup> or less, exfoliation of the chemical conversion layer can be suppressed.

The coating weight of the chemical conversion layer may be determined by a method appropriately selected from existing methods, such as measuring the proportions of elements whose content in the layer is known beforehand by X-ray fluorescence analysis of the layer.

**[0122]** The method of forming the chemical conversion layer is not particularly limited, and can be selected according to the required performance, manufacturing facilities, and so on. For example, the chemical conversion layer can be formed by continuously applying the chemical conversion treatment liquid on the coating layer using a roll coater, etc., followed by drying at a peak metal temperature (PMT) of about 60 °C to about 200 °C using hot blast, induction heating, or the like. In addition to a roll coater, other known means such as airless spray, electrostatic spray, curtain flow coater, or the like can be employed as appropriate for the application of the chemical conversion treatment liquid. Further, the chemical conversion layer may be in the form of either monolayer or multilayer, as long as it contains the aforementioned resins and metal compounds, and is not limited to any particular type.

**[0123]** As described above, in the pre-painted steel sheet disclosed herein, a paint layer is formed either directly on the coating layer or on a chemical conversion layer on top of the coating layer, and the paint layer comprises at least a primer paint layer.

**[0124]** According to the present disclosure, the primer paint layer contains a

polyester resin having a urethane bond and an inorganic compound including a vanadium compound, a phosphoric acid compound, and a magnesium oxide.

The inclusion of the polyester resin having a urethane bond and the inorganic compound in the primer paint layer allows improvement of corrosion resistance while enhancing the adhesion of the paint layer.

**[0125]** The primer paint layer contains the polyester resin having a urethane bond as its main component. The polyester resin having a urethane bond has both flexibility and strength, which makes it difficult for the primer paint layer to crack when subjected to processing, and its high affinity with the chemical conversion layer containing a urethane resin can contribute to improving corrosion resistance, especially, in the processed parts.

In this case, the term "main component" means the component with the highest content among the components contained in the primer paint layer.

**[0126]** As the polyester resin having a urethane bond, known resins such as those obtained by the reaction of polyester polyol and diisocyanate or polyisocyanate having two or more isocyanate groups can be used. Resins that are obtained by curing resins made by reacting the polyester polyol with the diisocyanate or polyisocyanate in excess of hydroxyl groups (urethane-modified polyester resins) with blocked polyisocyanate can also be used.

**[0127]** 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.

Examples of the polyhydric alcohol include glycol and trivalent or higher valent 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-hexanediol, 2-butyl-2-ethyl-1,3-propanediol, methylpropanediol, cyclohexanedimethanol, and 3,3-diethyl-1,5-pentanediol. Examples of the trivalent or higher valent alcohols include glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, and dipentaerythritol. These polyhydric alcohols can be used alone or in combination of two or more.

As the polybasic acid, a polyvalent carboxylic acid is usually used. However, monovalent fatty acids and other acids can be used in combination, if necessary.

Examples of the polyvalent carboxylic acid include phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, 4-methylhexahydrophthalic

acid, bicyclo[2,2,1]heptane-2,3-dicarboxylic acid, trimellitic acid, adipic acid, sebacic acid, succinic acid, azelaic acid, fumaric acid, maleic acid, itaconic acid, pyromellitic acid, dimeric acid, and their acid anhydrides, as well as 1,4-cyclohexanedicarboxylic acid, isophthalic acid, tetrahydroisophthalic acid, hexahydroisophthalic acid, and hexahydro terephthalic acid. These polybasic acids can be used alone or in combination of two or more.

**[0128]** Examples of the polyisocyanate include: aliphatic diisocyanates such as hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, and dimer diisocyanate; aromatic diisocyanates such as xylylene diisocyanate (XDI), meta-xylylene diisocyanate, tolylene diisocyanate (TDI), and 4,4-diphenylmethane diisocyanate (MDI); cyclic aliphatic diisocyanates such as isophorone diisocyanate, hydrogenated XDI, hydrogenated TDI, and hydrogenated MDI; and their adducts, biurets, and isocyanurates. These polyisocyanates can be used alone or in combination of two or more.

**[0129]** The hydroxyl group value of the polyester resin having a urethane bond is not particularly limited. However, from the viewpoint of solvent resistance and workability, the hydroxyl group value of the polyester resin having a urethane bond is preferably 5 mgKOH/g or more, more preferably 7 mgKOH/g or more, and even more preferably 10 mgKOH/g or more. It is preferably 120 mgKOH/g or less, more preferably 100 mgKOH/g or less, and even more preferably 80 mgKOH/g or less.

Furthermore, in terms of solvent resistance and workability, the number average molecular weight of the polyester resin having a urethane bond is preferably 500 or more, more preferably 700 or more, and even more preferably 800 or more. It is preferably 15,000 or less, more preferably 12,000 or less, and even more preferably 10,000 or less.

**[0130]** The content of the polyester resin having a urethane bond in the primer paint layer is preferably 40 mass% or more. It is preferably 88 mass% or less. If the content of the polyester resin having a urethane bond is less than 40 mass%, the binder function as the primer paint layer may decrease, while if the content of polyester resin having a urethane bond exceeds 88 mass%, the function by the inorganic substances as described below, such as inhibitor action, may decrease.

**[0131]** One of the inorganic compounds, a vanadium compound, acts as an inhibitor. Examples of the vanadium compound include vanadium pentoxide, metavanadate, ammonium metavanadate, vanadium oxytrichloride, vanadium

trioxide, vanadium dioxide, magnesium vanadate, vanadyl acetylacetonate, and vanadium acetylacetonate. Among these, in particular, it is desirable to use tetravalent vanadium compounds or tetravalent vanadium compounds obtained by reduction or oxidation.

5 The vanadium compound added to the primer paint layer may be the same as or different from the vanadium compound added to the chemical conversion layer. In the vanadate compound, it is believed that vanadate ions, which are gradually leached into moisture entering from the outside, react with ions on the surface of the zinc or zinc alloy coated steel sheet to form a passive layer  
10 with good adhesion, protecting exposed metal parts and preventing rust.

**[0132]** The content of the vanadium compound in the primer paint layer is not particularly limited. However, from the viewpoint of compatibility between corrosion resistance and moisture resistance, it is preferably 4 mass% or more. It is preferably 20 mass% or less. If the content of the vanadium compound is  
15 less than 4 mass%, the inhibitor effect may be reduced, resulting in a decrease in corrosion resistance. If the content of the vanadium compound exceeds 20 mass%, the moisture resistance of the primer paint layer may be reduced.

**[0133]** Phosphate compounds, one of the inorganic compounds, also act as inhibitors. Example of the phosphate compounds include phosphoric acid, ammonium salts of phosphoric acid, alkali metal salts of phosphoric acid, and  
20 alkaline earth metal salts of phosphoric acid. Alkali metal salts of phosphoric acid, such as calcium phosphate, are particularly suitable.

**[0134]** The content of the phosphoric acid compound in the primer paint layer is not limited. However, from the viewpoint of compatibility between corrosion  
25 resistance and moisture resistance, it is preferably 4 mass% or more. It is preferably 20 mass% or less. If the content of the phosphoric acid compound is less than 4 mass%, the inhibitor effect may decrease, resulting in a decrease in corrosion resistance. If the content of the phosphoric acid compound exceeds 20 mass%, the moisture resistance of the primer paint layer may decrease.

30 **[0135]** Magnesium oxide, one of the inorganic compounds, produces Mg-containing products at the time of initial corrosion and has the effect of increasing stability and improving corrosion resistance as an insoluble magnesium salt.

**[0136]** The content of the magnesium oxide in the primer paint layer is not  
35 particularly limited. However, from the viewpoint of compatibility between corrosion resistance and corrosion resistance in processed parts, it is preferably

4 mass% or more. It is preferably 20 mass% or less. If the content of the magnesium oxide is less than 4 mass%, the above effect may decrease and corrosion resistance may decrease. If the content of the magnesium oxide exceeds 20 mass%, the flexibility of the primer paint layer may decrease, resulting in reduced corrosion resistance in processed parts.

[0137] The primer paint layer may also contain components other than the polyester resin having a urethane bond and inorganic compounds mentioned above.

Examples of such components include a cross-linking agent used to form the primer paint layer. The cross-linking agent reacts with the polyester resin having a urethane bond to form a cross-linked paint layer. Examples of the cross-linking agent include oxazoline compounds, epoxy compounds, melamine compounds, isocyanate compounds, carbodiimide compounds, and silane coupling compounds. It is possible to use two or more cross-linking agents in combination. Among these, for example, blocked polyisocyanate compounds can be preferably used from the viewpoint of corrosion resistance in the processed parts of the resulting pre-painted steel sheet. Examples of the blocked polyisocyanate include one in which an isocyanate group of a polyisocyanate compound is blocked by alcohols such as butanol, oximes such as methyl ethyl ketoxime, lactams such as  $\epsilon$ -caprolactam, diketones such as acetoacetic acid diester diketones, imidazoles such as imidazole and 2-ethylimidazole, or phenols such as m-cresol.

[0138] Further, the primer paint layer may also contain various known components normally used in the field of paints, if necessary. Specifically, examples of such components include various surface adjustment agents such as leveling agents and defoamers, dispersants, anti-settling agents, UV absorbers, light stabilizers, various additives such as silane coupling agents and titanate coupling agents, various pigments such as colored pigments and body pigments, optical brightening materials, curing catalysts, and organic solvents.

[0139] The thickness of the primer paint layer is preferably 1.5  $\mu\text{m}$  or more. This is because the primer paint layer having a thickness of 1.5  $\mu\text{m}$  or more more reliably ensures the improvement of corrosion resistance and adhesion with the chemical conversion layer and a top coating layer formed on top of the primer paint layer.

[0140] There is no limitation on the method used to form the primer paint layer.

For the application method of the paint composition that constitutes the primer paint layer, the paint composition can preferably be applied by roll coater coating, curtain flow coating, or other methods. After the application, the applied paint composition is baked by heating means such as hot blast, infrared heating, or induction heating to form a primer paint layer. The baking is usually performed at a peak metal temperature approximately in the range of 180 °C to 270 °C for about 30 seconds to 3 minutes in this temperature range.

**[0141]** In the paint layer that constitutes the pre-painted steel sheet, it is preferable that a top coating layer be further formed on the primer paint layer.

In addition to being able to impart aesthetic qualities such as color, gloss, and surface conditions to the pre-painted steel sheet, the top coating layer can enhance various performances such as workability, weather resistance, chemical resistance, stain resistance, water resistance, and corrosion resistance.

**[0142]** The configuration of the top coating layer is not limited, and the material, thickness, and other conditions can be selected as appropriate according to the required performance.

For example, the top coating layer can be formed using polyester resin-based paint, silicon polyester resin-based paint, polyurethane resin-based paint, acrylic resin-based paint, fluoropolymer resin-based paint, or the like.

