

DESCRIPTION

TITLE

HOT DIP Al-Zn COATED STEEL SHEET, METHOD OF PRODUCING
5 SAME, SURFACE-TREATED STEEL SHEET, AND PREPAINTED STEEL
SHEET

TECHNICAL FIELD

[0001] The present disclosure relates to a hot-dip Al-Zn coated steel sheet, a
10 method of producing same, a surface-treated steel sheet and a prepainted steel
sheet.

BACKGROUND

[0002] Hot-dip Al-Zn coated steel sheets, as typified by 55 % Al-Zn coated
15 steel sheets, combine the sacrificial protection properties of Zn and the high
corrosion resistance of Al, and are therefore known to exhibit high corrosion
resistance among hot-dip galvanized steel sheets. Further, because of their
excellent corrosion resistance, hot-dip Al-Zn coated steel sheets are used
mainly in the field of building materials, as roofs, walls, and the like that are
20 exposed to outdoor environments for long periods of time, and in the field of
civil engineering and construction, as guardrails, wiring and piping,
soundproof walls, and the like. Demand for hot-dip Al-Zn coated steel sheets
has been increasing in recent years, in particular due to the demand for
materials having superior corrosion resistance and maintenance-free materials
25 under more severe operating environments, such as exposure to acid rain
caused by air pollution, exposure to snow-melting agents applied to prevent
roads from freezing in snowy regions, and in coastal area development.

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

[0004] Typically, hot-dip Al-Zn coated steel sheets are produced by using steel sheets hot rolled or cold rolled from slabs as base steel sheets and subjecting the base steel sheets to recrystallization annealing and hot dip coating treatment in a continuous galvanizing line annealing furnace.

5 Here, in addition to defined concentrations of Al and Zn, Si is usually added to a coating bath used in production of a hot-dip Al-Zn coated steel sheet in order to inhibit excessive growth of an interfacial alloy layer formed at the interface between the steel substrate and the coating. The action of Si can control the thickness of an interfacial alloy layer of a hot-dip Al-Zn coated
10 steel sheet to about 1 μm to 5 μm . When the coating thickness is uniform, the thinner the interfacial alloy layer and the thicker an upper layer that expresses high corrosion resistance, and therefore inhibiting growth of the interfacial alloy layer is thought to lead to improved corrosion resistance.

[0005] Further, it is known that impurities inevitably enter the coating bath
15 used in the production of hot-dip coated steel sheets due to impurities contained in the coating materials, liquation from the base steel sheet and bath equipment, and the like. There is no exception to inevitable impurity entering the bath for coating baths used in the production of hot-dip Al-Zn coated steel sheets, and components such as Fe, Cr, Ni, Cu, Co, and W are inevitably
20 contained in the coating.

[0006] Impurity in the coating bath may cause deterioration of properties such as appearance, corrosion resistance, and workability of a hot-dip coated steel sheet, and the presence or absence of impurity effects is determined by the composition and impurity concentration of the coating. That is, even impurities
25 of the same composition may be harmful or harmless to the properties of a coated steel sheet. Therefore, the effects of impurities on the properties of various hot-dip coated steel sheets have been investigated, and techniques have been developed to control impurity concentration to stably obtain required properties.

30 For example, Patent Literature (PTL) 2 describes a hot-dip Al-Zn coated steel sheet having a coating consisting of, in mass%, Al: 0.10 % to 0.6 %, Bi: 0.03 % to 0.3 %, with the balance being Zn and inevitable impurity, where the content of each of Pb, Sn, and Cd as inevitable impurity is controlled to 0.002 %.

35 Further, PTL 3 describes a hot-dip Zn-Al-Mg coated steel sheet having a coating consisting of, in mass%, Al: 4.4 % to 5.6 %, Mg: 0.3 % to 0.56 %, and the balance being Zn and inevitable impurity.

with the balance being Zn and inevitable impurity, where the content is controlled so that Ni is not contained in the inevitable impurity.

[0007] However, such hot-dip Al-Zn coated steel sheets have a problem that white rust occurs due to corrosion of the coating when used in a severe corrosion environment. White rust causes deterioration in the appearance of steel sheets, and therefore various technologies have been developed to improve anti-white rust property.

For example, PTL 4 describes a surface-treated steel sheet having an improved anti-white rust property by provision of a chemical conversion layer on a hot-dip Al-Zn coated steel sheet, the chemical conversion layer containing a water-soluble urethane resin having a carboxyl group and acid amide bond, N-methylpyrrolidone, a zirconium metal compound, and a silane coupling agent.

Further, PTL 5 describes a surface-treated steel sheet having an improved anti-white rust property by provision of a chemical conversion layer on a hot-dip Al-Zn coated steel sheet, the chemical conversion layer containing a resin having a glass transition temperature of -10°C or more selected from acrylic resins, polyester resins, or urethane resins and a compound selected from Si compounds, Zr compounds, or triazoles and tetrazoles.

[0008] Further, a prepainted steel sheet including a chemical conversion layer, a primer paint layer, a top coating layer, and the like formed on a surface of a hot-dip Al-Zn coated steel sheet is subjected to various working such as 90° bending and 180° bending by press forming, roll forming, or emboss forming, and is required to have long-term paint layer durability. In order to meet these requirements, there are prepainted steel sheets in which a chemical conversion layer containing chromate and a primer paint layer also containing chromate-based anti-corrosion pigments are formed on a hot-dip Al-Zn coated steel sheet, and a weather-resistant top coating layer such as a thermosetting polyester resin paint layer or a fluorine resin paint layer is formed thereon.

[0009] Recently, however, the use of chromate, an environmentally hazardous substance, has become a problem, and the development of prepainted steel sheets that can improve corrosion resistance even without chromate is strongly desired.

As a technology to meet these requirements, for example, PTL 6 describes a prepainted steel sheet that has improved corrosion resistance at a cut end surface, where an undercoat layer including a rust-prevention pigment

including Mg is applied to a surface of a hot-dip Al-Zn coated steel sheet and a top coating layer having a contact angle with respect to water of 80° or more and less than 130° is formed thereon.

Further, PTL 7 describes a prepainted steel sheet that has improved
5 corrosion resistance at a worked portion or cut end surface, where a chromate-free chemical conversion layer containing urethane resin, epoxy resin, vanadium compound, zirconium compound, and fluorine compound is formed on a surface of a hot-dip Al-Zn coated steel sheet, a primer paint layer containing ester resin as a main component, vanadium compound, phosphate
10 compound, and magnesium oxide is formed thereon, and a melamine-cured polyester top coating layer is formed thereon.

CITATION LIST

Patent Literature

- 15 **[0010]** PTL 1: JP S46-007161 B
PTL 2: JP 2004-285387 A
PTL 3: JP 2016-540885 A (publication in Japan of WO2015/052546 A1)
PTL 4: JP 2003-201578 A
PTL 5: JP 2013-237874 A
20 PTL 6: JP 2009-172553 A
PTL 7: JP 2016-176118 A

SUMMARY

(Technical Problem)

- 25 **[0011]** However, the effects of inevitable impurity on corrosion resistance of hot-dip Zn-Al coated steel sheets as described in PTL 2 and PTL 3 have not been sufficiently clarified, and development of a technology that can more reliably achieve superior corrosion resistance is desired.

In addition, the control of impurity in the production of hot-dip coated
30 steel sheets, not limited to hot-dip Al-Zn coated steel sheets, is mostly limited to concentration control only, and no technology has been established to control the size, distribution state, or other morphological control, and development of a technology that can more reliably achieve superior corrosion resistance is desired.

- 35 **[0012]** The above-mentioned technology to improve corrosion resistance by taking into account the effects of inevitable impurity is desired not only for

coated steel sheets but also for surface-treated steel sheets including an additional chemical conversion layer formed on the coating, and prepainted steel sheets including an additional paint layer formed directly on the coating or with a chemical conversion layer in-between.

5 **[0013]** Further, although a certain level of corrosion resistance and anti-white rust property is obtainable by using the surface-treated steel sheets of PTL 4 and PTL 5, the effect is not always sufficient, and a higher level of corrosion resistance and anti-white rust property is required.

10 Further, although a certain level of corrosion resistance at worked portions and cut ends is obtainable by using the prepainted steel sheets of PTL 6 and PTL 7, the effect may not be sufficient, and a higher level of corrosion resistance and worked portion corrosion resistance is required.

15 **[0014]** In view of these circumstances, it would be helpful to provide a hot-dip Al-Zn coated steel sheet that reliably and stably has excellent corrosion resistance and a method of producing same.

Further, it would be helpful to provide a surface-treated steel sheet that reliably and stably has excellent corrosion resistance and anti-white rust property, and a prepainted steel sheet that reliably and stably has excellent corrosion resistance and worked portion corrosion resistance.

20 (Solution to Problem)

25 **[0015]** As a result of studies to solve the technical problems described above, the inventors focused on the importance of controlling not only the concentration of Al, Zn, and Si but also controlling the concentration of impurity in the composition of the coating of a hot-dip Al-Zn coated steel sheet, and found that appropriate control of Ni content can effectively suppress degradation of corrosion resistance. Further, the inventors found that the degradation of corrosion resistance can be more stably suppressed by appropriately controlling the size and distribution state of Ni compounds that exist as impurity in the coating.

30 **[0016]** The present disclosure was completed based on these findings, and primary features of the present disclosure are as described below.

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

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Ni content in the inevitable impurity is 0.010 mass% or less of the total

mass of the coating.

[0017] 2. The hot-dip Al-Zn coated steel sheet according to 1, above, wherein the coating contains Ni compounds and the major axis length of the Ni compounds is 4.0 μm or less.

5 3. The hot-dip Al-Zn coated steel sheet according to 1 or 2, above, wherein the coating contains Ni compounds and the number of Ni compounds in a direction parallel to the surface of the base steel sheet is 5 or less per mm.

 4. The hot-dip Al-Zn coated steel sheet according to 1, above, wherein the coating does not contain Ni compounds.

10 **[0018]** 5. The hot-dip Al-Zn coated steel sheet according to any one of 1 to 4, above, wherein Al content in the coating is 50 mass% to 60 mass%.

[0019] 6. The hot-dip Al-Zn coated steel sheet according to any one of 1 to 5, above, wherein Co content in the inevitable impurity in the coating is 0.080 mass% or less of the total mass of the coating.

15 **[0020]** 7. A method of producing a hot-dip Al-Zn coated steel sheet including a coating, the method comprising:

 a hot-dip coating treatment to form the coating, the hot dip coating treatment including immersing a base steel sheet in a coating bath having a composition containing (consisting of) Al: 45 mass% to 65 mass% and Si: 1.0
20 mass% to 4.0 mass%, with the balance being Zn and inevitable impurity, and
 controlling Ni content in the inevitable impurity in the coating bath to be 0.010 mass% or less of the total mass of the coating bath.

[0021] 8. A surface-treated steel sheet comprising the coating according to any one of 1 to 6, above, and a chemical conversion layer formed on the coating,
25 wherein

 the chemical conversion layer contains: at least one resin selected from the group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin, an amino resin, and a fluororesin; and at least one metal compound selected from
30 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.

[0022] 9. A prepainted steel sheet comprising a paint layer formed either directly on the coating according to any one of 1 to 6, above, or on a chemical
35 conversion layer on top of the coating, 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 content ratio of (a) to (b), (a):(b), is in a range from 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 includes 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 a magnesium oxide.

(Advantageous Effect)

[0023] The present disclosure provides a hot-dip Al-Zn coated steel sheet that reliably and stably has excellent corrosion resistance.

Further, the present disclosure provides a surface-treated steel sheet that reliably and stably has excellent corrosion resistance and anti-white rust property, and a prepainted steel sheet that reliably and stably has excellent corrosion resistance and worked portion corrosion resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] In the accompanying drawings:

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

DETAILED DESCRIPTION

[0025] (Hot-dip Al-Zn coated steel sheet)

The hot-dip Al-Zn coated steel sheet disclosed herein includes a coating on a surface of the steel sheet.

The coating has a composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 4.0 mass%, with the balance being Zn and inevitable impurity.

[0026] From the viewpoint of balancing corrosion resistance with actual operation requirements, Al content in the coating is 45 mass% to 65 mass%. Al content in the coating is preferably 50 mass% to 60 mass%. This is because when the content of Al in the coating is at least 45 mass%, dendrite solidification of Al occurs and a coating structure mainly composed of α -Al phase dendrite solidification microstructure can be obtained. Such dendrite

solidification microstructure stacked in the thickness direction of the coating makes the corrosion path complex and improves corrosion resistance of the coating itself. Further, the more dendrite portions of α -Al phase are stacked, the more complex the corrosion path becomes, and the harder it is for corrosion to reach the base steel sheet, resulting in improved corrosion resistance. Therefore, the Al content is preferably 50 mass% or more. On the other hand, when the Al content in the coating exceeds 65 mass%, the microstructure changes to one in which most Zn is a solid solute in α -Al, a dissolution reaction of the α -Al phase cannot be suppressed, and the corrosion resistance of the Al-Zn coating deteriorates. For this reason, the Al content in the coating is 65 mass% or less. The Al content in the coating is preferably 60 mass% or less.

[0027] Si in the coating is mainly added to inhibit the growth of Fe-Al and/or Fe-Al-Si interfacial alloy layer that forms at the interface with the base steel sheet and to prevent deterioration of adhesion between the coating 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. At this point, the Fe-Al-Si alloy grows more slowly than the Fe-Al alloy, and therefore the higher the proportion of Fe-Al-Si alloy, the more the overall growth of the interfacial alloy layer is suppressed. Si content in the coating is therefore 1.0 mass% or more. On the other hand, when the Si content in the coating exceeds 4.0 mass%, not only does the 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. The Si content is therefore 4.0 mass% or less. Further, from the viewpoint of suppressing the presence of excess Si phase, the Si content in the coating is preferably 3.0 mass% or less.

[0028] Further, the coating contains Zn and inevitable impurity. Among these, the inevitable impurity contains Fe. Fe is inevitably contained in the coating as a result of inevitable liquation of the steel sheet or bath equipment into the coating bath and Fe supply by diffusion from the base steel sheet during the formation of the interfacial alloy layer. Fe content in the coating is usually around 0.3 mass% to 2.0 mass%.

Other inevitable impurity includes, for example, Cr, Ni, Cu, Co, and W. These components are inevitably included in the coating due to liquation into the coating bath of base steel sheets, stainless steel bath equipment, and W-C

and Co-Cr-W thermal sprayed coating applied to bath equipment, being contained as impurity in the metal ingots used as raw material for the coating bath, and use of pot or bath equipment used in the production of coated steel sheets to which these components are intentionally added.

5 **[0029]** The hot-dip Al-Zn coated steel sheet is characterized in that the Ni content in the inevitable impurity is 0.010 mass% or less of the total mass of the coating. Ni contained in the coating may deteriorate the corrosion resistance of the hot-dip Al-Zn coated steel sheet, and therefore the deterioration of corrosion resistance can be suppressed by suppressing Ni
10 content as inevitable impurity in addition to appropriate control of Al, Zn, and Si content in the coating. From the same perspective, the Ni content in the inevitable impurity is preferably 0.005 mass% or less of the total mass of the coating.

15 **[0030]** When Ni is contained in the inevitable impurity, Ni compounds may be included as impurity in the coating of the hot-dip Al-Zn coated steel sheet. The Ni compounds mainly include binary intermetallic compounds such as Ni-Al compounds and ternary intermetallic compounds such as Ni-Al-Fe compounds. Examples of Ni-Al compounds include intermetallic compounds such as NiAl_3 , and examples of Ni-Al-Fe compounds include intermetallic compounds such
20 as $(\text{Ni,Fe})\text{Al}_3$, in which a portion of Ni in NiAl_3 is replaced by Fe, but are not limited to these compounds.

25 **[0031]** Here, the presence of Ni compounds in the coating may be confirmed, for example, by utilizing a scanning electron microscope, observing the coating from the surface or cross-section with a secondary electron image or a reflected electron image, and analysis by energy dispersive X-ray spectroscopy (EDS). For example, the composition of Ni inclusions may be confirmed by arbitrarily selecting 5 to 10 locations of a coating cross-section of 100 μm , conducting observation and elemental mapping analysis at an accelerating voltage of 5 kV or less for each, and conducting further point analysis at portions where Ni is
30 detected. This method is only an example and by no means a limitation of the disclosure. Any method that can confirm the presence of Ni compounds may be used.

35 **[0032]** Further, when Ni compounds are included in the coating, the major axis length of the Ni compounds is preferably 4.0 μm or less.

Ni compounds present in the coating may function as a cathode in a corrosion environment and form a local battery with surrounding solidification

microstructure, causing degradation of corrosion resistance. In particular, when coarse Ni compounds are present in the coating, corrosion resistance of the hot-dip Al-Zn coated steel sheet may be significantly reduced. Therefore, in order to obtain the hot-dip Al-Zn coated steel sheet having superior corrosion resistance, controlling size of Ni compounds contained as impurity in the coating to be small is effective. Specifically, major axis length of the Ni compounds is preferably 4.0 μm or less. Major axis length of the Ni compounds is more preferably 3.0 μm or less. Major axis length of the Ni compounds is even more preferably 2.0 μm or less.

The major axis length of the Ni compounds may be measured, for example, by utilizing a scanning electron microscope, observing the coating from a cross-section with a reflected electron image, confirming presence of a Ni compound by EDS, and then observing a reflected electron image with the field of observation including the Ni compound enlarged. The major axis length of the Ni compounds is defined as the maximum major axis length of Ni compounds that can be confirmed in observation fields of the coating.

[0033] Further, when Ni compounds are included in the coating, reducing the amount of the Ni compounds, which are initiation points of corrosion, is effective from the viewpoint of obtaining more stable and higher corrosion resistance. Specifically, the number of particles of Ni compounds in the coating in the direction parallel to the surface of the base steel sheet is preferably 5 or less per mm. The number is more preferably 2 or less per mm. The number is most preferably 0 per mm (not present).

Therefore, by suppressing the amount of Ni compounds in the coating, degradation of corrosion resistance of the hot-dip Al-Zn coated steel sheet can be more reliably suppressed. In order to obtain such a coating structure (coating structure without Ni compounds), reducing the Ni content in the inevitable impurity is important, and specifically, reducing the Ni content to 0.005 mass% or less of the total mass of the coating is important.

The number of particles of Ni compounds may be calculated, for example, by utilizing a scanning electron microscope, continuously observing a cross-section of the coating parallel to the surface of the base steel sheet for a length of 1 mm or more in a reflected electron image, and dividing the number of Ni compounds confirmed by EDS by the measured length (mm) to calculate the number of Ni compounds present in a length range of 1 mm.

[0034] Further, the hot-dip Al-Zn coated steel sheet preferably has Co content

in the inevitable impurity of 0.080 mass% or less of the total mass of the coating. Co contained in the coating, like Ni, may deteriorate the corrosion resistance of the hot-dip Al-Zn coated steel sheet, and therefore suppressing Co content as inevitable impurity, in addition to appropriate control of Al, Zn, Si, and Ni content as inevitable impurity in the coating, is effective in suppressing the deterioration of corrosion resistance.

From the same perspective, the Co content in the inevitable impurity is preferably 0.020 mass% or less of the total mass of the coating. The Co content in the inevitable impurity is more preferably 0.010 mass% or less of the total mass of the coating.

[0035] The total content of the inevitable impurity in the coating is not particularly limited. Excessive content may affect various properties of the coated steel sheet, and therefore the total content of the inevitable impurity is preferably 5.0 mass% or less.

[0036] Further, the coating preferably contains at least one selected from the group consisting of V, Cr, Mn, Mg, Ca, and Sr in a total of 0.01 mass% to 10 mass%. These elements can improve the stability of corrosion products and delay the progress of corrosion when the coating is corroded.

The reason why the total content of the above-mentioned components is set in the range from 0.01 mass% to 10 mass% is that a sufficient corrosion retardation effect can be obtained and the effect is not saturated.

[0037] Further, in the hot-dip Al-Zn coated steel sheet, diffraction intensity of Si in the coating by X-ray diffraction preferably satisfies the following Relation (1), from the viewpoint of being able to improve corrosion resistance more stably after controlling the concentration of Al, Zn, Si, and Ni and Co as inevitable impurity.

$$\text{Si}(111) = 0 \quad \dots(1)$$

Here, Si(111) represents 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 Si phase as a cathodic site promotes the dissolution of surrounding α -Al phase. Accordingly, the best way to stabilize corrosion resistance is to make the coating free from Si phase (that is, to make the Si(111) diffraction peak intensity zero), as in Relation (1).

The method of measuring Si(111) by X-ray diffraction may include mechanically scraping off a part of the coating and performing X-ray

diffraction on the scraped off part in powder form (that is, powder X-ray diffraction measurement). For the measurement of diffraction intensity, the diffraction peak intensity of Si corresponding to an interplanar spacing d of 0.3135 nm is measured.

5 The amount of the coating required for powder X-ray diffraction measurement (that is, the amount of the coating to be scraped off) is 0.1 g or more from the viewpoint of measuring Si(111) with high precision. The amount is preferably 0.3 g or more. Further, although steel sheet components other than the coating may be included in the powder when the coating is scraped off,
10 these intermetallic compound phases are included only in the coating and the peak intensities are not affected. Further, X-ray diffraction is performed on the coating in powder form because calculating the proportions of phases correctly is difficult when X-ray diffraction is performed on the coating formed on the coated steel sheet due to the influence of planar orientation of coating
15 solidification microstructure.

[0038] There is no particular limitation on how to satisfy Relation (1). For example, the proportion of Si present (diffraction intensity of Si (111)) can be controlled by adjusting the balance of Si content and Al content in the coating. Regarding the balance between the Si content, the Mg content, the Ca content,
20 the Sr content, and the Al content in the coating, it does not necessarily follow that Relation (1) can be satisfied by simply setting a certain content ratio. For example, the content ratio of Al needs to be changed depending on the Si content in mass%. In addition to adjusting the balance between the Si content and the Al content in the coating, the diffraction intensity of Si(111) can be
25 controlled to satisfy Relation (1) by adjusting conditions during coating formation (for example, cooling conditions after coating).

[0039] The coating weight of the coating is preferably 45 g/m^2 to 120 g/m^2 per surface from the viewpoint of satisfying various properties. When the coating weight of the coating is 45 g/m^2 or more, sufficient corrosion resistance can be
30 obtained for applications requiring long-term corrosion resistance such as in building materials, and when the coating weight of the coating is 120 g/m^2 or less, excellent corrosion resistance can be achieved while suppressing the occurrence of defects such as coating cracks during working. From the same perspective, the coating weight of the coating is more preferably 45 g/m^2 to
35 100 g/m^2 .

[0040] The coating weight of the coating can be derived, for example, by

dissolving and stripping a specific area of the coating with a mixture of hydrochloric acid and hexamethylenetetramine as indicated in JIS H 0401:2013, and calculating the difference in weight of the steel sheet before and after the stripping. To determine the coating weight per surface using this method, the non-target surface may be sealed with tape prior to the dissolution so that the coated surface is not exposed.

[0041] Further, the chemical composition of the coating can be confirmed, as with the Ni content, by immersing the coating in hydrochloric acid or the like to dissolve the coating, and then analyzing the solution by ICP emission spectroscopy, atomic absorption spectroscopy, or the like. These methods are only examples and by no means a limitation of the disclosure. Any method that can accurately quantify the chemical composition of the coating may be used.

[0042] The composition of the coating of the hot-dip Al-Zn 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 can be precisely controlled by controlling the composition of the coating bath.

[0043] Further, regarding the base steel sheet of the hot-dip Al-Zn 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 required performance and standards.

Further, the method of obtaining the base steel sheet is not particularly limited. For example, in the case of a hot-rolled steel sheet, a hot-rolled steel sheet that has undergone hot rolling and pickling may be used, and in the case of a cold-rolled steel sheet, a cold-rolled steel sheet that has been additionally subjected to cold rolling may be used. Further, recrystallization annealing and the like may be carried out prior to the hot dip coating as appropriate for the required properties of the steel sheet.