In addition, the top coating layer may contain: colored pigments such as titanium oxide, red iron oxide, mica, carbon black, and the like; metallic pigments such as aluminum powder and mica; body pigments composed of carbonates, sulfates, and the like; fine particles such as silica particles, nylon resin beads, and acrylic resin beads; curing catalysts such as p-toluene sulfonic acid and dibutyl tin dilaurate; waxes; and other additives in appropriate quantities.

**[0143]** In terms of both appearance and workability, the thickness of the top coating layer is preferably 5 μm or more. It is preferably 30 μm or less. When the thickness of the top coating layer is 5 μm or more, the color appearance can be more reliably stabilized, and when the thickness of the top coating layer is 30 μm or less, the deterioration of workability (cracking of the top coating layer) can be more reliably suppressed.

**[0144]** The application method of the paint composition to form the top coating layer is not particularly limited. For example, the paint composition can be applied by roll coater coating, curtain flow coating, or other methods. After the application, the applied paint composition can be baked by heating

means such as hot blast, infrared heating, or induction heating to form a top coating layer. The baking is usually performed at a peak metal temperature approximately in the range of 180 °C to 270 °C for about 30 seconds to 3 minutes in this temperature range.

5

## EXAMPLES

### [0145] <Example 1: Samples 1-44>

Using cold-rolled steel sheets with a thickness of 0.8 mm prepared by a conventional method as base steel sheets, annealing and coating simulation was performed on a hot-dip coating simulator by RHESCA Co., Ltd. to produce hot-dip coated steel sheet samples 1-44 under the conditions listed in Table 1.

The composition of the coating bath used in the production of the hot-dip coated steel sheets was varied in the range of Al: 30 mass% to 75 mass%, Si: 0.5 mass% to 4.5 mass%, Mg: 0 mass% to 10 mass%, and Sr: 0.00 mass% to 0.15 mass%, so that the composition of the coating layer for each sample as listed in Table 1 was obtained. The bath temperature of the coating bath was controlled to be 590 °C in the case of Al being in the range of 30 mass% to 60 mass%, and to be 630°C in the case of Al being greater than 60 mass%, so that the sheet temperature of the base steel sheet at the time of entering the coating was the same as the bath temperature of the coating bath. Further, the coating process was carried out under the condition that the sheet temperature cooled down to the temperature range of 520 °C to 500 °C in 3 seconds.

The coating weight of the coating layer was controlled to be  $85 \pm 5$  g/m<sup>2</sup> per surface for samples 1-41 and 51 g/m<sup>2</sup> to 125 g/m<sup>2</sup> per surface for samples 42-44.

### [0146] (Evaluation)

The following evaluations were performed on each of the hot-dip coated steel sheet samples thus obtained. The evaluation results are presented in Table 1.

### [0147] (1) Configuration of Coating Layer (Coating Weight, Composition, and X-ray Diffraction Intensity)

For each sample after coating, 100 mmφ was punched out, the non-measured surface was sealed with tape, and the coating was dissolved and exfoliated with a mixture of hydrochloric acid and hexamethylenetetramine, as specified in JIS H 0401:2013. Then, from the mass difference before and after the exfoliation for each sample, the coating weight of the coating layer was calculated. The coating weight of each coating layer obtained by the

calculation is listed in Table 1.

The exfoliation solution was then filtered and the filtrate and solids were analyzed respectively. Specifically, the filtrate was analyzed by ICP emission spectrometry to quantify the components other than insoluble Si.

5 The solids were dried and ashed in a heating furnace at 650 °C and then melted by adding sodium carbonate and sodium tetraborate. In addition, the melt was dissolved in hydrochloric acid and the dissolved solution was analyzed by ICP emission spectrometry to quantify the insoluble Si. The concentration of Si in the coating layer is the concentration of soluble Si obtained by filtrate analysis  
10 plus the concentration of insoluble Si obtained by solids analysis. The composition of each coating layer obtained by the calculations is listed in Table 1.

After shearing each sample to a size of 100 mm × 100 mm, the coating layer on the surface to be evaluated was mechanically scraped off until the base steel  
15 sheet appeared. After mixing the obtained powder well, 0.3 g was taken out from the mixture and subjected to qualitative analysis using an X-ray diffractometer ("SmartLab" by Rigaku Corporation) under a set of conditions including X-ray used: Cu-K $\alpha$  (wavelength = 1.54178 Å), K $\beta$  ray removal: Ni filter, tube voltage: 40 kV, tube current: 30 mA, scanning speed: 4°/min,  
20 sampling interval: 0.020°, divergence slit: 2/3°, solar slit: 5°, detector: high-speed one-dimensional detector (D/teX Ultra). The diffraction intensities of the (111) plane of Mg<sub>2</sub>Si with an interplanar spacing d of 0.3668 nm and the (111) plane of Si with an interplanar spacing d of 0.3135 nm were measured, with each diffraction intensity (cps) being the peak intensity minus the base  
25 intensity. The measurement results are listed in Table 1.

#### **[0148]** (2) Evaluation of Corrosion Resistance

Each hot-dip coated steel sheet sample obtained was sheared to a size of 120 mm x 120 mm, and 10 mm from each edge of the surface to be evaluated as well as each end and the surface not to be evaluated of each sample were sealed  
30 with tape so that the surface to be evaluated was exposed at 100 mm x 100 mm in size. These were used as samples for evaluation. In each case, three identical samples were prepared for the evaluation.

Accelerated corrosion test was performed on the three evaluation samples thus prepared through the cycle as presented in FIG. 1. After 300 cycles of the  
35 accelerated corrosion test starting from wet, the corrosion loss of each sample was measured by the method prescribed in JIS Z 2383 and ISO 8407, and

evaluated according to the following criteria. The evaluation results are presented in Table 1.

⊙: Corrosion loss of all three samples was 45 g/m<sup>2</sup> or less.

○: Corrosion loss of all three samples was 70 g/m<sup>2</sup> or less.

5 ×: Corrosion loss of at least one sample exceeded 70 g/m<sup>2</sup>.

**[0149] (3) Surface Appearance**

The surface of the coating layer was observed visually on each hot-dip coated steel sheet sample obtained.

10 The observations were then evaluated according to the following criteria. The evaluation results are presented in Table 1.

⊙: No wrinkle-like defects were observed at all.

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

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

**[0150] (4) Workability**

Each hot-dip coated steel sheet sample obtained was sheared to a size of 70 mm × 150 mm and then subjected to 180° bending (8T bending) with eight sheets of the same thickness sandwiched inside. After bending, Sellotape® (Sellotape is a registered trademark in Japan, other countries, or both) was strongly attached to the outer surface of the bent portion and then pulled off. The surface condition of the coating layer on the outer surface of the bent portion and the presence of coating layer adhesion (exfoliation) on the surface of the tape used were visually observed, and workability was evaluated using the following criteria. The evaluation results are presented in Table 1.

○: Neither cracks nor exfoliation were observed in the coating layer.

Δ: Cracks were observed in the coating layer, but no exfoliation.

×: Both cracks and exfoliation were observed in the coating layer.

**[0151] (5) Bath Stability**

30 During the production of each hot-dip coated steel sheet sample, the condition of the bath surface of the coating bath was visually checked and compared with the bath surface of the coating bath used in the production of hot-dip Al-Zn coated steel sheets (i.e., the bath surface without Mg-containing oxides). Evaluations were made according to the following criteria, and the evaluation results are presented in Table 1.

○: Comparable to the hot-dip Al-Zn coating bath (a bath of 55 mass% Al - 1.6

mass% balance Zn).

Δ: More white oxides than those in the hot-dip Al-Zn coating bath (a bath of 55 mass% Al - 1.6 mass% balance Zn).

×: Black oxide formation was observed in the coating bath.

[0152] [Table 1]