[0044] (Method of producing hot-dip Al-Zn coated steel sheet)

The method of producing a hot-dip Al-Zn coated steel sheet according to the present disclosure is a method of producing a hot-dip Al-Zn coated steel sheet that includes the coating. The method includes hot-dip coating treatment to form the coating, the hot dip coating treatment including immersing the base steel sheet in a coating bath having a composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 4.0 mass%, with the balance being Zn and inevitable impurity.

The hot-dip coating treatment is not limited in any particular way, except for the coating bath conditions described below. For example, the method may include cleaning, heating, and dipping the base steel sheet in the coating bath in a continuous galvanizing line. In the heating of the steel sheet,
5 it is effective to perform recrystallization annealing in order to control the microstructure of the base steel sheet itself, and to perform the heating in a 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.

10 **[0045]** Further, regarding the coating bath used in the hot dip coating treatment, as described above, the composition of the coating as a whole is almost equivalent to the composition of the coating bath, and therefore a coating bath having a composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 4.0 mass%, with the balance being Zn and inevitable impurity, can be used.

15 **[0046]** Further, in the method of producing the hot-dip Al-Zn coated steel sheet, the Ni content in the inevitable impurity in the coating bath is controlled to be 0.010 mass% or less of the total mass of the coating bath. As mentioned above, Ni contained in the coating may deteriorate the corrosion resistance of the hot-dip Al-Zn coated steel sheet, and therefore the deterioration of corrosion
20 resistance can be suppressed by suppressing Ni content as inevitable impurity in addition to appropriate control of Al, Zn, and Si content in the coating bath.

Further, the Ni content as inevitable impurity in the coating bath needs to be controlled to 0.010 mass% or less of the total mass of the coating bath. The Ni content in the coating bath is preferably 0.005 mass% or less. When the
25 Ni content in the coating bath exceeds 0.005 mass%, the corrosion resistance of the produced hot-dip Al-Zn coated steel sheet may deteriorate, and when the Ni content exceeds 0.010 mass%, significant deterioration of corrosion resistance may occur. There is no limitation on the lower limit of Ni content, as Ni adversely affects corrosion resistance.

30 **[0047]** Here, the means to reduce the Ni content in the coating bath is not particularly limited.

For example, suppressing liquation of stainless steel bath equipment into the coating bath is effective, and therefore the surface of the bath equipment is preferably treated with a thermal sprayed coating or the like. This
35 is because the formation of the thermal sprayed coating or the like can provide the bath equipment with corrosion resistance to the coating bath, and can

suppress liquation of the bath equipment into the coating bath. The type of the thermal sprayed coating is not particularly limited. Coating having heat resistance and corrosion resistance such as WC or MoB types of coating may be selected. Further, using bath equipment made of a heat-resistant material that does not contain Ni is effective. In this case, an increase in Ni content can be prevented even in the case of liquation of bath equipment.

[0048] Further, as another means of reducing the Ni content in the coating bath, metal ingots with low Ni content as impurity are preferably used as raw material for the coating bath.

Further, avoiding use in the production of the hot-dip Al-Zn coated steel sheet of pots and bath equipment used in the production of coated steel sheets in which Ni is intentionally added is also effective. This is in order to prevent Ni-containing metal lumps that have adhered to the pots and bath equipment from dissolving and mixing into the coating bath.

[0049] In addition, the Co content as inevitable impurity in the coating bath is preferably controlled to 0.080 mass% or less of the total mass of the coating bath. The Co content in the coating bath is more preferably 0.020 mass% or less. The Co content in the coating bath is even more preferably 0.001 mass% or less. When the Co content in the coating bath is 0.080 mass% or less, the hot-dip Al-Zn coated steel sheet produced can have sufficiently good corrosion resistance, when 0.020 mass% or less, better corrosion resistance is obtainable, and when 0.010 mass% or less, particularly good corrosion resistance is obtainable. Thus, the lower the Co content in the coating bath, the better the corrosion resistance of the hot-dip Al-Zn coated steel sheet, and therefore there is no particular lower limit for the Co content.

[0050] Here, the means to reduce the Co content in the coating bath is not particularly limited.

For example, suppressing liquation into the coating bath of a Co-Cr-W thermal sprayed coating applied to the bath equipment is effective, and therefore a Co-free thermal sprayed coating is preferably applied.

[0051] Further, as another means of reducing the Co content in the coating bath, metal ingots with low Co content as impurity are preferably used as raw material for the coating bath.

Further, avoiding use in the production of the hot-dip Al-Zn coated steel sheet of pots and bath equipment used in the production of coated steel sheets in which Co is intentionally added is also effective. This is in order to

prevent Co-containing metal lumps that have adhered to the pots and bath equipment from dissolving and mixing into the coating bath.

[0052] Further, the bath temperature of the coating bath is not particularly limited. The bath temperature is preferably in a temperature range from
5 (melting point + 20 °C) to 650 °C.

The lower limit of the bath temperature is (melting point + 20 °C) because the bath temperature needs to be equal to or greater than the solidification point in order to carry out the hot-dip coating treatment, and (melting point + 20 °C) reliably prevents the components of the coating bath
10 from being solidified due to a localized drop of the bath temperature of the coating bath. On the other hand, the upper limit of the bath temperature is 650 °C because a bath temperature exceeding 650 °C may make rapid cooling of the coating difficult, thereby increasing the thickness of the interfacial alloy layer formed between the coating and the steel sheet.

[0053] Further, the temperature of the base steel sheet entering the coating bath (entering sheet temperature) is not particularly limited. From the viewpoint of securing proper coating characteristics in the continuous hot-dip coating operation and preventing change in the bath temperature, the entering sheet temperature is preferably controlled to be in ± 20 °C relative to the
15 temperature of the coating bath.

[0054] Further, the time during which the base steel sheet is immersed in the coating bath is preferably 0.5 s or more. This is because when the immersion time is less than 0.5 s, there is a possibility that a sufficient coating cannot be formed on the surface of the base steel sheet. The upper limit of immersion
20 time is not particularly limited. A long immersion time may result in a thicker interfacial alloy layer forming between the coating and the steel sheet, and therefore the immersion time is preferably 8 s or less.

[0055] In the hot-dip Al-Zn coated steel sheet, a paint layer may be formed either directly on the coating or on an intermediate layer on top of the coating,
25 depending on required performance.

[0056] The method of forming the paint layer is not particularly limited, and may be selected as appropriate depending on required performance. For example, roll coater coating, curtain flow coating, spray coating, or other formation methods may be used. The paint layer may be formed by applying a
30 paint containing an organic resin, and then heating and drying the applied paint
35 by means of hot air drying, infrared heating, induction heating, or the like.

[0057] Further, the intermediate layer is also not particularly limited as long as the intermediate layer is formed between the coating and the paint layer of the hot-dip coated steel sheet.

[0058] (Surface-treated steel sheet)

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

 The configuration of the coating is the same as that of the coating of the hot-dip Al-Zn coated steel sheet according to the present disclosure, as
10 described above.

[0059] According to the surface-treated steel sheet, the chemical conversion layer is formed on the coating.

 The chemical conversion layer may be formed on at least one surface of the surface-treated steel sheet, and may be formed on both surfaces of the
15 surface-treated steel sheet depending on the application and required performance.

[0060] In the surface-treated steel sheet according to the present disclosure, the chemical conversion layer contains: at least one resin selected from the group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic
20 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, a Mo compound, a Zr compound, a Ti compound, and a Ca compound.

25 By forming the chemical conversion layer on the coating, enhancing the anti-rust and barrier effects of the chemical conversion layer is possible, in addition to increasing affinity with the coating and enabling uniform formation of the chemical conversion layer on the coating. As a result, corrosion resistance and anti-white rust property of the surface-treated steel sheet may
30 be stably achieved.

[0061] The resin of the chemical conversion layer, from the viewpoint of improving corrosion resistance, may be at least one selected from the group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic
35 silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin, an amino resin, and a fluororesin. From the same perspective, the resin preferably contains at least one of a urethane resin or an acrylic resin. Examples of the

resin of the chemical conversion layer also include addition polymerization products of the resins listed above.

[0062] 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; aliphatic epoxy resins; alicyclic epoxy resins; and polyether epoxy resins.

[0063] Examples of the urethane resin include oil-modified polyurethane resins, alkyd polyurethane resins, polyester polyurethane resins, polyether polyurethane resins, and polycarbonate polyurethane resins.

[0064] 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.

[0065] 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. In addition to corrosion resistance, excellent weather resistance may be obtained when the acrylic silicon resin is used.

[0066] 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.

[0067] 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 terephthalate, polytrimethylene terephthalate, polyethylene naphthalate, and polybutylene naphthalate. Further, acrylic-modified products of these polyester resins may also be used.

[0068] Examples of the polyalkylene resins include: ethylene copolymers such

as ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, 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 may also be used.

[0069] Examples of the amino resin include thermosetting resins formed by the reaction of an amine or amide compound with an aldehyde, including melamine resins, guanamine resins, and thiourea resins. Among these, melamine resins are preferred 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 waterborne melamine resins.

[0070] Examples of the fluororesin include fluoroolefin polymers and copolymers of fluoroolefins and alkyl vinyl ethers, synchroalkyl vinyl ethers, carboxylic acid-modified vinyl esters, hydroxyalkyl allyl ethers, tetrafluoropropyl vinyl ethers, and the like. When using these fluororesins, not only excellent corrosion resistance, but also excellent weather resistance and hydrophobicity can be obtained.

[0071] Further, a curing agent is preferably used 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 melamine resins or butyl ether melamine resins), butylated urea-melamine resins, amino resins such as benzoguanamine resins, block isocyanates, oxazoline compounds, or phenol resins may be used as appropriate.

[0072] Further, the metal compound of the chemical conversion layer is 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. From the same perspective, the metal compound preferably contains at least one of a P compound, a Si compound, or a V compound.

[0073] Here, the P compound can improve corrosion resistance and perspiration resistance by being included in the chemical conversion layer. 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 salts thereof.

[0074] As the inorganic phosphoric acid, organic phosphoric acid, and salts

thereof, any compounds may 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. The salt is more preferably a metal salt. The salt is preferably at least one selected from the group consisting of alkali metal salts and alkaline earth metal salts.

[0075] When a chemical conversion treatment liquid containing the P compound is applied to the hot-dip Al-Zn coated steel sheet, the P compound causes the surface of the coating to be etched, thereby forming, on the coating side of the chemical conversion layer, an enriched layer in which the constituent elements of the coating, 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, improving the adhesion of the chemical conversion layer.

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%. When 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 flat parts but also in reduced corrosion resistance and perspiration resistance in defective parts, cut edges, and those parts of the coating or coating damaged by working or the like. From the same perspective, the concentration of the P compound is preferably 0.35 mass% or more. The concentration of the P compound is more preferably 0.50 % or more. On the other hand, when the concentration of the P compound exceeds 5 mass%, not only is the life of the chemical conversion treatment liquid shortened, but the appearance after the formation of the coating 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 compound is preferably 3.5 mass% or less. The concentration of the P compound is 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/m² to 100 mg/m².

[0076] 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 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.

[0077] The silica may be any silica without any particular limitation. For example, at least one of wet silica or dry silica may 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, and the like produced by Nissan Chemical Corporation may be suitably used. As the dry silica, for example, AEROSIL 50, 130, 200, 300, 380, and the like produced by Nippon Aerosil Co., Ltd. may be suitably used.

[0078] The trialkoxysilane may be any trialkoxysilane without any particular limitation. For example, 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) are preferred. Such trialkoxysilanes include, for example, trimethoxysilane, triethoxysilane, and methyltriethoxysilane.

[0079] The tetraalkoxysilane may be any tetraalkoxysilane without any particular limitation. For example, tetraalkoxysilanes represented by the general formula: $Si(OR)_4$ (where R is the same or different alkyl group having 1-5 carbon atoms) are preferred. Such tetraalkoxysilanes include, for example, tetramethoxysilane, tetraethoxysilane, and tetrapropoxysilane.

[0080] The silane coupling agent may be any silane coupling agent without any particular limitation. Examples of the silane coupling agent include γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -

aminopropylmethyldiethoxysilane, γ -aminopropyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -mercaptopropylmethyldimethoxysilane, and γ -mercaptopropyltrimethoxysilane, vinyltriethoxysilane, and γ -isocyanate propyltriethoxysilane.

[0081] By including the Si compound in the chemical conversion layer, the Si compound dehydrates and condenses to form an amorphous chemical conversion layer with siloxane bonds that have a high barrier effect in shielding against corrosion factors. Further, the chemical conversion layer with higher barrier properties is formed by bonding with any of the aforementioned resins. Further, in a corrosion environment, dense and stable corrosion products are formed in defective parts or those parts of the coating or coating damaged by working, thereby providing the combined effect with the coating 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 and dry silica as the Si compound.

[0082] 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%. When 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 resistance in defective parts, cut edges, and those parts damaged by working or the like, in addition to improved corrosion resistance in flat parts. When 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 compound in the range from 0.2 mass% to 9.5 mass%, the coating weight of Si in the chemical conversion layer after drying can be 2 mg/m² to 95 mg/m².

[0083] The Co compound and the Ni compound 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 in a corrosion environment. Further, Co and Ni are 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, the enriched layer becomes a barrier against

corrosion, resulting in improved blackening resistance.

[0084] 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. A cobalt salt is preferred as the Co compound. Use of at least one of cobalt sulfate, cobalt carbonate, or cobalt chloride as the cobalt salt is more preferable.

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. A nickel salt is preferred as the Ni compound. Use of at least one of nickel sulfate, nickel carbonate, and nickel chloride as the nickel salt is more preferable.

[0085] The concentration of the Co compound and/or the Ni compound in the chemical conversion treatment liquid is not particularly limited, yet can be 0.25 mass% to 5 mass% in total. When the concentration of the Co compound and/or the Ni compound 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 resistance in defective parts, cut edges, and those parts of the coating or coating damaged by working or the like may be reduced. From the same perspective, the total concentration is preferably 0.5 mass% or more. The total concentration is more preferably 0.75 mass% or more. On the other hand, when the total concentration of the Co compound and/or the Ni compound exceeds 5 mass%, the appearance after the formation of the coating is likely to become non-uniform and corrosion resistance may decrease. From the same perspective, the total concentration is preferably 4.0 mass% or less. The total concentration is more preferably 3.0 mass% or less. By applying and drying a chemical conversion treatment liquid with a total concentration of 0.25 mass% to 5 mass% of the Co compound and/or the Ni compound, the total coating weight of Co and Ni in the chemical conversion layer after drying can be 5 mg/m² to 100 mg/m².

[0086] 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 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. **[0087]** 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.

5 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
10 chloride, magnesium oxide, and magnesium hydroxide.

[0088] 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% to 5 mass%. When the total concentration is 0.25 mass% or more, the aforementioned enriched layer can be formed more effectively,
15 resulting in further improvement of corrosion resistance. When 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 damaged by working or the like.

20 **[0089]** The inclusion of the V compound in the chemical conversion layer allows 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 corrosion that
25 propagates not only in flat parts of the steel sheet, but also in defective parts, those parts of the coating damaged by working, cut edges to flat parts, and so on.

[0090] 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.
30

[0091] The V compound in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.05 mass% to 4 mass%. When 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,
35 improving corrosion resistance in defective parts, cut edges, and those parts of the coating damaged by working. When 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.

[0092] The Mo compound may 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.

[0093] The concentration of the Mo compound in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.01 mass% to 3 mass%. When 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. When 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.

[0094] 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.

[0095] 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 may 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.

[0096] 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 acetylacetonate, titanium octyleneglycolate, and titanium ethylacetoacetate may be used.

[0097] The total concentration of the Zr compound and/or the Ti compound in the chemical conversion treatment liquid to form the chemical conversion layer is preferably 0.2 mass% to 20 mass%. When the total concentration of the Zr

compound and/or the Ti compound 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 defective parts, cut edges, and those parts of the coating damaged by working. When the
5 total concentration of the Zr compound and/or the Ti compound is 20 mass% or less, the life of the chemical conversion treatment liquid can be further extended.

[0098] The Ca compound has the effect of reducing the corrosion rate when included in the chemical conversion layer.

10 **[0099]** 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, CaCO₃, Ca(OH)₂, Ca(NO₃)₂·4H₂O, and CaSO₄·2H₂O. The content of the Ca compound in the chemical conversion layer is not particularly limited.

15 **[0100]** 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, ultraviolet absorbers, light stabilizers, silane coupling agents, and titanate coupling
20 agents; pigments such as colored pigments, body pigments, and optical brightening agents; curing catalysts; organic solvents; and lubricants.

[0101] In the surface-treated steel sheet, the chemical conversion layer preferably does not contain harmful components such as hexavalent chromium, trivalent chromium, and fluorine. The chemical conversion treatment liquid
25 used to form the chemical conversion layer not containing these harmful components increases safety and is less harmful to the environment.

[0102] The coating weight of the chemical conversion layer is not particularly limited. For example, from the viewpoint of preventing exfoliation of the chemical conversion layer while ensuring more reliable corrosion resistance,
30 the coating weight of the chemical conversion layer is preferably 0.1 g/m² to 3.0 g/m². The coating weight of the chemical conversion layer is more preferably 0.5 g/m² to 2.5 g/m². By setting the coating weight of the chemical conversion layer to 0.1 g/m² or more, corrosion resistance can be more reliably secured, and by setting the coating weight of the chemical conversion layer to
35 3.0 g/m² or less, cracking and exfoliation of the chemical conversion layer may 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.

5 **[0103]** The method of forming the chemical conversion layer is not particularly limited, and may 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 using a roll coater, etc., followed by drying at a peak
10 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 may be employed as appropriate for the application of the chemical conversion treatment liquid. Further, the chemical conversion layer may be in the form of
15 either monolayer or multilayer, as long as it contains the aforementioned resins and metal compounds, and is not limited to any particular type.

[0104] In the surface-treated steel sheet according to the present disclosure, a paint layer may be formed on the chemical conversion layer, as required.

[0105] (Prepainted steel sheet)

20 The prepainted steel sheet according to the present disclosure is a prepainted steel sheet in which a paint layer is formed either directly on the coating or on the chemical conversion layer on top of the coating.

The configuration of the coating is the same as that of the coating of the hot-dip Al-Zn coated steel sheet according to the present disclosure, as
25 described above.

[0106] According to the prepainted steel sheet, the chemical conversion layer can be formed on the coating.

The chemical conversion layer may be formed on at least one surface of the prepainted steel sheet, and can be formed on both surfaces of the
30 prepainted steel sheet depending on the application and required performance.

[0107] According to the prepainted steel sheet, 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),
35 (a):(b), is in the range from 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, the strength and adhesion of the chemical conversion layer can be improved, while corrosion resistance can also be enhanced.

[0108] The resin component of the chemical conversion layer contains the anionic polyurethane resin (a) having an ester bond and the epoxy resin (b) having a bisphenol skeleton.

[0109] 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.

[0110] 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 ϵ -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 (for example, prepolymers obtained by reaction with polyols, modified polyisocyanates such as carbodiimide compounds of diphenylmethane diisocyanate).

[0111] 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 become water soluble (water dispersion). 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.

[0112] 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 a bisphenol-A epoxy resin is more preferred. The epoxy resin (b) having a bisphenol skeleton can be dispersed in a liquid such as water using a known method to obtain a chemical conversion treatment liquid.

[0113] 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 destroyed (exfoliated) when subjected to working because of its flexibility. The epoxy resin (b) having a bisphenol skeleton can achieve the effect of improving the adhesion with the Al-Zn coated steel sheet as the base steel sheet with the primer paint layer thereon.

The resin component is contained in a total of 30 mass% to 50 mass% in the chemical conversion layer. When the content of the resin component is less than 30 mass%, the binder effect of the chemical conversion layer is reduced, and when the content exceeds 50 mass%, the function of the inorganic components described below, such as inhibitor action, is reduced. From the same perspective, the content of the resin component in the chemical conversion layer is preferably 35 mass% to 45 mass%.

[0114] Further, in the resin component, the content ratio of the anionic polyurethane resin (a) having an ester bond to the epoxy resin (b) having a bisphenol skeleton, (a):(b), is required to be in the range from 3:97 to 60:40 by mass. When 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 in a range from 10:90 to 55:45.

[0115] 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 (that is, other resin components), depending on required performance. The other resin components include, but are not limited to, for

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.

5 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) having a bisphenol skeleton is preferably 50 mass% or more. The total content is more preferably 75 mass% or more. This is to more reliably obtain flexibility and adhesion as the chemical conversion treatment layer.

[0116] The chemical conversion layer also contains, as inorganic compounds, 10 2 mass% to 10 mass% of a vanadium compound, 40 mass% to 60 mass% of a zirconium compound, and 0.5 mass% to 5 mass% of a fluorine compound.

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

[0117] The vanadium compound is added to the chemical conversion treatment 15 liquid to act as an anti-rust agent (inhibitor). The inclusion of the vanadium 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 20 can further enhance corrosion resistance against corrosion that propagates not only in flat parts of the steel sheet, but also in defective parts, those parts of the coating damaged by working, cut edges to flat parts, and so on.

Examples of the vanadium compound include vanadium pentoxide, metavanadate, ammonium metavanadate, vanadium oxytrichloride, vanadium 25 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.

[0118] The content of the vanadium compound in the chemical conversion 30 layer is 2 mass% to 10 mass%. When the content of the vanadium compound in the chemical conversion layer is less than 2 mass%, the inhibitor effect is not sufficient, resulting in a decrease in corrosion resistance. When the content of the vanadium compound exceeds 10 mass%, the moisture resistance of the chemical conversion layer decreases.

35 **[0119]** The zirconium compound is contained in the chemical conversion layer and is expected to improve the strength and corrosion resistance of the

chemical conversion layer by reacting with the coating metal and coexisting with the resin components. Further, the zirconium compound itself contributes to the formation of a dense chemical conversion layer and exhibits good covering properties, and is therefore expected to have a barrier effect.

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

[0120] The content of the zirconium compound in the chemical conversion layer is 40 mass% to 60 mass%. When the content of the zirconium compound in the chemical conversion layer is less than 40 mass%, the strength and corrosion resistance as the chemical conversion layer decreases. When the content of the zirconium compound exceeds 60 mass%, the chemical conversion layer becomes brittle, resulting in destruction and stripping of the chemical conversion layer under severe working.

15 **[0121]** The fluorine compound is contained in the chemical conversion layer and acts as an agent to impart adhesion with the coating. 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 fluorides may be used. Among these, fluoride salts such as ammonium fluoride, sodium fluoride, and potassium fluoride are preferred.

20 **[0122]** The content of the fluorine compound in the chemical conversion layer is 0.5 mass% to 5 mass%. When the content of the fluorine compound in the chemical conversion layer is less than 0.5 mass%, sufficient adhesion cannot be obtained in worked portions. When the content of the fluorine compound exceeds 5 mass%, the moisture resistance of the chemical conversion layer is reduced.

[0123] The coating weight of the chemical conversion layer is not particularly 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/m² to 0.5 g/m². By setting the coating weight of the chemical conversion layer to 0.025 g/m² or more, corrosion resistance can be more reliably obtained, and by setting the coating weight of the chemical conversion layer to 0.5 g/m² or less, exfoliation of the chemical conversion layer can be suppressed.

35 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.

5 [0124] The method of forming the chemical conversion layer is not particularly limited, and may 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 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, 10 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 may 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. 15

[0125] As described above, in the prepainted steel sheet according to the present disclosure, a paint layer is formed either directly on the coating or on a chemical conversion layer on top of the coating, and the paint layer comprises at least a primer paint layer.

20 [0126] 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 25 resistance while enhancing the adhesion of the paint layer.

[0127] The primer paint layer contains a 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 working, and its high affinity with the chemical 30 conversion layer containing a urethane resin can contribute to improving corrosion resistance, especially in worked portions.

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

35 [0128] 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. Further,

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 may also be used.

- 5 **[0129]** 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, as required. 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.

[0130] 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.

[0131] The hydroxyl group value of the polyester resin having a urethane bond

is not particularly limited. From the viewpoint of solvent resistance and workability, the hydroxyl group value is preferably 5 mg KOH/g to 120 mg KOH/g. The hydroxyl group value is more preferably 7 mg KOH/g to 100 mg KOH/g. The hydroxyl group value is even more preferably 10 mg KOH/g to 80 mg KOH/g.