Table 1

| No. | Coating layer       |     |     |      |      |                                    |                                 |                | Corrosion resistance               |     |     |            | Surface appearance | Workability | Bath stability | Remarks             |
|-----|---------------------|-----|-----|------|------|------------------------------------|---------------------------------|----------------|------------------------------------|-----|-----|------------|--------------------|-------------|----------------|---------------------|
|     | Composition (mass%) |     |     |      |      | Coating weight (g/m <sup>2</sup> ) | Si(111)/Mg <sub>2</sub> Si(111) | Si(111) (kpcs) | Corrosion loss (g/m <sup>2</sup> ) |     |     | Evaluation |                    |             |                |                     |
|     | Al                  | Si  | Mg  | Fe   | Sr   |                                    |                                 |                | N1                                 | N2  | N3  |            |                    |             |                |                     |
| 1   | 55                  | 0.5 | 4.4 | 1.05 | 0.11 | 85                                 | 0.00                            | 0.00           | 97                                 | 98  | 95  | ×          | ◎                  | ×           | ○              | Comparative example |
| 2   | 55                  | 1.0 | 4.4 | 0.68 | 0.11 | 85                                 | 0.00                            | 0.00           | 42                                 | 43  | 45  | ◎          | ◎                  | △           | ○              | Example             |
| 3   | 55                  | 1.5 | 0.0 | 0.51 | 0.00 | 82                                 | without Mg <sub>2</sub> Si      | 1.19           | 111                                | 105 | 102 | ×          | ◎                  | ○           | ○              | Comparative example |
| 4   | 55                  | 1.5 | 0.0 | 0.51 | 0.11 | 85                                 | without Mg <sub>2</sub> Si      | 1.18           | 104                                | 99  | 100 | ×          | ◎                  | ○           | ○              | Comparative example |
| 5   | 55                  | 1.5 | 1.1 | 0.58 | 0.10 | 84                                 | without Mg <sub>2</sub> Si      | 0.88           | 80                                 | 82  | 78  | ×          | ◎                  | △           | ○              | Comparative example |
| 6   | 55                  | 1.6 | 1.5 | 0.63 | 0.10 | 82                                 | 0.85                            | 0.75           | 75                                 | 77  | 66  | ×          | ◎                  | △           | ○              | Comparative example |
| 7   | 54                  | 1.5 | 1.9 | 0.39 | 0.00 | 85                                 | 0.58                            | 0.62           | 45                                 | 44  | 51  | ○          | ×                  | △           | ○              | Comparative example |
| 8   | 55                  | 1.5 | 2.0 | 0.43 | 0.05 | 84                                 | 0.55                            | 0.62           | 46                                 | 48  | 50  | ○          | ◎                  | △           | ○              | Example             |
| 9   | 55                  | 1.5 | 1.9 | 0.62 | 0.11 | 81                                 | 0.60                            | 0.63           | 49                                 | 40  | 50  | ○          | ◎                  | △           | ○              | Example             |
| 10  | 55                  | 1.5 | 3.4 | 0.59 | 0.09 | 85                                 | 0.00                            | 0.00           | 45                                 | 43  | 45  | ◎          | ◎                  | △           | ○              | Example             |
| 11  | 32                  | 1.5 | 4.5 | 0.58 | 0.10 | 85                                 | 0.00                            | 0.00           | 89                                 | 98  | 90  | ×          | ◎                  | △           | ○              | Comparative example |
| 12  | 48                  | 1.5 | 4.5 | 0.60 | 0.10 | 84                                 | 0.00                            | 0.00           | 42                                 | 44  | 43  | ◎          | ◎                  | △           | ○              | Example             |
| 13  | 50                  | 1.5 | 4.5 | 0.59 | 0.01 | 87                                 | 0.00                            | 0.00           | 40                                 | 39  | 37  | ◎          | ◎                  | △           | ○              | Example             |
| 14  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 85                                 | 0.00                            | 0.00           | 39                                 | 41  | 40  | ◎          | ◎                  | △           | ○              | Example             |
| 15  | 60                  | 1.5 | 4.5 | 0.63 | 0.10 | 85                                 | 0.00                            | 0.00           | 38                                 | 44  | 39  | ◎          | ◎                  | △           | ○              | Example             |
| 16  | 64                  | 1.6 | 4.3 | 0.61 | 0.02 | 83                                 | 0.00                            | 0.00           | 44                                 | 43  | 44  | ◎          | ◎                  | △           | ○              | Example             |
| 17  | 68                  | 1.5 | 4.5 | 0.60 | 0.10 | 85                                 | 0.00                            | 0.00           | 96                                 | 88  | 82  | ×          | ◎                  | △           | ○              | Comparative example |
| 18  | 73                  | 1.6 | 4.5 | 0.58 | 0.10 | 86                                 | 0.00                            | 0.00           | 99                                 | 94  | 92  | ×          | ◎                  | △           | ○              | Comparative example |
| 19  | 55                  | 1.5 | 5.9 | 0.63 | 0.09 | 85                                 | 0.00                            | 0.00           | 29                                 | 26  | 31  | ◎          | ◎                  | △           | △              | Example             |
| 20  | 55                  | 2.3 | 0.0 | 0.57 | 0.00 | 86                                 | without Mg <sub>2</sub> Si      | 4.21           | 105                                | 103 | 97  | ×          | ◎                  | ○           | ○              | Comparative example |
| 21  | 55                  | 2.3 | 0.0 | 0.60 | 0.09 | 85                                 | without Mg <sub>2</sub> Si      | 3.98           | 104                                | 113 | 104 | ×          | ◎                  | ○           | ○              | Comparative example |
| 22  | 55                  | 2.3 | 0.9 | 0.58 | 0.11 | 83                                 | without Mg <sub>2</sub> Si      | 3.13           | 111                                | 98  | 96  | ×          | ◎                  | △           | ○              | Comparative example |
| 23  | 55                  | 2.2 | 2.0 | 0.55 | 0.10 | 85                                 | 3.26                            | 2.15           | 81                                 | 64  | 72  | ×          | ◎                  | △           | ○              | Comparative example |
| 24  | 55                  | 2.3 | 2.7 | 0.58 | 0.10 | 87                                 | 1.67                            | 1.23           | 68                                 | 89  | 79  | ×          | ◎                  | △           | ○              | Comparative example |
| 25  | 55                  | 2.2 | 3.1 | 0.55 | 0.10 | 85                                 | 0.87                            | 0.75           | 83                                 | 67  | 76  | ×          | ◎                  | △           | ○              | Comparative example |
| 26  | 55                  | 2.2 | 3.4 | 0.61 | 0.10 | 85                                 | 0.12                            | 0.30           | 62                                 | 59  | 60  | ○          | ◎                  | △           | ○              | Example             |
| 27  | 55                  | 2.2 | 4.3 | 0.56 | 0.00 | 82                                 | 0.13                            | 0.13           | 55                                 | 56  | 51  | ○          | ×                  | △           | ○              | Comparative example |
| 28  | 55                  | 2.3 | 4.4 | 0.60 | 0.03 | 85                                 | 0.09                            | 0.15           | 43                                 | 31  | 63  | ○          | ◎                  | △           | ○              | Example             |
| 29  | 55                  | 2.3 | 4.3 | 0.59 | 0.09 | 83                                 | 0.10                            | 0.16           | 53                                 | 60  | 49  | ○          | ◎                  | △           | ○              | Example             |
| 30  | 55                  | 2.2 | 4.3 | 0.60 | 0.11 | 86                                 | 0.10                            | 0.12           | 54                                 | 58  | 60  | ○          | ◎                  | △           | ○              | Example             |
| 31  | 55                  | 2.2 | 5.9 | 0.57 | 0.10 | 85                                 | 0.03                            | 0.10           | 59                                 | 56  | 55  | ○          | ◎                  | △           | △              | Example             |
| 32  | 55                  | 2.2 | 6.4 | 0.55 | 0.00 | 82                                 | 0.03                            | 0.99           | 60                                 | 54  | 48  | ○          | ×                  | △           | △              | Comparative example |
| 33  | 55                  | 2.9 | 2.0 | 0.60 | 0.00 | 85                                 | 3.56                            | 3.24           | 89                                 | 94  | 87  | ×          | ×                  | △           | ○              | Comparative example |
| 34  | 55                  | 2.9 | 3.2 | 0.61 | 0.10 | 85                                 | 0.88                            | 0.85           | 85                                 | 91  | 80  | ×          | ○                  | △           | ○              | Comparative example |
| 35  | 55                  | 2.9 | 5.5 | 0.60 | 0.11 | 85                                 | 0.12                            | 0.13           | 41                                 | 45  | 50  | ○          | ◎                  | △           | △              | Example             |
| 36  | 55                  | 3.1 | 4.5 | 0.62 | 0.10 | 87                                 | 0.34                            | 0.87           | 55                                 | 43  | 48  | ○          | ◎                  | △           | ○              | Example             |
| 37  | 55                  | 3.6 | 4.4 | 0.63 | 0.09 | 86                                 | 0.35                            | 1.22           | 61                                 | 55  | 60  | ○          | ◎                  | △           | ○              | Example             |
| 38  | 55                  | 3.9 | 3.6 | 0.61 | 0.10 | 85                                 | 0.95                            | 1.81           | 93                                 | 85  | 82  | ×          | ○                  | △           | ○              | Comparative example |
| 39  | 55                  | 4.0 | 5.8 | 0.60 | 0.11 | 83                                 | 0.88                            | 1.46           | 68                                 | 79  | 74  | ×          | ◎                  | △           | △              | Comparative example |
| 40  | 55                  | 4.1 | 4.4 | 0.58 | 0.09 | 82                                 | 0.90                            | 1.49           | 96                                 | 89  | 82  | ×          | ○                  | △           | ○              | Comparative example |
| 41  | 55                  | 2.9 | 9.7 | 0.61 | 0.09 | 86                                 | 0.00                            | 0.00           | 61                                 | 43  | 43  | ○          | ◎                  | △           | △              | Example             |
| 42  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 51                                 | 0.00                            | 0.00           | 39                                 | 44  | 39  | ◎          | ◎                  | △           | ○              | Example             |
| 43  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 100                                | 0.00                            | 0.00           | 40                                 | 41  | 43  | ◎          | ◎                  | △           | ○              | Example             |
| 44  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 125                                | 0.00                            | 0.00           | 39                                 | 41  | 39  | ◎          | ◎                  | ×           | ○              | Example             |

**[0153]** It can be seen from the results in Table 1 that all of our samples are superior to the comparative samples in terms of corrosion resistance, surface appearance, workability, and bath stability in a well-balanced manner.

**[0154]** <Example 2: Samples 1-112>

- 5 (1) Using the cold-rolled steel sheets with a thickness of 0.8 mm prepared by a conventional method as base steel sheets, annealing and coating simulation was performed on a hot-dip coating simulator by RHESCA Co., Ltd. to produce hot-dip coated steel sheet samples under the coating film conditions listed in Tables 3 and 4.
- 10 The composition of the coating bath used in the production of hot-dip coated steel sheets was varied in the range of Al: 30 mass% to 75 mass%, Si: 0.5 mass% to 4.5 mass%, Mg: 0 mass% to 10 mass%, and Sr: 0.00 mass% to 0.15 mass%, so that the composition of the coating layer for each sample as listed in Table 2 was obtained. The bath temperature of the coating bath was
- 15 controlled to be 590 °C in the case of Al being in the range of 30 mass% to 60 mass%, and to be 630°C in the case of Al being greater than 60 mass%, so that the sheet temperature of the base steel sheet at the time of entering the coating was the same as the bath temperature of the coating bath. Further, the coating process was carried out under the condition that the sheet temperature cooled
- 20 down to the temperature range of 520 °C to 500 °C in 3 seconds.
- The coating weight of the coating layer was controlled to be  $85 \pm 5$  g/m<sup>2</sup> per surface for samples 1-82 and 95-112 and 51 g/m<sup>2</sup> to 125 g/m<sup>2</sup> per surface for samples 83-94.
- (2) Then, a chemical conversion treatment liquid was applied to the coating
- 25 layer of each of the prepared hot-dip coated steel sheet samples using a bar coater and dried in a hot air oven (heating rate: 60 °C/s, PMT: 120°C) to form a chemical conversion layer. As a result, surface-treated steel sheet samples were prepared as presented in Tables 3 and 4.
- For the chemical conversion treatment liquids, surface-treatment solutions A-
- 30 F were prepared by dissolving the corresponding components in water as a solvent. The types of the components (resins and metal compounds) contained in the surface treatment solutions were as follows.

(Resins)

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

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

(Metal compounds)

P compound: aluminum dihydrogen triphosphosphate

Si compound: silica

V compound: sodium metavanadate

Mo compound: molybdic acid

5 Zr compound: potassium zirconyl carbonate

The compositions of the prepared chemical conversion treatment liquids A-F and the coating weight of the formed chemical conversion layers are listed in Table 2. The concentration of each component in Table 2 is the concentration of solid content (in mass %).

10 **[0155]** [Table 2]

Table 2

| Chemical conversion treatment | Chemical conversion treatment liquid |               |                  |                                      |             |                     |               |                              | Coating weight of chemical conversion layer (g/m <sup>2</sup> ) |
|-------------------------------|--------------------------------------|---------------|------------------|--------------------------------------|-------------|---------------------|---------------|------------------------------|-----------------------------------------------------------------|
|                               | Resin (mass%)                        |               |                  | Metal compound mass(%)               |             |                     |               |                              |                                                                 |
|                               | Urethane resin                       |               | Acrylic resin    | P compound                           | Si compound | V compound          | Mo compound   | Zr compound                  |                                                                 |
|                               | SUPERFLEX 130                        | SUPERFLEX 126 | VONCOAT EC-740EF | aluminum dihydrogen triphosphosphate | silica      | sodium metavanadate | molybdic acid | potassium zirconyl carbonate |                                                                 |
| A                             | 8.0                                  | -             | 2.0              | 0.5                                  | 1.0         | 1.0                 | 0.3           | -                            | 1.6                                                             |
| B                             | 8.0                                  | -             | 2.0              | 0.5                                  | 1.0         | 1.0                 | 0.5           | -                            | 1.6                                                             |
| C                             | 8.0                                  | -             | 2.0              | 0.5                                  | 1.0         | 1.0                 | 0.8           | -                            | 1.6                                                             |
| D                             | 9.0                                  | 1.0           | -                | 0.5                                  | 1.0         | 1.0                 | 0.3           | -                            | 1.6                                                             |
| E                             | -                                    | -             | -                | 1.5                                  | 1.0         | 1.5                 | -             | 6.0                          | 0.7                                                             |
| F                             | 10.0                                 | -             | -                | -                                    | -           | -                   | -             | -                            | 2.0                                                             |

**[0156]** (Evaluation)

The following evaluations were performed on each hot-dip coated steel sheet sample and each surface-treated steel sheet sample obtained as described above.