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

[0132] The content of the polyester resin having a urethane bond in the primer paint layer is preferably 40 mass% to 88 mass%. When 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 when the content of polyester resin having a urethane bond exceeds 88 mass%, the function by the inorganic substances as below, such as inhibitor action, may decrease.

[0133] The vanadium compound, one of the inorganic compounds, 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.

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. According to 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 with good adhesion, protecting exposed metal parts and preventing rust.

[0134] The content of the vanadium compound in the primer paint layer is not particularly limited. From the viewpoint of compatibility between corrosion resistance and moisture resistance, the content of the vanadium compound in the primer paint layer is preferably 4 mass% to 20 mass%. When the content of the vanadium compound is less than 4 mass%, the inhibitor effect may be reduced, resulting in a decrease in corrosion resistance. When the content of

the vanadium compound exceeds 20 mass%, the moisture resistance of the primer paint layer may be reduced.

5 **[0135]** The phosphate compound, one of the inorganic compounds, also acts as an inhibitor. Example of the phosphate compound include phosphoric acid, ammonium salts of phosphoric acid, alkali metal salts of phosphoric acid, and alkaline earth metal salts of phosphoric acid. Alkali metal salts of phosphoric acid, such as calcium phosphate, are particularly suitable.

10 **[0136]** The content of the phosphoric acid compound in the primer paint layer is not particularly limited. From the viewpoint of compatibility between corrosion resistance and moisture resistance, the content of the phosphoric acid compound in the primer paint later is preferably 4 mass% to 20 mass%. When the content of the phosphoric acid compound is less than 4 mass%, the inhibitor effect may decrease, resulting in a decrease in corrosion resistance. When the content of the phosphoric acid compound exceeds 20 mass%, the moisture
15 resistance of the primer paint layer may decrease.

[0137] Magnesium oxide, one of the inorganic compounds, produces Mg-containing products due to initial corrosion and has the effect of increasing stability and improving corrosion resistance as an insoluble magnesium salt.

20 **[0138]** The content of the magnesium oxide in the primer paint layer is not particularly limited. From the viewpoint of compatibility between corrosion resistance and corrosion resistance in worked portions, the content of the magnesium oxide in the primer paint layer is preferably 4 mass% to 20 mass%. When the content of the magnesium oxide is less than 4 mass%, the above effect may decrease and corrosion resistance may decrease. When the content
25 of the magnesium oxide exceeds 20 mass%, the flexibility of the primer paint layer may decrease, resulting in reduced corrosion resistance in worked portions.

30 **[0139]** 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 a component is a crosslinking agent used to form the primer paint layer. The crosslinking agent reacts with the polyester resin having a urethane bond to form a cross-linked paint layer. Examples of the crosslinking agent include oxazoline compounds, epoxy compounds, melamine
35 compounds, isocyanate compounds, carbodiimide compounds, and silane coupling compounds. Two or more crosslinking agents may be used in

combination. Among these, blocked polyisocyanate compounds, for example, are preferably used from the viewpoint of corrosion resistance in worked portions of the resulting prepainted 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 ϵ -caprolactam, diketones such as acetoacetic acid diester diketones, imidazoles such as imidazole and 2-ethylimidazole, or phenols such as m-cresol.

[0140] Further, the primer paint layer may also contain various known components normally used in the field of paints, as required. Specifically, examples of such components include various surface adjustment agents such as leveling agents and defoamers, dispersants, anti-settling agents, ultraviolet 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.

[0141] The thickness of the primer paint layer is preferably 1.5 μm or more. The primer paint layer having a thickness of 1.5 μm or more helps reliably obtain 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.

[0142] There is no particular limitation on the method used to form the primer paint layer. As the application method of the paint composition of the primer paint layer, the paint composition may preferably be applied by roll coater coating, curtain flow coating, or the like. After the application, the applied paint composition is baked by heating means such as hot blast, infrared heating, or induction heating to form the primer paint layer. The baking is typically performed at a peak metal temperature approximately in a range from 180 $^{\circ}\text{C}$ to 270 $^{\circ}\text{C}$ for about 30 s to 3 min in this temperature range.

[0143] Further, in the paint layer of the prepainted steel sheet, the top coating layer is preferably formed on the primer paint layer.

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

[0144] The configuration of the top coating layer is not particularly limited, and the material, thickness, and other conditions may be selected as appropriate

according to required performance.

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

5 Further, 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; microparticles such as silica microparticles, nylon resin beads, and acrylic resin beads; curing catalysts such as p-toluene
10 sulfonic acid and dibutyl tin dilaurate; waxes; and other additives in appropriate quantities.

[0145] The thickness of the top coating layer is preferably 5 μm to 30 μm in terms of both appearance and workability. When the thickness of the top coating layer is 5 μm or more, color appearance can be more reliably stabilized,
15 and when the thickness of the top coating layer is 30 μm or less, deterioration of workability (cracking of the top coating layer) can be more reliably suppressed.

[0146] The method of applying the paint composition to form the top coating layer is not particularly limited. For example, the paint composition can be
20 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 the top coating layer. The baking is typically performed at a peak metal temperature approximately in a range from 180 $^{\circ}\text{C}$ to 270 $^{\circ}\text{C}$ for about 30 s to 3 min in this temperature
25 range.

EXAMPLES

[0147] <Example 1: Samples 1 to 47>

Using cold-rolled steel sheets having a thickness of 0.8 mm prepared
30 by a conventional method as base steel sheets, annealing and coating simulation was performed on a hot-dip coating simulator produced by Rhesca Co., Ltd. to produce hot-dip coated steel sheet Samples 1 to 47 under the conditions listed in Table 1.

For the composition of the coating bath used in the production of hot-
35 dip coated steel sheets, the composition of the coating bath was varied within the following ranges: Al: 5 mass% to 70 mass%, Si: 0.0 mass% to 4.4 mass%,

Ni: 0.000 mass% to 0.025 mass%, Co: 0.001 mass% to 0.092 mass%, V: 0.0 mass% to 0.1 mass%, Cr: 0.0 mass% to 0.2 mass%, Mn: 0.0 mass% to 0.1 mass%, Mg: 0.0 mass% to 4.0 mass%, Ca: 0.0 mass% to 1.0 mass%, and Sr: 0.0 mass% to 1.0 mass% so that the composition of the coating for each Sample listed in Table 1 was obtained. The bath temperature of the coating bath used was 450 °C when Al was 5 mass%, 480 °C when Al was 18 mass%, 600 °C when Al was 36 mass% to 55 mass%, and 660 °C when Al was more than 60 mass%, and the entering sheet temperature of the base steel sheet was controlled to be the same temperature as the coating bath temperature. Further, when Al was 30 mass% to 60 mass%, the coating treatment was conducted under the condition that the sheet temperature cooled down to the temperature range from 520 °C to 500 °C in 3 s.

The coating weight of the coating was controlled to be $85 \pm 5 \text{ g/m}^2$ per side for Samples 1 to 44, $50 \pm 5 \text{ g/m}^2$ per side for Sample 45, $100 \pm 5 \text{ g/m}^2$ per side for Sample 46, and $125 \pm 5 \text{ g/m}^2$ per side for Sample 47.

[0148] <Evaluation>

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

[0149] (1) Coating (composition, coating weight, Ni compounds)

For each Sample after coating, a 100 mm diameter was punched out, the non-measured surface was sealed with tape, and the coating was dissolved and stripped with a mixture of hydrochloric acid and hexamethylenetetramine, as specified in JIS H 0401:2013. Then, from the mass difference before and after the stripping for each sample, the coating weight of the coating was calculated. The coating weight of each coating obtained by the calculation is listed in Table 1.

The stripping solution was then filtered and the filtrate and solids were analyzed respectively. Specifically, the filtrate was analyzed by ICP emission spectroscopy 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 spectroscopy to quantify the insoluble Si. The concentration of Si in the coating was the concentration of soluble Si obtained by filtrate analysis plus the concentration of insoluble Si obtained by solids

analysis. The composition of each coating obtained by the calculations is listed in Table 1.

Further, each Sample was sheared to a size of 15 mm × 15 mm, embedded in electrically conductive resin so that the cross-section of the steel sheet could be observed, and then mechanically polished. Subsequently, a scanning electron microscope (ULTRA 55, produced by Carl Zeiss AG) was used to obtain reflected electron images continuously at an accelerating voltage of 3 kV with a width of 100 μm for an arbitrarily selected continuous cross-section of the coating having a length of 2 mm or more in a direction parallel to the surface of the base steel sheet. Further, elemental mapping analysis (Al, Zn, Si, Fe, and Ni) of each cross-section was performed using the same apparatus and an energy-dispersive X-ray spectrometer (Ultim Extreme, produced by Oxford Instruments) at an accelerating voltage of 3 kV. The portions of high Ni intensity detected in this analysis were subjected to point analysis using the same spectrometer at an accelerating voltage of 3 kV, and substances were identified from the semi-quantitative values of the components obtained. The major axis length was measured for all Ni compounds identified in the observation field, and the largest major axis length was determined. The number of Ni compound particles per mm parallel to the base steel sheet surface was calculated by counting the number of all Ni compound particles present in the observed continuous cross-section and dividing by the observed cross-section length (mm). The portions of high Ni intensity detected in this analysis were subjected to point analysis using the same spectrometer at an accelerating voltage of 3 kV, and substances were identified from the semi-quantitative values of the components obtained. The results of analysis are listed in Table 1.

[0150] (2) Evaluation of corrosion resistance

Each Sample of the hot-dip coated steel sheets obtained was sheared to a size of 120 mm × 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 were sealed with tape so that the exposed size of the surface to be evaluated was 100 mm × 100 mm. These were used as evaluation samples. In each case, three identical evaluation samples were prepared.

Accelerated corrosion tests were performed on the three evaluation samples thus prepared through the cycle as illustrated in FIG. 1. After 150 cycles of the accelerated corrosion test starting from wet, the corrosion loss of

each sample was measured by the method described in JIS Z 2383 and ISO 8407, and evaluated according to the following criteria. The evaluation results are listed in Table 1.

- 5 ◎: Corrosion loss of all three samples was 60 g/m² or less
 ○: Corrosion loss of all three samples was 75 g/m² or less
 ×: Corrosion loss of at least one sample exceeded 75 g/m²

[0151] (3) Surface appearance

Each Sample of the hot-dip coated steel sheets obtained was sheared to a size of 70 mm × 150 mm and then subjected to 180° bending (8T bending)
10 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 on the outer surface of the bent portion and the presence of coating adhesion (peeling) on the surface of the
15 tape used were visually observed, and workability was evaluated using the following criteria. The evaluation results are listed in Table 1.