15 The evaluation results are presented in Tables 3 and 4.

**[0157]** (1) Configuration of Coating Layer (Coating Weight, Composition, and X-ray Diffraction Intensity)

For each hot-dip coated steel sheet sample, 100 mmφ was punched out, the non-measured surface was sealed with tape, and the coating was dissolved and exfoliated with a mixture of hydrochloric acid and hexamethylenetetramine, as specified in JIS H 0401:2013. Then, from the mass difference before and after the exfoliation for each sample, the coating weight of the coating layer was calculated. The coating weight of each coating layer obtained by the calculation is listed in Tables 3 and 4.

25 The exfoliation solution was then filtered and the filtrate and solids were analyzed respectively. Specifically, the filtrate was analyzed by ICP emission spectrometry to quantify the components other than insoluble Si.

The solids were dried and ashed in a heating furnace at 650 °C and then melted by adding sodium carbonate and sodium tetraborate. In addition, the melt was

dissolved in hydrochloric acid and the dissolved solution was analyzed by ICP emission spectrometry to quantify the insoluble Si. The concentration of Si in the coating layer is the concentration of soluble Si obtained by filtrate analysis plus the concentration of insoluble Si obtained by solids analysis. The composition of each coating layer obtained by the calculation is listed in Tables 3 and 4.

After shearing each sample to a size of 100 mm × 100 mm, the coating layer on the surface to be evaluated was mechanically scraped off until the base steel sheet appeared. After mixing the obtained powder well, 0.3 g was taken out from the mixture and subjected to qualitative analysis using an X-ray diffractometer ("SmartLab" by Rigaku Corporation) under a set of conditions including X-ray used: Cu-K $\alpha$  (wavelength = 1.54178 Å), K $\beta$  ray removal: 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°, detector: high-speed one-dimensional detector (D/teX Ultra). The diffraction intensities of the (111) plane of Mg<sub>2</sub>Si with an interplanar spacing *d* of 0.3668 nm and the (111) plane of Si with an interplanar spacing *d* of 0.3135 nm were measured, with each diffraction intensity (cps) being the peak intensity minus the base intensity. The measurement results are listed in Tables 3 and 4.

## **[0158] (2) Evaluation of Corrosion Resistance**

Each hot-dip coated steel sheet sample and each surface-treated steel sheet sample were sheared to a size of 120 mm x 120 mm, and 10 mm from each edge of the surface to be evaluated as well as each end and the surface not to be evaluated of each sample were sealed with tape so that the surface to be evaluated was exposed at 100 mm x 100 mm in size. These were used as samples for evaluation. In each case, three identical samples were prepared for the evaluation.

Accelerated corrosion test was performed on the three evaluation samples thus prepared through the cycle as presented in FIG. 1. After 300 cycles of the accelerated corrosion test starting from wet, the corrosion loss of each sample was measured by the method prescribed in JIS Z 2383 and ISO 8407, and evaluated according to the following criteria. The evaluation results are presented in Tables 3 and 4.

◎: Corrosion loss of all three samples was 30 g/m<sup>2</sup> or less.

○: Corrosion loss of all three samples was 50 g/m<sup>2</sup> or less.

×: Corrosion loss of at least one sample exceeded 50 g/m<sup>2</sup>.

**[0159] (3) Anti-white Rust Property**

Each hot-dip coated steel sheet sample and each surface-treated steel sheet sample were sheared to a size of 120 mm x 120 mm, and 10 mm from each edge of the surface to be evaluated as well as each end and the surface not to be evaluated of each sample were sealed with tape so that the surface to be evaluated was exposed at 100 mm x 100 mm in size. These were used as samples for evaluation.

Using the above samples for evaluation, the salt spray test prescribed in JIS Z 2371 was conducted for 90 hours, and the samples were evaluated based on the following criteria. The evaluation results are presented in Tables 3 and 4.

◎: No white rust was observed on the flat parts.

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

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

**[0160] (4) Surface Appearance**

The surface of the coating layer was observed visually on each hot-dip coated steel sheet sample.

The observations were then evaluated according to the following criteria. The evaluation results are presented in Tables 3 and 4.

◎: No wrinkle defects were observed at all.

○: 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.

**[0161] (5) Workability**

Each hot-dip coated steel sheet sample was sheared to a size of 70 mm × 150 mm and then subjected to 180° bending (8T bending) with eight sheets of the same thickness sandwiched inside. After bending, Sellotape® was strongly attached to the outer surface of the bent portion and then pulled off. The surface condition of the coating layer on the outer surface of the bent portion and the presence or absence of coating layer adhesion (exfoliation) on the surface of the tape used were visually observed, and workability was evaluated using the following criteria. The evaluation results are presented in Tables 3 and 4.

○: Neither cracks nor exfoliation were observed in the coating layer.

Δ: Cracks were observed in the coating layer, but no exfoliation.

×: Both cracks and exfoliation were observed in the coating layer.

**[0162] (5) Bath Stability**

During the hot-dip coating, the condition of the bath surface of the coating bath was visually checked and compared with the bath surface of the coating bath used in the production of hot-dip Al-Zn coated steel sheets (i.e., the bath surface without Mg-containing oxides). Evaluations were made according to  
5 the following criteria, and the evaluation results are presented in Tables 3 and 4.

○: Comparable to the hot-dip Al-Zn coating bath (a bath of 55 mass% Al - 1.6 mass% balance Zn).

Δ: More white oxides than those in the hot-dip Al-Zn coating bath (a bath of  
10 55 mass% Al - 1.6 mass% balance Zn).

×: Black oxide formation was observed in the coating bath.

[0163] [Table 3]

Table 3

| No. | Coating layer       |     |     |      |      |                                    |                                 |                | Chemical conversion treatment | Corrosion resistance               |     |     |            | Anti-white rust property | Surface appearance | Workability | Bath stability | Remarks             |
|-----|---------------------|-----|-----|------|------|------------------------------------|---------------------------------|----------------|-------------------------------|------------------------------------|-----|-----|------------|--------------------------|--------------------|-------------|----------------|---------------------|
|     | Composition (mass%) |     |     |      |      | Coating weight (g/m <sup>2</sup> ) | Si(111)/Mg <sub>2</sub> Si(111) | Si(111) (kcps) |                               | Corrosion loss (g/m <sup>2</sup> ) |     |     | Evaluation |                          |                    |             |                |                     |
|     | Al                  | Si  | Mg  | Fe   | Sr   |                                    |                                 |                |                               | N1                                 | N2  | N3  |            |                          |                    |             |                |                     |
| 1   | 55                  | 0.5 | 4.4 | 1.05 | 0.11 | 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 | 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 | 82                                 | without Mg <sub>2</sub> 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 | 85                                 | without Mg <sub>2</sub> 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 | 84                                 | without Mg <sub>2</sub> 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 | 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 | 85                                 | 0.58                            | 0.62           | -                             | 45                                 | 44  | 51  | ×          | ×                        | ×                  | △           | ○              | Comparative example |
| 14  |                     |     |     |      |      |                                    |                                 |                | A                             | 33                                 | 29  | 38  | ○          | ○                        |                    |             |                | Comparative example |
| 15  | 55                  | 1.5 | 2.0 | 0.43 | 0.05 | 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 | 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 | 85                                 | 0.00                            | 0.00           | -                             | 45                                 | 43  | 45  | ○          | ×                        | ◎                  | △           | ○              | Comparative example |
| 20  |                     |     |     |      |      |                                    |                                 |                | A                             | 29                                 | 25  | 24  | ◎          | ◎                        |                    |             |                | Example             |
| 21  | 32                  | 1.5 | 4.5 | 0.58 | 0.10 | 85                                 | 0.00                            | 0.00           | -                             | 89                                 | 98  | 90  | ×          | ×                        | ◎                  | △           | ○              | Comparative example |
| 22  |                     |     |     |      |      |                                    |                                 |                | A                             | 68                                 | 77  | 74  | ×          | ○                        |                    |             |                | Comparative example |
| 23  | 48                  | 1.5 | 4.5 | 0.60 | 0.10 | 84                                 | 0.00                            | 0.00           | -                             | 42                                 | 44  | 43  | ○          | ×                        | ◎                  | △           | ○              | Comparative example |
| 24  |                     |     |     |      |      |                                    |                                 |                | A                             | 23                                 | 20  | 27  | ◎          | ◎                        |                    |             |                | Example             |
| 25  | 50                  | 1.5 | 4.5 | 0.59 | 0.01 | 87                                 | 0.00                            | 0.00           | -                             | 40                                 | 39  | 37  | ○          | ×                        | ◎                  | △           | ○              | Comparative example |
| 26  |                     |     |     |      |      |                                    |                                 |                | A                             | 28                                 | 28  | 26  | ◎          | ◎                        |                    |             |                | Example             |
| 27  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 85                                 | 0.00                            | 0.00           | -                             | 39                                 | 41  | 40  | ○          | ×                        | ◎                  | △           | ○              | Comparative example |
| 28  |                     |     |     |      |      |                                    |                                 |                | A                             | 24                                 | 25  | 26  | ◎          | ◎                        |                    |             |                | Example             |
| 29  | 60                  | 1.5 | 4.5 | 0.63 | 0.10 | 85                                 | 0.00                            | 0.00           | -                             | 38                                 | 44  | 39  | ○          | ×                        | ◎                  | △           | ○              | Comparative example |
| 30  |                     |     |     |      |      |                                    |                                 |                | A                             | 22                                 | 23  | 24  | ◎          | ◎                        |                    |             |                | Example             |
| 31  | 64                  | 1.6 | 4.3 | 0.61 | 0.02 | 83                                 | 0.00                            | 0.00           | -                             | 44                                 | 43  | 44  | ○          | ×                        | ◎                  | △           | ○              | Comparative example |
| 32  |                     |     |     |      |      |                                    |                                 |                | A                             | 25                                 | 23  | 26  | ◎          | ◎                        |                    |             |                | Example             |
| 33  | 68                  | 1.5 | 4.5 | 0.60 | 0.10 | 85                                 | 0.00                            | 0.00           | -                             | 96                                 | 88  | 82  | ×          | ×                        | ◎                  | △           | ○              | Comparative example |
| 34  |                     |     |     |      |      |                                    |                                 |                | A                             | 66                                 | 77  | 65  | ×          | ○                        |                    |             |                | Comparative example |
| 35  | 73                  | 1.6 | 4.5 | 0.58 | 0.10 | 86                                 | 0.00                            | 0.00           | -                             | 99                                 | 94  | 92  | ×          | ×                        | ◎                  | △           | ○              | Comparative example |
| 36  |                     |     |     |      |      |                                    |                                 |                | A                             | 70                                 | 74  | 76  | ×          | ○                        |                    |             |                | Comparative example |
| 37  | 55                  | 1.5 | 5.9 | 0.63 | 0.09 | 85                                 | 0.00                            | 0.00           | -                             | 29                                 | 26  | 31  | ○          | ×                        | ◎                  | △           | △              | Comparative example |
| 38  |                     |     |     |      |      |                                    |                                 |                | A                             | 23                                 | 21  | 25  | ◎          | ◎                        |                    |             |                | Example             |
| 39  | 55                  | 2.3 | 0.0 | 0.57 | 0.00 | 86                                 | without Mg <sub>2</sub> Si      | 4.21           | -                             | 105                                | 103 | 97  | ×          | ×                        | ◎                  | ○           | ○              | Comparative example |
| 40  |                     |     |     |      |      |                                    |                                 |                | A                             | 78                                 | 76  | 75  | ×          | ○                        |                    |             |                | Comparative example |
| 41  | 55                  | 2.3 | 0.0 | 0.60 | 0.09 | 85                                 | without Mg <sub>2</sub> Si      | 3.98           | -                             | 104                                | 113 | 104 | ×          | ×                        | ◎                  | ○           | ○              | Comparative example |
| 42  |                     |     |     |      |      |                                    |                                 |                | A                             | 80                                 | 85  | 79  | ×          | ○                        |                    |             |                | Comparative example |
| 43  | 55                  | 2.3 | 0.9 | 0.58 | 0.11 | 83                                 | without Mg <sub>2</sub> Si      | 3.13           | -                             | 111                                | 98  | 96  | ×          | ×                        | ◎                  | △           | ○              | Comparative example |
| 44  |                     |     |     |      |      |                                    |                                 |                | A                             | 77                                 | 72  | 75  | ×          | ○                        |                    |             |                | Comparative example |