- : Neither cracks nor peeling were observed in the coating
 △: Cracks were observed in the coating, but no peeling
 ×: Both cracks and peeling were observed in the coating

[0152] [Table 1]

Table 1

No.	Coating										Corrosion resistance					Workability	Remarks
	Chemical composition (mass%)						Ni compounds				Corrosion loss (g/m ²)			Evaluation			
	Al	Si	Fe	Ni	Co	Other	Coating weight (g/m ²)	Type	Amount present (/10 mm)	Major axis length (μm)	N1	N2	N3				
1	5	0.0	0.39	0.003	0.0002	-	85	-	0.0	-	182	175	218	×	○	Comparative Example	
2	18	0.5	0.41	0.002	0.0002	-	85	-	0.0	-	92	106	111	×	○	Comparative Example	
3	36	1.5	0.49	0.003	0.0003	-	84	-	0.0	-	81	96	80	×	○	Comparative Example	
4	46	1.5	0.55	0.003	0.0002	-	85	-	0.0	-	65	68	64	○	○	Example	
5	55	0.5	1.05	0.003	0.0001	-	85	-	0.0	-	78	81	75	×	×	Comparative Example	
6	55	1.0	0.68	0.003	0.0002	-	85	-	0.0	-	52	49	52	⊙	○	Example	
7	55	1.5	0.54	0.001	0.0002	-	86	-	0.0	-	48	51	50	⊙	○	Example	
8	55	1.5	0.51	0.003	0.0008	-	82	-	0.0	-	56	52	51	⊙	○	Example	
9	55	1.5	0.53	0.008	0.0002	-	84	Ni-Al	2.5	1.9	68	72	65	○	○	Example	
10	55	1.5	0.56	0.010	0.0002	-	85	Ni-Al, Ni-Al-Fe	4.3	2.9	71	74	70	○	○	Example	
11	55	1.5	0.58	0.013	0.0002	-	86	Ni-Al, Ni-Al-Fe	6.0	5.4	86	91	88	×	○	Comparative Example	
12	55	1.5	0.55	0.025	0.0002	-	84	Ni-Al, Ni-Al-Fe	8.7	6.6	126	138	134	×	○	Comparative Example	
13	65	1.5	0.71	0.003	0.0002	-	85	-	0.0	-	59	58	58	⊙	○	Example	
14	70	1.5	0.82	0.003	0.0004	-	86	-	0.0	-	99	105	92	×	○	Comparative Example	
15	55	2.3	0.59	0.003	0.0000	-	85	-	0.0	-	59	56	59	⊙	○	Example	
16	55	2.3	0.61	0.008	0.0002	-	85	Ni-Al	1.5	2.8	72	68	71	○	○	Example	
17	55	2.3	0.58	0.010	0.0003	-	85	Ni-Al	4.7	3.6	69	75	72	○	○	Example	
18	55	2.3	0.58	0.018	0.0002	-	85	Ni-Al, Ni-Al-Fe	6.8	7.9	131	129	141	×	○	Comparative Example	
19	55	2.9	0.58	0.003	0.0002	-	84	-	0.0	-	65	64	60	○	○	Example	
20	55	3.2	0.57	0.003	0.0001	-	85	-	0.0	-	61	66	65	○	△	Example	
21	55	3.9	0.57	0.003	0.0002	-	85	-	0.0	-	68	73	72	○	△	Example	
22	55	4.4	0.58	0.003	0.0002	-	86	-	0.0	-	79	84	86	×	×	Comparative Example	
23	55	1.5	0.53	0.003	0.0198	-	84	-	0.0	-	58	57	59	⊙	○	Example	
24	55	1.5	0.55	0.003	0.0503	-	85	-	0.0	-	64	63	64	○	○	Example	
25	55	1.5	0.52	0.003	0.0821	-	86	-	0.0	-	69	68	68	○	○	Example	
26	55	1.5	0.54	0.003	0.0920	-	85	-	0.0	-	74	75	72	○	○	Example	
27	55	1.5	0.53	0.008	0.0002	V: 0.1	85	-	0.0	-	52	48	46	⊙	○	Example	
28	55	1.5	0.61	0.013	0.0002	V: 0.1	85	Ni-Al, Ni-Al-Fe	5.7	5.5	70	78	81	×	○	Comparative Example	
29	55	1.5	0.59	0.008	0.0002	Cr: 0.2	85	-	0.0	-	52	58	58	⊙	○	Example	
30	55	1.5	0.62	0.014	0.0001	Cr: 0.2	85	Ni-Al, Ni-Al-Fe	6.0	6.3	76	77	72	×	○	Comparative Example	
31	55	1.5	0.58	0.008	0.0002	Mn: 0.1	84	-	0.0	-	48	53	55	⊙	○	Example	
32	55	1.5	0.58	0.015	0.0002	Mn: 0.1	85	Ni-Al, Ni-Al-Fe	6.5	6.2	78	90	76	×	○	Comparative Example	
33	55	1.5	0.62	0.008	0.0003	Mg: 3.0	84	-	0.0	-	16	18	14	⊙	△	Example	
34	55	1.5	0.59	0.108	0.0002	Mg: 3.0	85	Ni-Al, Ni-Al-Fe	8.5	7.1	77	68	65	×	△	Comparative Example	
35	55	1.5	0.57	0.008	0.0002	Ca: 1.0	85	-	0.0	-	58	56	56	⊙	△	Example	
36	55	1.5	0.61	0.020	0.0001	Ca: 1.0	86	Ni-Al, Ni-Al-Fe	7.2	6.8	98	85	80	×	△	Comparative Example	
37	55	1.5	0.64	0.008	0.0002	Sr: 1.0	85	-	0.0	-	56	58	52	⊙	△	Example	
38	55	1.5	0.58	0.012	0.0002	Sr: 1.0	85	Ni-Al, Ni-Al-Fe	5.8	5.8	76	82	79	×	△	Comparative Example	
39	55	1.5	0.58	0.008	0.0002	Mg: 2.0, Ca: 0.1	84	-	0.0	-	20	22	26	⊙	△	Example	
40	55	1.5	0.61	0.048	0.0002	Mg: 2.0, Ca: 0.1	85	Ni-Al, Ni-Al-Fe	12.1	8.9	78	76	70	×	△	Comparative Example	
41	55	1.5	0.56	0.008	0.0002	Mg: 2.0, Cr: 0.2	85	-	0.0	-	19	16	23	⊙	△	Example	
42	55	1.5	0.59	0.075	0.0002	Mg: 2.0, Cr: 0.2	86	Ni-Al, Ni-Al-Fe	13.2	11.3	91	76	81	×	△	Comparative Example	
43	55	1.5	0.62	0.008	0.0001	Mg: 4.0, Sr: 0.1	86	-	0.0	-	18	19	21	⊙	△	Example	
44	55	1.5	0.63	0.105	0.0002	Mg: 4.0, Sr: 0.1	85	Ni-Al, Ni-Al-Fe	14.8	14.2	80	76	73	×	△	Comparative Example	
45	55	1.5	0.51	0.003	0.0002	-	46	-	0.0	-	68	72	58	○	○	Example	
46	55	1.5	0.51	0.003	0.0002	-	100	-	0.0	-	54	48	52	⊙	○	Example	
47	55	1.5	0.51	0.003	0.0003	-	126	-	0.0	-	51	50	50	⊙	△	Example	

[0153] The results in Table 1 demonstrate that each of the Samples of Examples of the present disclosure has superior and balanced corrosion resistance and workability compared to each of the Samples of Comparative Examples.

5 **[0154]** <Example 2: Samples 1 to 118>

(1) Using cold-rolled steel sheets having 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 produced by Rhesca Co., Ltd. to obtain hot-dip coated steel sheet Samples under the coating
10 conditions listed in Tables 3 to 5.

For the composition of the coating bath used in the production of hot-dip coated steel sheets, the composition of the coating bath was varied within the following ranges: Al: 5 mass% to 70 mass%, Si: 0.0 mass% to 4.4 mass%, Ni: 0.000 mass% to 0.025 mass%, V: 0.0 mass% to 0.1 mass%, Cr: 0.0 mass%
15 to 0.2 mass%, Mn: 0.0 mass% to 0.1 mass%, Mg: 0.0 mass% to 4.0 mass%, Ca: 0.0 mass% to 1.0 mass%, and Sr: 0.0 mass% to 1.0 mass% so that the composition of the coating for each Sample listed in Table 1 was obtained. The bath temperature of the coating bath was 450 °C when Al was 5 mass%, 480 °C when Al was 18 mass%, 600 °C when Al was 36 mass% to 55 mass%, and
20 660 °C when Al was more than 60 mass%, and the entering sheet temperature of the base steel sheet was controlled to be the same temperature as the coating bath temperature. Further, when Al was 30 mass% to 60 mass%, the coating treatment was conducted under the condition that the sheet temperature cooled down to the temperature range from 520 °C to 500 °C in 3 s.

25 The coating weight of the coating was controlled to be 85 ± 5 g/m² per side for Samples 1 to 88 and 95 to 118, 50 ± 5 g/m² per side for Samples 89 and 90, 100 ± 5 g/m² per side for Samples 91 and 92, and $125 \text{ g/m}^2 \pm 5 \text{ g/m}^2$ per side for Samples 93 and 94.

[0155] (2) Then, a chemical conversion treatment liquid was applied to the
30 coating 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 listed in Tables 3 to 5.

For the chemical conversion treatment liquids, surface-treatment
35 solutions A to 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 (produced by DKS Co. Ltd.)

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

(Metal compounds)

P compound: aluminum dihydrogen tripolyphosphate

Si compound: silica

V compound: sodium metavanadate

10 Mo compound: molybdic acid

Zr compound: potassium zirconyl carbonate

The compositions of the prepared chemical conversion treatment liquids A to 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
15 concentration of solid content (in mass%).

[0156] [Table 2]

[illegible]

[0157] <Evaluation>

The following evaluations were performed on each hot-dip coated steel sheet Sample and each surface-treated steel sheet Sample obtained as described
5 above. The evaluation results are listed in Tables 3 to 5.

(1) Coating (composition, coating weight, Ni compounds)

For each hot-dip coated steel sheet Sample, a 100 mm diameter was punched out, the non-measured surface was sealed with tape, and the coating as dissolved and stripped with a mixture of hydrochloric acid and
10 hexamethylenetetramine, as specified in JIS H 0401:2013. Then, from the mass difference before and after the stripping for each sample, the coating weight of the coating was calculated. The coating weight of each coating obtained by the calculation is listed in Tables 3 to 5.

The stripping solution was then filtered and the filtrate and solids were
15 analyzed respectively. Specifically, the filtrate was analyzed by ICP emission spectroscopy 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
20 analyzed by ICP emission spectroscopy to quantify the insoluble Si. The concentration of Si in the coating was the concentration of soluble Si obtained by filtrate analysis plus the concentration of insoluble Si obtained by solids analysis. The composition of each coating obtained by the calculations is listed in Tables 3 to 5.

25 Further, each Sample was sheared to a size of 15 mm × 15 mm, embedded in electrically conductive resin so that the cross-section of the steel sheet could be observed, and then mechanically polished. Subsequently, a scanning electron microscope (ULTRA 55, produced by Carl Zeiss AG) was used to obtain reflected electron images continuously at an accelerating voltage
30 of 3 kV with a width of 100 μm for an arbitrarily selected continuous cross-section of the coating having a length of 2 mm or more in a direction parallel to the surface of the base steel sheet. Further, elemental mapping analysis (Al, Zn, Si, Fe, and Ni) of each cross-section was performed using the same apparatus and an energy-dispersive X-ray spectrometer (Ultim Extreme,
35 produced by Oxford Instruments) at an accelerating voltage of 3 kV. The portions of high Ni intensity detected in this analysis were subjected to point

analysis using the same spectrometer at an accelerating voltage of 3 kV, and substances were identified from the semi-quantitative values of the components obtained. The major axis length was measured for all Ni compounds identified in the observation field, and the largest major axis length was determined. The number of Ni compound particles per mm parallel to the base steel sheet surface was calculated by counting the number of all Ni compound particles present in the observed continuous cross-section and dividing by the observed cross-section length (mm). The portions of high Ni intensity detected in this analysis were subjected to point analysis using the same spectrometer at an accelerating voltage of 3 kV, and substances were identified from the semi-quantitative values of the components obtained. The analysis results are listed in Tables 3 to 5.

[0158] (2) Evaluation of corrosion resistance

Each hot-dip coated steel sheet Sample and each surface-treated steel sheet Sample was sheared to a size of 120 mm × 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 exposed size of the surface to be evaluated was 100 mm × 100 mm. These were used as evaluation samples. In each case, three identical evaluation samples were prepared.

Accelerated corrosion tests were performed on the three evaluation samples thus prepared through the cycle as illustrated in FIG. 1. After 150 cycles of the accelerated corrosion test starting from wet, the corrosion loss of each sample was measured by the method described in JIS Z 2383 and ISO 8407, and evaluated according to the following criteria. The evaluation results are listed in Tables 3 to 5.

◎: Corrosion loss of all three samples was 40 g/m² or less

○: Corrosion loss of all three samples was 60 g/m² or less

×: Corrosion loss of at least one sample exceeds 60 g/m²

[0159] (3) Anti-white rust property

Each hot-dip coated steel sheet Sample and each surface-treated steel sheet Sample was sheared to a size of 120 mm × 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 exposed size of the surface to be evaluated was 100 mm × 100 mm. These were used as evaluation samples.

Using the evaluation samples, the salt spray test described in JIS Z 2371 was conducted for 90 h, and evaluation was based on the following criteria. The evaluation results are listed in Tables 3 to 5.

- 5 ⊙: No white rust 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) 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
10 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 on the outer surface of the bent portion and the presence of coating adhesion (peeling) on the surface of the tape used were
15 visually observed, and workability was evaluated using the following criteria. The evaluation results are listed in Tables 3 to 5.