Table 3 (cont'd)

| No. | Coating layer       |     |     |      |      |                                    |                                 |                | Chemical conversion treatment | Corrosion resistance               |    |    |            | Anti-white rust property | Surface appearance | Workability | Bath stability | Remarks             |
|-----|---------------------|-----|-----|------|------|------------------------------------|---------------------------------|----------------|-------------------------------|------------------------------------|----|----|------------|--------------------------|--------------------|-------------|----------------|---------------------|
|     | Composition (mass%) |     |     |      |      | Coating weight (g/m <sup>2</sup> ) | Si(111)/Mg <sub>2</sub> Si(111) | Si(111) (kcps) |                               | Corrosion loss (g/m <sup>2</sup> ) |    |    | Evaluation |                          |                    |             |                |                     |
|     | Al                  | Si  | Mg  | Fe   | Sr   |                                    |                                 |                |                               | N1                                 | N2 | N3 |            |                          |                    |             |                |                     |
| 45  | 55                  | 2.2 | 2.0 | 0.55 | 0.10 | 85                                 | 3.26                            | 2.15           | -                             | 81                                 | 64 | 72 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 46  |                     |     |     |      |      |                                    |                                 |                | A                             | 43                                 | 45 | 51 | ×          | ○                        |                    |             |                | Comparative example |
| 47  | 55                  | 2.3 | 2.7 | 0.58 | 0.10 | 87                                 | 1.67                            | 1.23           | -                             | 68                                 | 89 | 79 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 48  |                     |     |     |      |      |                                    |                                 |                | A                             | 61                                 | 68 | 55 | ×          | ○                        |                    |             |                | Comparative example |
| 49  | 55                  | 2.2 | 3.1 | 0.55 | 0.10 | 85                                 | 0.87                            | 0.75           | -                             | 83                                 | 67 | 76 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 50  |                     |     |     |      |      |                                    |                                 |                | A                             | 54                                 | 57 | 51 | ×          | ○                        |                    |             |                | Comparative example |
| 51  | 55                  | 2.2 | 3.4 | 0.61 | 0.10 | 85                                 | 0.12                            | 0.30           | -                             | 62                                 | 59 | 60 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 52  |                     |     |     |      |      |                                    |                                 |                | A                             | 36                                 | 40 | 42 | ○          | ○                        |                    |             |                | Example             |
| 53  | 55                  | 2.2 | 4.3 | 0.56 | 0.00 | 82                                 | 0.13                            | 0.13           | -                             | 55                                 | 56 | 51 | ×          | ×                        | ×                  | Δ           | ○              | Comparative example |
| 54  |                     |     |     |      |      |                                    |                                 |                | A                             | 35                                 | 41 | 38 | ○          | ○                        |                    |             |                | Comparative example |
| 55  | 55                  | 2.3 | 4.4 | 0.60 | 0.03 | 85                                 | 0.09                            | 0.15           | -                             | 43                                 | 31 | 63 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 56  |                     |     |     |      |      |                                    |                                 |                | A                             | 28                                 | 30 | 35 | ○          | ○                        |                    |             |                | Example             |
| 57  | 55                  | 2.3 | 4.3 | 0.59 | 0.09 | 83                                 | 0.10                            | 0.16           | -                             | 53                                 | 60 | 49 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 58  |                     |     |     |      |      |                                    |                                 |                | A                             | 39                                 | 41 | 38 | ○          | ○                        |                    |             |                | Example             |
| 59  | 55                  | 2.2 | 4.3 | 0.60 | 0.11 | 86                                 | 0.10                            | 0.12           | -                             | 54                                 | 58 | 60 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 60  |                     |     |     |      |      |                                    |                                 |                | A                             | 38                                 | 40 | 42 | ○          | ○                        |                    |             |                | Example             |
| 61  | 55                  | 2.2 | 5.9 | 0.57 | 0.10 | 85                                 | 0.03                            | 0.10           | -                             | 59                                 | 56 | 55 | ×          | ×                        | ◎                  | Δ           | Δ              | Comparative example |
| 62  |                     |     |     |      |      |                                    |                                 |                | A                             | 42                                 | 40 | 39 | ○          | ○                        |                    |             |                | Example             |
| 63  | 55                  | 2.2 | 6.4 | 0.55 | 0.00 | 82                                 | 0.03                            | 0.99           | -                             | 60                                 | 54 | 48 | ×          | ×                        | ×                  | Δ           | Δ              | Comparative example |
| 64  |                     |     |     |      |      |                                    |                                 |                | A                             | 38                                 | 40 | 35 | ○          | ○                        |                    |             |                | Comparative example |
| 65  | 55                  | 2.9 | 2.0 | 0.60 | 0.00 | 85                                 | 3.56                            | 3.24           | -                             | 89                                 | 94 | 87 | ×          | ×                        | ×                  | Δ           | ○              | Comparative example |
| 66  |                     |     |     |      |      |                                    |                                 |                | A                             | 74                                 | 72 | 66 | ×          | ○                        |                    |             |                | Comparative example |
| 67  | 55                  | 2.9 | 3.2 | 0.61 | 0.10 | 85                                 | 0.88                            | 0.85           | -                             | 85                                 | 91 | 80 | ×          | ×                        | ○                  | Δ           | ○              | Comparative example |
| 68  |                     |     |     |      |      |                                    |                                 |                | A                             | 73                                 | 65 | 71 | ×          | ○                        |                    |             |                | Comparative example |
| 69  | 55                  | 2.9 | 5.5 | 0.60 | 0.11 | 85                                 | 0.12                            | 0.13           | -                             | 41                                 | 45 | 50 | ○          | ×                        | ◎                  | Δ           | Δ              | Comparative example |
| 70  |                     |     |     |      |      |                                    |                                 |                | A                             | 28                                 | 31 | 27 | ○          | ○                        |                    |             |                | Example             |
| 71  | 55                  | 3.1 | 4.5 | 0.62 | 0.10 | 87                                 | 0.34                            | 0.87           | -                             | 55                                 | 43 | 48 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 72  |                     |     |     |      |      |                                    |                                 |                | A                             | 42                                 | 40 | 33 | ○          | ○                        |                    |             |                | Example             |
| 73  | 55                  | 3.6 | 4.4 | 0.63 | 0.09 | 86                                 | 0.35                            | 1.22           | -                             | 61                                 | 55 | 60 | ×          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 74  |                     |     |     |      |      |                                    |                                 |                | A                             | 44                                 | 39 | 45 | ○          | ○                        |                    |             |                | Example             |
| 75  | 55                  | 3.9 | 3.6 | 0.61 | 0.10 | 85                                 | 0.95                            | 1.81           | -                             | 93                                 | 85 | 82 | ×          | ×                        | ○                  | Δ           | ○              | Comparative example |
| 76  |                     |     |     |      |      |                                    |                                 |                | A                             | 73                                 | 73 | 65 | ×          | ○                        |                    |             |                | Comparative example |
| 77  | 55                  | 4.0 | 5.8 | 0.60 | 0.11 | 83                                 | 0.88                            | 1.46           | -                             | 68                                 | 79 | 74 | ×          | ×                        | ◎                  | Δ           | Δ              | Comparative example |
| 78  |                     |     |     |      |      |                                    |                                 |                | A                             | 57                                 | 53 | 51 | ×          | ○                        |                    |             |                | Comparative example |
| 79  | 55                  | 4.1 | 4.4 | 0.58 | 0.09 | 82                                 | 0.90                            | 1.49           | -                             | 96                                 | 89 | 82 | ×          | ×                        | ○                  | Δ           | ○              | Comparative example |
| 80  |                     |     |     |      |      |                                    |                                 |                | A                             | 71                                 | 76 | 69 | ×          | ○                        |                    |             |                | Comparative example |
| 81  | 55                  | 2.9 | 9.7 | 0.61 | 0.09 | 86                                 | 0.00                            | 0.00           | -                             | 61                                 | 43 | 43 | ×          | ×                        | ◎                  | Δ           | Δ              | Comparative example |
| 82  |                     |     |     |      |      |                                    |                                 |                | A                             | 39                                 | 37 | 33 | ○          | ○                        |                    |             |                | Example             |
| 83  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 51                                 | 0.00                            | 0.00           | -                             | 39                                 | 44 | 39 | ○          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 84  |                     |     |     |      |      |                                    |                                 |                | A                             | 21                                 | 26 | 25 | ◎          | ○                        |                    |             |                | Example             |
| 85  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 100                                | 0.00                            | 0.00           | -                             | 40                                 | 41 | 43 | ○          | ×                        | ◎                  | Δ           | ○              | Comparative example |
| 86  |                     |     |     |      |      |                                    |                                 |                | A                             | 26                                 | 24 | 27 | ◎          | ○                        |                    |             |                | Example             |
| 87  | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 125                                | 0.00                            | 0.00           | -                             | 39                                 | 41 | 39 | ○          | ×                        | ◎                  | ×           | ○              | Comparative example |
| 88  |                     |     |     |      |      |                                    |                                 |                | A                             | 28                                 | 29 | 25 | ◎          | ○                        |                    |             |                | Example             |

[0164] [Table 4]

Table 4

| No. | Coating layer       |     |     |      |      |                                    |                                  |                | Chemical conversion treatment | Corrosion resistance               |    |    |            | Anti-white rust property | Surface appearance | Workability | Bath stability | Remarks             |
|-----|---------------------|-----|-----|------|------|------------------------------------|----------------------------------|----------------|-------------------------------|------------------------------------|----|----|------------|--------------------------|--------------------|-------------|----------------|---------------------|
|     | Composition (mass%) |     |     |      |      | Coating weight (g/m <sup>2</sup> ) | Si(111) /Mg <sub>2</sub> Si(111) | Si(111) (kcps) |                               | Corrosion loss (g/m <sup>2</sup> ) |    |    | Evaluation |                          |                    |             |                |                     |
|     | Al                  | Si  | Mg  | Fe   | Sr   |                                    |                                  |                |                               | N1                                 | N2 | N3 |            |                          |                    |             |                |                     |
| 89  | 55                  | 1.7 | 1.9 | 0.42 | 0.03 | 71                                 | 0.55                             | 0.60           | A                             | 33                                 | 39 | 35 | ○          | ○                        | ◎                  | △           | ○              | Example             |
| 90  |                     |     |     |      |      |                                    |                                  |                | B                             | 32                                 | 37 | 33 | ○          | ○                        |                    |             |                | Example             |
| 91  |                     |     |     |      |      |                                    |                                  |                | C                             | 35                                 | 36 | 38 | ○          | ○                        |                    |             |                | Example             |
| 92  |                     |     |     |      |      |                                    |                                  |                | D                             | 39                                 | 34 | 33 | ○          | ○                        |                    |             |                | Example             |
| 93  |                     |     |     |      |      |                                    |                                  |                | E                             | 40                                 | 39 | 41 | ○          | ×                        |                    |             |                | Comparative example |
| 94  |                     |     |     |      |      |                                    |                                  |                | F                             | 47                                 | 43 | 44 | ○          | ×                        |                    |             |                | Comparative example |
| 95  | 55                  | 1.6 | 2.0 | 0.45 | 0.00 | 80                                 | 0.53                             | 0.63           | A                             | 30                                 | 35 | 36 | ○          | ○                        | ×                  | △           | ○              | Comparative example |
| 96  |                     |     |     |      |      |                                    |                                  |                | B                             | 34                                 | 35 | 37 | ○          | ○                        |                    |             |                | Comparative example |
| 97  |                     |     |     |      |      |                                    |                                  |                | C                             | 31                                 | 38 | 33 | ○          | ○                        |                    |             |                | Comparative example |
| 98  |                     |     |     |      |      |                                    |                                  |                | D                             | 34                                 | 36 | 35 | ○          | ○                        |                    |             |                | Comparative example |
| 99  |                     |     |     |      |      |                                    |                                  |                | E                             | 38                                 | 43 | 44 | ○          | ×                        |                    |             |                | Comparative example |
| 100 |                     |     |     |      |      |                                    |                                  |                | F                             | 42                                 | 43 | 39 | ○          | ×                        |                    |             |                | Comparative example |
| 101 | 55                  | 1.5 | 4.4 | 0.55 | 0.10 | 85                                 | 0.00                             | 0.00           | A                             | 24                                 | 25 | 26 | ◎          | ◎                        | ◎                  | △           | ○              | Example             |
| 102 |                     |     |     |      |      |                                    |                                  |                | B                             | 22                                 | 23 | 26 | ◎          | ◎                        |                    |             |                | Example             |
| 103 |                     |     |     |      |      |                                    |                                  |                | C                             | 28                                 | 24 | 25 | ◎          | ◎                        |                    |             |                | Example             |
| 104 |                     |     |     |      |      |                                    |                                  |                | D                             | 21                                 | 28 | 25 | ◎          | ◎                        |                    |             |                | Example             |
| 105 |                     |     |     |      |      |                                    |                                  |                | E                             | 28                                 | 27 | 29 | ◎          | ○                        |                    |             |                | Example             |
| 106 |                     |     |     |      |      |                                    |                                  |                | F                             | 35                                 | 30 | 33 | ○          | ○                        |                    |             |                | Example             |
| 107 | 55                  | 2.3 | 4.3 | 0.59 | 0.09 | 83                                 | 0.09                             | 0.16           | A                             | 39                                 | 41 | 38 | ○          | ○                        | ◎                  | △           | ○              | Example             |
| 108 |                     |     |     |      |      |                                    |                                  |                | B                             | 37                                 | 36 | 33 | ○          | ○                        |                    |             |                | Example             |
| 109 |                     |     |     |      |      |                                    |                                  |                | C                             | 39                                 | 38 | 36 | ○          | ○                        |                    |             |                | Example             |
| 110 |                     |     |     |      |      |                                    |                                  |                | D                             | 36                                 | 35 | 32 | ○          | ○                        |                    |             |                | Example             |
| 111 |                     |     |     |      |      |                                    |                                  |                | E                             | 39                                 | 40 | 37 | ○          | ○                        |                    |             |                | Example             |
| 112 |                     |     |     |      |      |                                    |                                  |                | F                             | 46                                 | 42 | 48 | ○          | ○                        |                    |             |                | Example             |

[0165] It can be seen from the results in Tables 3 and 4 that all of our samples are superior to the comparative samples in terms of corrosion resistance, anti-white rust property, surface appearance, workability, and bath stability in a well-balanced manner.

It can also be seen from the results in Table 4 that those samples subjected to chemical conversion treatments A-D exhibited excellent anti-white rust properties.

[0166] <Example 3: Samples 1-44>

(1) Using the cold-rolled steel sheets with a thickness of 0.8 mm prepared by a conventional method as base steel sheets, annealing and coating simulation was performed on a hot-dip coating simulator by RHESCA Co., Ltd. to obtain hot-dip coated steel sheet samples with the coating layer conditions listed in Table 6.

The composition of the coating bath used in the production of hot-dip coated steel sheets was varied in the range of Al: 30 mass% to 75 mass%, Si: 0.5 mass% to 4.5 mass%, Mg: 0 mass% to 10 mass%, and Sr: 0.00 mass% to 0.15 mass%, so that the composition of the coating layer for each sample as listed in Table 6 was obtained. The bath temperature of the coating bath was controlled to be 590 °C in the case of Al being in the range of 30 mass% to 60

mass%, and to be 630°C in the case of Al being greater than 60 mass%, so that the sheet temperature of the base steel sheet at the time of entering the coating was the same as the bath temperature of the coating bath. Further, the coating process was carried out under the condition that the sheet temperature cooled  
5 down to the temperature range of 520 °C to 500 °C in 3 seconds.

The coating weight of the coating layer was controlled to be  $85 \pm 5$  g/m<sup>2</sup> per surface for samples 1-41 and 42 g/m<sup>2</sup> to 125 g/m<sup>2</sup> per surface for samples 42-44.

**[0167]** (2) Then, a chemical conversion treatment liquid listed in Table 5 was  
10 applied to the coating layer of each of the prepared hot-dip coated steel sheet samples using a bar coater and dried in a hot-air drying furnace (peak metal temperature: 90 °C) to form a chemical conversion layer with a coating weight of 0.1 g/m<sup>2</sup>.

The chemical conversion treatment liquids used were chemical conversion  
15 treatment liquids with a pH of 8 to 10, prepared by dissolving the corresponding components in water as a solvent. The types of the components (resin components and inorganic compounds) contained in the chemical conversion treatment liquids were as follows.

(Resin Components)

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

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

25 (Inorganic Compounds)

Vanadium compound: organic vanadium compound chelated with acetylacetone

Zirconium compound: ammonium zirconium carbonate

Fluorine compound: ammonium fluoride

**[0168]** (3) Then, a primer paint was applied to each chemical conversion layer  
30 formed as described above using a bar coater, and baking was performed at an end-point temperature of each steel sheet of 230 °C for a baking time of 35 seconds to form primer paint layers with the chemical compositions as listed in Table 5. Then, a top coating paint composition was applied to each primer paint layer thus formed using a bar coater, and baking was performed at an end-  
35 point temperature of each steel sheet in the range of 230 °C to 260°C for a baking time of 40 seconds to form top coating layers with the resin conditions

and layer thicknesses as listed in Table 5. In this way, pre-painted steel sheet samples were prepared.

The primer paint was obtained by mixing the components and stirring the mixture in a ball mill for approximately 1 hour. The resin components and inorganic compounds that constitute each primer paint layer were as follows.

(Resin Components)

Resin  $\alpha$ : urethane-modified polyester resin (obtained by reacting 455 mass parts of polyester resin with 45 mass parts of isophorone diisocyanate, with a resin acid number of 3, an average molecular weight of 5,600, and a hydroxyl group value of 36) cured with blocked isocyanate

The polyester resin to be urethane modified was prepared under the following conditions. In a flask equipped with a stirrer, a rectifying column, a water separator, a cooling pipe, and a thermometer, 320 parts by mass of isophthalic acid, 200 parts by mass of adipic acid, 60 parts by mass of trimethylolpropane, and 420 parts by mass of cyclohexanedimethanol were supplied, heated, and stirred. The temperature was increased at a constant rate from 160 °C to 230 °C over a period of 4 hours while allowing the condensation water generated to evaporate out of the system. After the temperature reached 230 °C, 20 parts by mass of xylene were added gradually, and the condensation reaction was continued while maintaining the temperature at 230 °C. The reaction was terminated when the acid number became 5 or less, and after cooling to 100 °C, 120 parts by mass of Solvesso 100 (trade name by ExxonMobil, an aromatic hydrocarbon solvent with a high boiling point) and 100 parts by mass of butyl cellosolve were added to obtain a polyester resin solution.

Resin  $\beta$ : urethane-cured polyester resin ("Evaclad 4900" by Kansai Paint Co., Ltd.)

(Inorganic Compounds)

Vanadium compound: magnesium vanadate

Phosphate compound: calcium phosphate

Magnesium oxide compound: magnesium oxide

The following paints were used for the resins used in the top coating layer.