- : Neither cracks nor peeling were observed in the coating
 △: Cracks were observed in the coating, but no peeling
 ×: Both cracks and peeling were observed in the coating

[0161] [Table 3]

Table 3

No.	Coating										Chemical conversion treatment	Corrosion resistance					Workability	Remarks
	Chemical composition (mass%)						Coating weight (g/m ²)	Ni compounds				Corrosion loss (g/m ²)			Evaluation	Anti-white rust property		
	Al	Si	Fe	Ni	Co	Other		Type	Amount present (/10 mm)	Major axis length (μm)		N1	N2	N3				
1	5	0.0	0.39	0.003	0.0002	-	85	-	0.0	-	-	182	175	218	x	x	○	Comparative Example
2											A	108	98	92	x	x		Comparative Example
3	18	0.5	0.41	0.002	0.0002	-	85	-	0.0	-	-	92	106	111	x	x	○	Comparative Example
4											A	76	85	89	x	x		Comparative Example
5	36	1.5	0.49	0.003	0.0003	-	84	-	0.0	-	-	81	96	80	x	x	○	Comparative Example
6											A	72	61	64	x	○		Comparative Example
7	46	1.5	0.55	0.003	0.0002	-	85	-	0.0	-	-	65	68	64	x	x	○	Comparative Example
8											A	48	44	42	○	○		Example
9	55	0.5	1.05	0.003	0.0001	-	85	-	0.0	-	-	78	81	75	x	x	x	Comparative Example
10											A	62	58	56	x	○		Comparative Example
11	55	1.0	0.68	0.003	0.0002	-	85	-	0.0	-	-	52	49	52	○	x	○	Comparative Example
12											A	31	33	33	⊗	⊗		Example
13	55	1.5	0.54	0.001	0.0002	-	86	-	0.0	-	-	48	51	50	○	x	○	Comparative Example
14											A	25	30	28	⊗	⊗		Example
15	55	1.5	0.51	0.003	0.0008	-	82	-	0.0	-	-	56	52	51	○	x	○	Comparative Example
16											A	31	32	33	⊗	⊗		Example
17	55	1.5	0.53	0.008	0.0002	-	84	Ni-Al	2.5	1.9	-	68	72	65	x	x	○	Comparative Example
18											A	53	46	49	○	○		Example
19	55	1.5	0.56	0.010	0.0002	-	85	Ni-Al, Ni-Al-Fe	4.3	2.9	-	71	74	70	x	x	○	Comparative Example
20											A	58	57	55	○	○		Example
21	55	1.5	0.58	0.013	0.0002	-	86	Ni-Al, Ni-Al-Fe	6.0	5.4	-	86	91	88	x	x	○	Comparative Example
22											A	66	67	64	x	○		Comparative Example
23	55	1.5	0.55	0.025	0.0002	-	84	Ni-Al, Ni-Al-Fe	8.7	6.6	-	126	138	134	x	x	○	Comparative Example
24											A	98	87	98	x	x		Comparative Example
25	65	1.5	0.71	0.003	0.0002	-	85	-	0.0	-	-	59	58	58	○	x	○	Comparative Example
26											A	36	38	37	⊗	⊗		Example
27	70	1.5	0.82	0.003	0.0004	-	86	-	0.0	-	-	99	105	92	x	x	○	Comparative Example
28											A	72	75	73	x	○		Comparative Example
29	55	2.3	0.59	0.003	0.0000	-	85	-	0.0	-	-	61	56	59	x	x	○	Comparative Example
30											A	39	39	38	○	⊗		Example
31	55	2.3	0.61	0.008	0.0002	-	85	Ni-Al	1.5	2.8	-	72	68	71	x	x	○	Comparative Example
32											A	53	51	53	○	○		Example
33	55	2.3	0.58	0.010	0.0003	-	85	Ni-Al	4.7	3.6	-	69	75	72	x	x	○	Comparative Example
34											A	56	55	53	○	○		Example
35	55	2.3	0.58	0.018	0.0002	-	85	Ni-Al, Ni-Al-Fe	6.8	7.9	-	131	129	141	x	x	○	Comparative Example
36											A	98	111	105	x	x		Comparative Example
37	55	2.9	0.58	0.003	0.0002	-	84	-	0.0	-	-	65	64	60	x	x	○	Comparative Example
38											A	43	39	41	○	○		Example
39	55	3.2	0.57	0.003	0.0001	-	85	-	0.0	-	-	61	66	65	x	x	Δ	Comparative Example
40											A	45	43	43	○	○		Example
41	55	3.9	0.57	0.003	0.0002	-	85	-	0.0	-	-	68	73	72	x	x	Δ	Comparative Example
42											A	51	46	48	○	○		Example
43	55	4.4	0.58	0.003	0.0002	-	86	-	0.0	-	-	79	84	86	x	x	x	Comparative Example
44											A	61	59	63	x	○		Comparative Example
45	55	1.5	0.53	0.003	0.0198	-	84	-	0.0	-	-	58	57	59	○	x	○	Comparative Example
46											A	38	38	39	⊗	⊗		Example
47	55	1.5	0.55	0.003	0.0503	-	85	-	0.0	-	-	64	63	64	x	x	○	Comparative Example
48											A	42	45	45	○	○		Example
49	55	1.5	0.52	0.003	0.0821	-	86	-	0.0	-	-	69	68	68	x	x	○	Comparative Example
50											A	48	51	48	○	○		Example
51	55	1.5	0.54	0.003	0.0920	-	85	-	0.0	-	-	74	75	72	x	x	○	Comparative Example
52											A	52	56	55	○	○		Example

[0162] [Table 4]

Table 4

No.	Coating										Chemical conversion treatment	Corrosion resistance				Anti-white rust property	Workability	Remarks
	Chemical composition (mass%)						Ni compounds			Corrosion loss (g/m ²)			Evaluation					
	Al	Si	Fe	Ni	Co	Other	Coating weight (g/m ²)	Type	Amount present (per 10 mm)	Major axis length (μm)		N1		N2	N3			
53	55	1.5	0.53	0.008	0.0002	V: 0.1	85	-	0.0	-	-	52	48	46	○	×	○	Comparative Example
54											A	31	30	30	◎	◎		Example
55	55	1.5	0.61	0.013	0.0002	V: 0.1	85	Ni-Al, Ni-Al-Fe	5.7	5.5	-	70	78	81	×	×	○	Comparative Example
56											A	62	59	64	×	○		Comparative Example
57	55	1.5	0.59	0.008	0.0002	Cr: 0.2	85	-	0.0	-	-	52	58	58	○	×	○	Comparative Example
58											A	33	34	33	◎	◎		Example
59	55	1.5	0.62	0.014	0.0001	Cr: 0.2	85	Ni-Al, Ni-Al-Fe	6.0	6.3	-	76	77	72	×	×	○	Comparative Example
60											A	60	62	61	×	○		Comparative Example
61	55	1.5	0.58	0.008	0.0002	Mn: 0.1	84	-	0.0	-	-	48	53	55	○	×	○	Comparative Example
62											A	22	21	19	◎	◎		Example
63	55	1.5	0.58	0.015	0.0002	Mn: 0.1	85	Ni-Al, Ni-Al-Fe	6.5	6.2	-	78	90	76	×	×	○	Comparative Example
64											A	63	59	62	×	○		Comparative Example
65	55	1.5	0.62	0.008	0.0003	Mg: 3.0	84	-	0.0	-	-	16	18	14	◎	×	△	Comparative Example
66											A	2	3	2	◎	◎		Example
67	55	1.5	0.59	0.108	0.0002	Mg: 3.0	85	Ni-Al, Ni-Al-Fe	8.5	7.1	-	77	68	65	×	×	△	Comparative Example
68											A	61	52	58	×	○		Comparative Example
69	55	1.5	0.57	0.008	0.0002	Ca: 1.0	85	-	0.0	-	-	58	56	56	○	×	△	Comparative Example
70											A	35	36	36	◎	◎		Example
71	55	1.5	0.61	0.020	0.0001	Ca: 1.0	86	Ni-Al, Ni-Al-Fe	7.2	6.8	-	98	85	80	×	×	△	Comparative Example
72											A	68	75	69	×	○		Comparative Example
73	55	1.5	0.64	0.008	0.0002	Sr: 1.0	85	-	0.0	-	-	56	58	52	○	×	△	Comparative Example
74											A	38	37	35	◎	◎		Example
75	55	1.5	0.58	0.012	0.0002	Sr: 1.0	85	Ni-Al, Ni-Al-Fe	5.8	5.8	-	76	82	79	×	×	△	Comparative Example
76											A	64	60	61	×	○		Comparative Example
77	55	1.5	0.58	0.008	0.0002	Mg: 2.0 Ca: 0.1	84	-	0.0	-	-	20	22	26	◎	×	△	Comparative Example
78											A	5	5	2	◎	◎		Example
79	55	1.5	0.61	0.048	0.0002	Mg: 2.0 Ca: 0.1	85	Ni-Al, Ni-Al-Fe	12.1	8.9	-	78	76	70	×	×	△	Comparative Example
80											A	61	58	59	×	○		Comparative Example
81	55	1.5	0.56	0.008	0.0002	Mg: 2.0 Cr: 0.2	85	-	0.0	-	-	19	16	23	◎	×	△	Comparative Example
82											A	2	3	1	◎	◎		Example
83	55	1.5	0.59	0.075	0.0002	Mg: 2.0 Cr: 0.2	86	Ni-Al, Ni-Al-Fe	13.2	11.3	-	91	76	81	×	×	△	Comparative Example
84											A	65	70	68	×	○		Comparative Example
85	55	1.5	0.62	0.008	0.0001	Mg: 4.0 Sr: 0.1	86	-	0.0	-	-	18	19	21	◎	×	△	Comparative Example
86											A	4	2	3	◎	◎		Example
87	55	1.5	0.63	0.105	0.0002	Mg: 4.0 Sr: 0.1	85	Ni-Al, Ni-Al-Fe	14.8	14.2	-	80	76	73	×	×	△	Comparative Example
88											A	60	62	58	×	○		Comparative Example
89	55	1.5	0.51	0.003	0.0002	-	46	-	0.0	-	-	68	72	58	×	×	○	Comparative Example
90											A	42	38	40	○	○		Example
91	55	1.5	0.51	0.003	0.0002	-	100	-	0.0	-	-	54	48	52	○	×	○	Comparative Example
92											A	32	35	36	◎	◎		Example
93	55	1.5	0.51	0.003	0.0003	-	126	-	0.0	-	-	51	50	50	○	×	△	Comparative Example
94											A	28	30	33	◎	◎		Example

[0163] [Table 5]

No.		Coating										Chemical conversion treatment	Corrosion resistance			Anti-white rust property	Workability	Remarks										
		Chemical composition (mass%)						Coating weight (g/m ²)	Ni compounds																			
		Al	Si	Fe	Ni	Co	Other		Type	Amount present (per 10 mm)	Major axis length (μm)																	
95											A	32	33	35	◎		Example											
96											B	36	39	32	◎		Example											
97	55	1.5	0.53	0.002	0.0002	-	83	-	0.0	-	C	34	35	31	◎	○	Example											
36												31	33	◎	Example													
41												38	40	○	Example													
43												44	42	○	Example													
100											F	59	55	57	○		Example											
101											A	56	58	55	○		Example											
102											B	55	56	58	○		Example											
103	55	1.5	0.55	0.010	0.0002	-	84	Ni-Al, Ni-Al-Fe	4.5	2.7	D	59	54	59	○	○	Example											
63												63	61	×	Comparative Example													
64												60	58	×	Comparative Example													
42												39	40	○	Example													
107											A	40	42	40	○		Example											
108											B	43	42	39	○		Example											
109											C	43	44	40	○		Example											
110	55	2.3	0.52	0.003	0.0002	-	85	-	0.0	-	D	53	56	55	○	×	Comparative Example											
53												51	57	○	×		Comparative Example											
57												55	54	○	○		Example											
56												57	56	○	○		Example											
113											B	57	58	55	○		Example											
114											C	56	56	54	○		Example											
115	55	2.3	0.54	0.010	0.0002	-	85	Ni-Al	4.8	3.8	E	65	63	60	×	×	Comparative Example											
61												62	59	×	×		Comparative Example											

Table 5

[0164] The results in Tables 3 to 5 demonstrate that each of the Samples of Examples of the present disclosure have superior and balanced corrosion resistance, anti-white rust property, and workability compared to each of the Samples of Comparative Examples.