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

Resin II: organosol-based baking-type fluororesin paint (Precolor #8800HR by BASF Japan Ltd.) with the mass ratio of polyvinylidene fluoride to acrylic resin of 80:20

[0169] [Table 5]

Table 5

| Paint layer condition | Chemical conversion layer |                 |                           |                            |                           | Primer paint layer |                 |                           |                                  |                                  |                                 | Top coating layer |                            | Remarks             |
|-----------------------|---------------------------|-----------------|---------------------------|----------------------------|---------------------------|--------------------|-----------------|---------------------------|----------------------------------|----------------------------------|---------------------------------|-------------------|----------------------------|---------------------|
|                       | Resin                     |                 | Vanadium compound (mass%) | Zirconium compound (mass%) | Fluorine compound (mass%) | Resin              |                 | Vanadium compound (mass%) | Phosphoric acid compound (mass%) | Magnesium oxide compound (mass%) | Others (pigments, etc.) (mass%) | Resin             |                            |                     |
|                       | Type                      | Content (mass%) |                           |                            |                           | Type               | Content (mass%) |                           |                                  |                                  |                                 | Type              | Paint layer thickness (μm) |                     |
| T1                    | A                         | 30              | 6                         | 50                         | 1                         | α                  | 60              | 12                        | 12                               | 6                                | 10                              | I                 | 15                         | Example             |
| T2                    | A                         | 30              | 6                         | 50                         | 1                         | α                  | 60              | 12                        | 12                               | 6                                | 10                              | II                | 23                         | Example             |
| T3                    | B                         | 30              | 6                         | 50                         | 1                         | α                  | 60              | 12                        | 12                               | 6                                | 10                              | I                 | 15                         | Comparative example |
| T4                    | A                         | 30              | 0                         | 50                         | 1                         | α                  | 60              | 12                        | 12                               | 6                                | 10                              | I                 | 15                         | Comparative example |
| T5                    | A                         | 30              | 6                         | 0                          | 1                         | α                  | 60              | 12                        | 12                               | 6                                | 10                              | I                 | 15                         | Comparative example |
| T6                    | A                         | 30              | 6                         | 50                         | 0                         | α                  | 60              | 12                        | 12                               | 6                                | 10                              | I                 | 15                         | Comparative example |
| T7                    | A                         | 30              | 6                         | 50                         | 1                         | β                  | 60              | 12                        | 12                               | 6                                | 10                              | I                 | 15                         | Comparative example |
| T8                    | A                         | 30              | 6                         | 50                         | 1                         | α                  | 60              | 0                         | 12                               | 6                                | 10                              | I                 | 15                         | Comparative example |
| T9                    | A                         | 30              | 6                         | 50                         | 1                         | α                  | 60              | 12                        | 0                                | 6                                | 10                              | I                 | 15                         | Comparative example |
| T10                   | A                         | 30              | 6                         | 50                         | 1                         | α                  | 60              | 12                        | 12                               | 0                                | 10                              | I                 | 15                         | Comparative example |

[0170] (Evaluation)

The following evaluations were performed on the pre-painted steel sheet samples thus obtained. The evaluation results are presented in Table 6.

[0171] (1) Configuration of Coating Layer (Coating Weight, Composition, and X-ray Diffraction Intensity)

For each hot-dip coated steel sheet sample, 100 mmφ was punched out, the non-measured surface was sealed with tape, and the coating was dissolved and exfoliated with a mixture of hydrochloric acid and hexamethylenetetramine, as specified in JIS H 0401:2013. Then, from the mass difference before and after the exfoliation for each sample, the coating weight of the coating layer was calculated. The coating weight of each coating layer obtained by the calculation is listed in Table 6.

The exfoliation solution was then filtered and the filtrate and solids were analyzed respectively. Specifically, the filtrate was analyzed by ICP emission spectrometry to quantify the components other than insoluble Si.

The solids were dried and ashed in a heating furnace at 650 °C and then melted by adding sodium carbonate and sodium tetraborate. In addition, the melt was dissolved in hydrochloric acid and the dissolved solution was analyzed by ICP emission spectrometry to quantify the insoluble Si. The concentration of Si in the coating layer is the concentration of soluble Si obtained by filtrate analysis plus the concentration of insoluble Si obtained by solids analysis. The composition of each coating layer obtained by the calculations is listed in Table 6.

After shearing each sample to a size of 100 mm × 100 mm, the coating layer on the surface to be evaluated was mechanically scraped off until the base steel sheet appeared. After mixing the obtained powder well, 0.3 g was taken out from the mixture and subjected to qualitative analysis using an X-ray diffractometer ("SmartLab" by Rigaku Corporation) under a set of conditions including X-ray used: Cu-K $\alpha$  (wavelength = 1.54178 Å), K $\beta$  ray removal: 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°, detector: high-speed one-dimensional detector (D/teX Ultra). The diffraction intensities of the (111) plane of Mg<sub>2</sub>Si with an interplanar spacing  $d$  of 0.3668 nm and the (111) plane of Si with an interplanar spacing  $d$  of 0.3135 nm were measured, with each diffraction intensity (cps) being the peak intensity minus the base intensity. The measurement results are listed in Table 6.

#### [0172] (2) Evaluation of Corrosion Resistance

Each pre-painted steel sheet sample was sheared to a size of 120 mm x 120 mm, and 10 mm from edges of the surface to be evaluated on freely-selected three sides as well as ends on the three sides and the surface not to be evaluated of each sample were sealed with tape so that the surface to be evaluated was exposed at 100 mm x 100 mm in size. These were used as samples for evaluation. In each case, three identical samples were prepared for the evaluation.

Accelerated corrosion test was performed on the three evaluation samples thus prepared through the cycle as presented in FIG. 1. The accelerated corrosion test was started from wet, and samples were taken out after every 20 cycles and visually observed after water washing and drying to check for the occurrence of red rust on the sheared end on the side that was not tape-sealed. The number of cycles when red rust was observed was then evaluated according to the following criteria. The evaluation results are presented in Table 6.

◎: number of cycles to initial red rust in 3 samples  $\geq$  600 cycles

○: 600 cycles > number of cycles to initial red rust in 3 samples  $\geq$  500 cycles

×: number of cycles to initial red rust in at least one sample < 500 cycles

#### [0173] (3) Appearance after Painting

The surface of each pre-painted steel sheet sample was observed visually. The observations were then evaluated according to the following criteria. The evaluation results are presented in Table 6.

◎: No wrinkle defects were observed at all.

○: 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.

5 **[0174]** (5) Workability after Coating

Each pre-painted steel sheet sample was sheared to a size of 70 mm × 150 mm and then subjected to 180° bending (8T bending) with eight sheets of the same thickness sandwiched inside. After bending, Sellotape® was strongly attached to the outer surface of the bent portion and then pulled off. The surface condition of the paint layer on the outer surface of the bent portion and the presence or absence of paint layer adhesion (exfoliation) on the surface of the tape used were visually observed, and workability was evaluated using the following criteria. The evaluation results are presented in Table 6.

○: Neither cracks nor exfoliation were observed in the coating layer.

15 Δ: Cracks were observed in the coating layer, but no exfoliation.

×: Both cracks and exfoliation were observed in the coating layer.

**[0175]** (5) Bath Stability

During the hot-dip coating, the condition of the bath surface of the coating bath was visually checked and compared with the bath surface of the coating bath used in the production of hot-dip Al-Zn coated steel sheets (i.e., the bath surface without Mg-containing oxides). Evaluations were made according to the following criteria, and the evaluation results are presented in Table 6.

○: Comparable to the hot-dip Al-Zn coating bath (a bath of 55 mass% Al - 1.6 mass% balance Zn).

25 Δ: More white oxides than those in the hot-dip Al-Zn coating bath (a bath of 55 mass% Al - 1.6 mass% balance Zn).

×: Black oxide formation was observed in the coating bath.

[0176] [Table 6]

Table 6

| No. | Coating layer       |     |     |      |      |                                    |                                  |                | Paint layer condition | Corrosion resistance              |     |     |            | Appearance after painting | Workability after painting | Bath stability | Remarks             |
|-----|---------------------|-----|-----|------|------|------------------------------------|----------------------------------|----------------|-----------------------|-----------------------------------|-----|-----|------------|---------------------------|----------------------------|----------------|---------------------|
|     | Composition (mass%) |     |     |      |      | Coating weight (g/m <sup>2</sup> ) | Si(111) /Mg <sub>2</sub> Si(111) | Si(111) (kcps) |                       | Time to initial red rust (cycles) |     |     | Evaluation |                           |                            |                |                     |
|     | Al                  | Si  | Mg  | Fe   | Sr   |                                    |                                  |                |                       | N1                                | N2  | N3  |            |                           |                            |                |                     |
| 1   | 55                  | 0.5 | 4.4 | 1.01 | 0.11 | 86                                 | 0.00                             | 0.00           | T1                    | 400                               | 360 | 340 | ×          | ◎                         | ×                          | ○              | Comparative example |
| 2   | 55                  | 1.0 | 4.4 | 0.65 | 0.11 | 83                                 | 0.00                             | 0.00           | T1                    | 620                               | 640 | 640 | ◎          | ◎                         | △                          | ○              | Example             |
| 3   | 55                  | 1.5 | 0.0 | 0.49 | 0.00 | 84                                 | without Mg <sub>2</sub> Si       | 1.25           | T1                    | 320                               | 300 | 320 | ×          | ◎                         | ○                          | ○              | Comparative example |
| 4   | 55                  | 1.5 | 0.0 | 0.48 | 0.11 | 82                                 | without Mg <sub>2</sub> Si       | 1.24           | T1                    | 280                               | 320 | 320 | ×          | ◎                         | ○                          | ○              | Comparative example |
| 5   | 55                  | 1.5 | 1.1 | 0.55 | 0.10 | 85                                 | without Mg <sub>2</sub> Si       | 0.92           | T1                    | 420                               | 460 | 460 | ×          | ◎                         | △                          | ○              | Comparative example |
| 6   | 55                  | 1.6 | 1.5 | 0.58 | 0.10 | 86                                 | 0.85                             | 0.76           | T1                    | 460                               | 480 | 460 | ×          | ◎                         | △                          | ○              | Comparative example |
| 7   | 54                  | 1.5 | 1.9 | 0.36 | 0.00 | 83                                 | 0.58                             | 0.65           | T1                    | 540                               | 520 | 560 | ○          | ×                         | △                          | ○              | Example             |
| 8   | 55                  | 1.5 | 2.0 | 0.41 | 0.05 | 82                                 | 0.55                             | 0.61           | T1                    | 560                               | 580 | 580 | ○          | ◎                         | △                          | ○              | Example             |
| 9   | 55                  | 1.5 | 1.9 | 0.59 | 0.11 | 83                                 | 0.60                             | 0.65           | 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 | 84                                 | 0.00                             | 0.00           | T1                    | 660                               | 680 | 680 | ◎          | ◎                         | △                          | ○              | Example             |
| 11  | 32                  | 1.5 | 4.5 | 0.55 | 0.10 | 86                                 | 0.00                             | 0.00           | T1                    | 380                               | 400 | 360 | ×          | ◎                         | △                          | ○              | Comparative example |
| 12  | 48                  | 1.5 | 4.5 | 0.58 | 0.10 | 85                                 | 0.00                             | 0.00           | T1                    | 720                               | 680 | 680 | ◎          | ◎                         | △                          | ○              | Example             |
| 13  | 50                  | 1.5 | 4.5 | 0.56 | 0.01 | 87                                 | 0.00                             | 0.00           | T1                    | 700                               | 680 | 680 | ◎          | ◎                         | △                          | ○              | Example             |
|     |                     |     |     |      |      |                                    |                                  |                | T2                    | 680                               | 660 | 680 | ◎          | ◎                         | △                          |                | Example             |
| 14  | 55                  | 1.5 | 4.4 | 0.52 | 0.10 | 84                                 | 0.00                             | 0.00           | T1                    | 640                               | 700 | 660 | ◎          | ◎                         | △                          | ○              | Example             |
| 15  | 60                  | 1.5 | 4.5 | 0.59 | 0.10 | 83                                 | 0.00                             | 0.00           | T1                    | 680                               | 660 | 680 | ◎          | ◎                         | △                          | ○              | Example             |
| 16  | 64                  | 1.6 | 4.3 | 0.58 | 0.02 | 86                                 | 0.00                             | 0.00           | T1                    | 660                               | 700 | 660 | ◎          | ◎                         | △                          | ○              | Example             |
| 17  | 68                  | 1.5 | 4.5 | 0.60 | 0.10 | 85                                 | 0.00                             | 0.00           | T1                    | 360                               | 460 | 400 | ×          | ◎                         | △                          | ○              | Comparative example |
| 18  | 73                  | 1.6 | 4.5 | 0.55 | 0.10 | 88                                 | 0.00                             | 0.00           | T1                    | 380                               | 360 | 400 | ×          | ◎                         | △                          | ○              | Comparative example |
| 19  | 55                  | 1.5 | 5.9 | 0.61 | 0.09 | 84                                 | 0.00                             | 0.00           | T1                    | 680                               | 680 | 700 | ◎          | ◎                         | △                          | △              | Example             |
| 20  | 55                  | 2.3 | 0.0 | 0.54 | 0.00 | 83                                 | without Mg <sub>2</sub> Si       | 4.36           | T1                    | 300                               | 280 | 340 | ×          | ◎                         | ○                          | ○              | Comparative example |
| 21  | 55                  | 2.3 | 0.0 | 0.56 | 0.09 | 86                                 | without Mg <sub>2</sub> Si       | 4.22           | T1                    | 340                               | 360 | 300 | ×          | ◎                         | ○                          | ○              | Comparative example |
| 22  | 55                  | 2.3 | 0.9 | 0.52 | 0.11 | 85                                 | without Mg <sub>2</sub> Si       | 3.46           | T1                    | 420                               | 380 | 400 | ×          | ◎                         | △                          | ○              | Comparative example |
| 23  | 55                  | 2.2 | 2.0 | 0.52 | 0.10 | 84                                 | 3.26                             | 2.28           | T1                    | 460                               | 500 | 480 | ×          | ◎                         | △                          | ○              | Comparative example |
| 24  | 55                  | 2.3 | 2.7 | 0.58 | 0.10 | 87                                 | 1.67                             | 1.23           | T1                    | 460                               | 480 | 460 | ×          | ◎                         | △                          | ○              | Comparative example |
| 25  | 55                  | 2.2 | 3.1 | 0.55 | 0.10 | 85                                 | 0.87                             | 0.75           | T1                    | 500                               | 480 | 440 | ×          | ◎                         | △                          | ○              | Comparative example |
| 26  | 55                  | 2.2 | 3.4 | 0.58 | 0.10 | 87                                 | 0.12                             | 0.35           | T1                    | 520                               | 560 | 500 | ○          | ◎                         | △                          | ○              | Example             |
| 27  | 55                  | 2.2 | 4.3 | 0.52 | 0.00 | 86                                 | 0.13                             | 0.20           | T1                    | 520                               | 540 | 580 | ○          | ×                         | △                          | ○              | Example             |
| 28  | 55                  | 2.3 | 4.4 | 0.59 | 0.03 | 84                                 | 0.09                             | 0.18           | T1                    | 560                               | 600 | 560 | ○          | ◎                         | △                          | ○              | Example             |
|     |                     |     |     |      |      |                                    |                                  |                | T2                    | 540                               | 560 | 580 | ○          | ◎                         | △                          |                | Example             |
| 29  | 55                  | 2.3 | 4.3 | 0.56 | 0.09 | 85                                 | 0.10                             | 0.21           | T1                    | 620                               | 560 | 600 | ○          | ◎                         | △                          | ○              | Example             |
| 30  | 55                  | 2.2 | 4.3 | 0.57 | 0.11 | 87                                 | 0.10                             | 0.15           | T1                    | 580                               | 580 | 600 | ○          | ◎                         | △                          | ○              | Example             |
| 31  | 55                  | 2.2 | 5.9 | 0.55 | 0.10 | 84                                 | 0.03                             | 0.12           | T1                    | 580                               | 560 | 580 | ○          | ◎                         | △                          | △              | Example             |
| 32  | 55                  | 2.2 | 6.4 | 0.53 | 0.00 | 83                                 | 0.03                             | 1.05           | T1                    | 560                               | 540 | 580 | ○          | ×                         | △                          | △              | Example             |
| 33  | 55                  | 2.9 | 2.0 | 0.60 | 0.00 | 85                                 | 3.56                             | 3.24           | T1                    | 440                               | 380 | 420 | ×          | ×                         | △                          | ○              | Comparative example |
| 34  | 55                  | 2.9 | 3.2 | 0.61 | 0.10 | 85                                 | 0.88                             | 0.85           | T1                    | 400                               | 440 | 380 | ×          | ○                         | △                          | ○              | Comparative example |
| 35  | 55                  | 2.9 | 5.5 | 0.60 | 0.11 | 85                                 | 0.12                             | 0.13           | T1                    | 540                               | 600 | 600 | ○          | ◎                         | △                          | △              | Example             |
| 36  | 55                  | 3.1 | 4.5 | 0.54 | 0.10 | 85                                 | 0.34                             | 0.98           | T1                    | 600                               | 580 | 600 | ○          | ◎                         | △                          | ○              | Example             |
| 37  | 55                  | 3.6 | 4.4 | 0.57 | 0.09 | 87                                 | 0.35                             | 1.24           | T1                    | 520                               | 560 | 540 | ○          | ◎                         | △                          | ○              | Example             |
| 38  | 55                  | 3.9 | 3.6 | 0.61 | 0.10 | 85                                 | 0.95                             | 1.81           | T1                    | 420                               | 420 | 380 | ×          | ○                         | △                          | ○              | Comparative example |
| 39  | 55                  | 4.0 | 5.8 | 0.60 | 0.11 | 83                                 | 0.88                             | 1.46           | T1                    | 480                               | 540 | 520 | ×          | ◎                         | △                          | △              | Comparative example |
| 40  | 55                  | 4.1 | 4.4 | 0.58 | 0.09 | 82                                 | 0.90                             | 1.49           | T1                    | 360                               | 380 | 360 | ×          | ○                         | △                          | ○              | Comparative example |
| 41  | 55                  | 2.9 | 9.7 | 0.57 | 0.09 | 88                                 | 0.00                             | 0.00           | T1                    | 500                               | 560 | 520 | ○          | ◎                         | △                          | △              | Example             |
| 42  | 55                  | 1.5 | 4.4 | 0.50 | 0.10 | 52                                 | 0.00                             | 0.00           | T1                    | 640                               | 620 | 600 | ◎          | ◎                         | △                          | ○              | Example             |
| 43  | 55                  | 1.5 | 4.4 | 0.52 | 0.10 | 98                                 | 0.00                             | 0.00           | T1                    | 660                               | 660 | 640 | ◎          | ◎                         | △                          | ○              | Example             |
| 44  | 55                  | 1.5 | 4.4 | 0.54 | 0.10 | 128                                | 0.00                             | 0.00           | T1                    | 720                               | 720 | 700 | ◎          | ◎                         | ×                          | ○              | Example             |

[0177] It can be seen from the results in Table 6 that all of our samples are superior to the comparative samples in terms of corrosion resistance, appearance after coating, workability after coating, and bath stability in a well-balanced manner.

5

#### INDUSTRIAL APPLICABILITY

[0178] The present disclosure provides a hot-dip Al-Zn-Si-Mg-Sr coated steel sheet that stably exhibits excellent corrosion resistance and good surface appearance.

10 The present disclosure also provides a surface-treated steel sheet that stably exhibits excellent corrosion resistance and anti-white rust property.

The present disclosure also provides a pre-painted steel sheet that stably exhibits excellent corrosion resistance and excellent corrosion resistance in processed parts.

## CLAIMS

[Claim 1] A hot-dip Al-Zn-Si-Mg-Sr coated steel sheet comprising a coating layer, wherein

5 the coating layer has a composition containing Al: 45 mass% to 65 mass%, Si: 1.0 mass% to 4.0 mass%, Mg: 1.0 mass% to 10.0 mass%, and Sr: 0.01 mass% to 1.0 mass%, with the balance being Zn and inevitable impurities, and

10 diffraction intensities of Si and Mg<sub>2</sub>Si in the coating layer as measured by an X-ray diffraction method satisfy the following relation (1):

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

15 where Si(111) represents a diffraction intensity for a (111) plane of Si with an interplanar spacing d of 0.3135 nm, and

Mg<sub>2</sub>Si(111) represents a diffraction intensity for a (111) plane of Mg<sub>2</sub>Si with an interplanar spacing d of 0.3668 nm.

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

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

25 [Claim 3] The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to any one of claim 1 or 2, wherein a content of Al in the coating layer is 50 mass% to 60 mass%.

30 [Claim 4] The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to any one of claims 1 to 3, wherein a content of Si in the coating layer is 1.0 mass% to 3.0 mass%.

[Claim 5] The hot-dip Al-Zn-Si-Mg-Sr coated steel sheet according to any one of claims 1 to 4, wherein a content of Mg in the coating layer is 1.0 mass% to 5.0 mass%.

[Claim 6] A surface-treated steel sheet comprising the coating layer as recited in any one of claims 1 to 5 and a chemical conversion layer formed on the coating layer, wherein

the chemical conversion layer contains: at least one resin selected from  
5 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 metal 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,  
10 a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

[Claim 7] A pre-painted steel sheet comprising a paint layer formed either directly on the coating layer as recited in any one of claims 1 to 5 or on a chemical conversion layer on top of the coating layer, wherein

15 the chemical conversion layer contains: a resin component containing (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%, in which a content ratio of (a) to (b), (a):(b), is in the range of 3:97 to 60:40 by mass; and an inorganic compound containing 2 mass% to 10 mass% of a  
20 vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound, and

the paint layer has at least a primer paint layer, the primer paint layer containing: a polyester resin having a urethane bond; and an inorganic compound containing a vanadium compound, a phosphoric acid compound, and  
25 a magnesium oxide.