5 Further, the results in Table 5 demonstrate that the anti-white rust property of each Sample subjected to chemical conversion treatments A to D exhibited particularly excellent results.

[0165] <Example 3: Samples 1 to 47>

10 (1) Using cold-rolled steel sheets having 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 produced by Rhesca Co., Ltd. to produce hot-dip coated steel sheet Samples 1 to 47 under the conditions listed in Table 7.

15 The composition of the coating bath was varied within the following ranges: Al: 5 mass% to 70 mass%, Si: 0.0 mass% to 4.4 mass%, Ni: 0.000 mass% to 0.025 mass%, Co: 0.001 mass% to 0.092 mass%, V: 0.0 mass% to 0.1 mass%, Cr: 0.0 mass% to 0.2 mass%, Mn: 0.0 mass% to 0.1 mass%, Mg: 0.0 mass% to 4.0 mass%, Ca 0.0 mass% to 1.0 mass%, and Sr: 0.0 mass% to 1.0 mass%. The bath temperature of the coating bath was 450 °C when Al was 5 mass%, 480 °C when Al was 18 mass%, 600 °C when Al was 36 mass% to 55 mass%, and 660 °C when Al was more than 60 mass%, and the entering sheet temperature of the base steel sheet was controlled to be the same temperature as the coating bath temperature. Further, when Al was 30 mass% to 60 mass%, the coating treatment was conducted under the condition that the sheet temperature cooled down to the temperature range from 520 °C to 500 °C in 3 s.

 The coating weight of the coating was controlled to be 85 ± 5 g/m² per side for Samples 1 to 44, 50 ± 5 g/m² per side for Sample 45, 100 ± 5 g/m² per side for Sample 46, and 125 ± 5 g/m² per side for Sample 47.

30 **[0166]** (2) Then, a chemical conversion treatment liquid listed in Table 6 was applied to the coating 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 having a coating weight of 0.1 g/m².

35 The chemical conversion treatment liquids used were chemical conversion 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)

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

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

(Inorganic compounds)

Vanadium compound: organic vanadium compound chelated with acetylacetone

Zirconium compound: ammonium zirconium carbonate

15 Fluorine compound: ammonium fluoride

[0167] (3) A primer paint was applied to each chemical conversion layer 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 s to form primer paint layers with the chemical compositions as listed in Table
20 6. Subsequently, a top coating layer paint composition was applied to each primer paint layer thus formed using a bar coater, and baking was performed at an end-point temperature of each steel sheet in the range from 230 °C to 260 °C for a baking time of 40 s to form top coating layers with the resin conditions and layer thicknesses as listed in Table 6. In this way, prepainted steel sheet
25 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 of each primer paint layer were as follows.

(Resin components)

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

35 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 h while allowing the condensation
5 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, produced
10 by ExxonMobil, an aromatic hydrocarbon solvent having a high boiling point) and 100 parts by mass of butyl Cellosolve were added to obtain a polyester resin solution.

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

15 (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
20 layers listed in Table 6.

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

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

[0168] [Table 6]

Table 6

Paint layer Conditions	Chemical conversion layer				Primer paint layer						Top coating layer		Remarks	
	Resin		Vanadium compound (mass%)	Zirconium compound (mass%)	Fluorine compound (mass%)	Resin		Vanadium compound (mass%)	Phosphate compound (mass%)	Magnesium oxide compound (mass%)	Other (pigments, etc.) (mass%)	Resin		Paint layer thickness (μm)
	Type	Content (mass%)				Type	Content (mass%)					Type		
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

[0169] <Evaluation>

The following evaluations were performed on the prepainted steel sheet Samples thus obtained. The evaluation results are listed in Table 7.

5 **[0170]** (1) Coating (composition, coating weight, Ni compounds)

For each hot-dip coated steel sheet Sample, a 100 mm diameter was punched out, the non-measured surface was sealed with tape, and the coating as dissolved and stripped with a mixture of hydrochloric acid and hexamethylenetetramine, as specified in JIS H 0401:2013. Then, from the mass
10 difference before and after the stripping for each sample, the coating weight of the coating was calculated. The coating weight of each coating according to the calculation is listed in Table 7.

The stripping solution was then filtered and the filtrate and solids were analyzed respectively. Specifically, the filtrate was analyzed by ICP emission
15 spectroscopy 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 spectroscopy to quantify the insoluble Si. The
20 concentration of Si in the coating was the concentration of soluble Si obtained by filtrate analysis plus the concentration of insoluble Si obtained by solids analysis. The composition of each coating as obtained by the calculations is listed in Table 7.

Further, each Sample was sheared to a size of 15 mm × 15 mm,
25 embedded in electrically conductive resin so that the cross-section of the steel sheet could be observed, and then mechanically polished. Subsequently, a scanning electron microscope (ULTRA 55, produced by Carl Zeiss AG) was used to obtain reflected electron images continuously at an accelerating voltage of 3 kV with a width of 100 μm for an arbitrarily selected continuous cross-
30 section of the coating having a length of 2 mm or more in a direction parallel to the surface of the base steel sheet. Further, elemental mapping analysis (Al, Zn, Si, Mg, Fe, Sr, and Ni) of each cross-section was performed using the same apparatus and an energy-dispersive X-ray spectrometer (Ultim Extreme, produced by Oxford Instruments) at an accelerating voltage of 3 kV. The
35 portions of high Ni intensity detected in this analysis were subjected to point analysis using the same spectrometer at an accelerating voltage of 3 kV, and

substances were identified from the semi-quantitative values of the components obtained. The major axis length was measured for all Ni compounds identified in the observation field, and the largest major axis length was determined. The number of Ni compound particles per mm parallel to the base steel sheet surface was calculated by counting the number of all Ni compound particles present in the observed continuous cross-section and dividing by the observed cross-section length (mm). The portions of high Ni intensity detected in this analysis were subjected to point analysis using the same spectrometer at an accelerating voltage of 3 kV, and substances were identified from the semi-quantitative values of the components obtained. The results of each analysis are listed in Table 7.

[0171] (2) Evaluation of corrosion resistance

Each prepainted steel sheet Sample was sheared to a size of 120 mm × 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 exposed size of the surface to be evaluated was 100 mm × 100 mm. These were used as evaluation samples. In each case, three identical evaluation samples were prepared.

Accelerated corrosion tests were performed on the three evaluation samples thus prepared through the cycle as illustrated 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 listed in Table 7.

◎: Number of cycles to initial red rust in 3 samples $\geq$ 300 cycles

○: 300 cycles > number of cycles to initial red rust in 3 samples $\geq$ 200 cycles

×: Number of cycles to initial red rust in at least one sample < 200 cycles

[0172] (3) Workability after coating

Each prepainted 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® (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 paint layer on the outer surface of the bent portion and the presence of paint layer adhesion (peeling) on the surface of the tape used were visually observed, and workability was evaluated using the following criteria.

5 The evaluation results are listed in Table 7.

○: Neither cracks nor peeling were observed in the paint layer

△: Cracks were observed in the paint layer, but no peeling

×: Both cracks and peeling were observed in the paint layer

[0173] [Table 7]

Table 7

No.	Coating										Paint layer conditions	Corrosion resistance					Remarks
	Chemical composition (mass%)						Coating weight (g/m ²)	Ni compounds				Time to initial red rust (cycles)			Evaluation	Workability	
	Al	Si	Fe	Ni	Co	Other		Type	Amount present (/10 mm)	Major axis length (μm)		N1	N2	N3			
1	5	0.0	0.39	0.003	0.0002	-	85	-	0.0	-	T1	80	100	100	×	○	Comparative Example
2	18	0.5	0.41	0.002	0.0002	-	85	-	0.0	-	T1	120	100	120	×	○	Comparative Example
3	36	1.5	0.49	0.003	0.0003	-	84	-	0.0	-	T1	160	180	100	×	○	Comparative Example
4	46	1.5	0.55	0.003	0.0002	-	85	-	0.0	-	T1	240	260	240	○	○	Example
5	55	0.5	1.05	0.003	0.0001	-	85	-	0.0	-	T1	180	160	180	×	×	Comparative Example
6	55	1.0	0.68	0.003	0.0002	-	85	-	0.0	-	T1	320	320	320	⊗	○	Example
7	55	1.5	0.54	0.001	0.0002	-	86	-	0.0	-	T1	340	320	320	⊗	○	Example
											T2	320	300	320	⊗	○	Example
8	55	1.5	0.51	0.003	0.0008	-	82	-	0.0	-	T1	300	320	320	⊗	○	Example
9	55	1.5	0.53	0.008	0.0002	-	84	Ni-Al	2.5	1.9	T1	260	240	240	○	○	Example
10	55	1.5	0.56	0.010	0.0002	-	85	Ni-Al, Ni-Al-Fe	4.3	2.9	T1	200	220	200	○	○	Example
11	55	1.5	0.58	0.013	0.0002	-	86	Ni-Al, Ni-Al-Fe	6.0	5.4	T1	160	140	160	×	○	Comparative Example
12	55	1.5	0.55	0.025	0.0002	-	84	Ni-Al, Ni-Al-Fe	8.7	6.6	T1	120	120	140	×	○	Comparative Example
13	65	1.5	0.71	0.003	0.0002	-	85	-	0.0	-	T1	300	300	300	⊗	○	Example
14	70	1.5	0.82	0.003	0.0004	-	86	-	0.0	-	T1	140	160	140	×	○	Comparative Example
15	55	2.3	0.59	0.003	0.0000	-	85	-	0.0	-	T1	300	300	300	⊗	○	Example
16	55	2.3	0.61	0.008	0.0002	-	85	Ni-Al	1.5	2.8	T1	200	220	200	○	○	Example
											T2	220	200	200	○	○	Example
											T3	180	160	180	×	○	Comparative Example
											T4	160	180	200	×	○	Comparative Example
											T5	160	140	140	×	○	Comparative Example
											T6	160	180	200	×	○	Comparative Example
											T7	200	160	160	×	○	Comparative Example
											T8	180	160	180	×	○	Comparative Example
											T9	180	180	180	×	○	Comparative Example
T10	160	180	140	×	○	Comparative Example											
17	55	2.3	0.58	0.010	0.0003	-	85	Ni-Al	4.7	3.6	T1	200	200	200	○	○	Example
18	55	2.3	0.58	0.018	0.0002	-	85	Ni-Al, Ni-Al-Fe	6.8	7.9	T1	140	120	120	×	○	Comparative Example
19	55	2.9	0.58	0.003	0.0002	-	84	-	0.0	-	T1	260	240	240	○	○	Example
20	55	3.2	0.57	0.003	0.0001	-	85	-	0.0	-	T1	220	240	220	○	△	Example
21	55	3.9	0.57	0.003	0.0002	-	85	-	0.0	-	T1	220	200	200	○	△	Example
22	55	4.4	0.58	0.003	0.0002	-	86	-	0.0	-	T1	180	180	180	×	×	Comparative Example
23	55	1.5	0.53	0.003	0.0198	-	84	-	0.0	-	T1	300	320	300	⊗	○	Example
24	55	1.5	0.55	0.003	0.0503	-	85	-	0.0	-	T1	240	240	260	○	○	Example
25	55	1.5	0.52	0.003	0.0821	-	86	-	0.0	-	T1	220	200	220	○	○	Example
26	55	1.5	0.54	0.003	0.0920	-	85	-	0.0	-	T1	200	200	200	○	○	Example
27	55	1.5	0.53	0.008	0.0002	V: 0.1	85	-	0.0	-	T1	300	320	300	⊗	○	Example
28	55	1.5	0.61	0.013	0.0002	V: 0.1	85	Ni-Al, Ni-Al-Fe	5.7	5.5	T1	180	160	180	×	○	Comparative Example
29	55	1.5	0.59	0.008	0.0002	Cr: 0.2	85	-	0.0	-	T1	300	300	300	⊗	○	Example
30	55	1.5	0.62	0.014	0.0001	Cr: 0.2	85	Ni-Al, Ni-Al-Fe	6.0	6.3	T1	200	180	180	×	○	Comparative Example
31	55	1.5	0.58	0.008	0.0002	Mn: 0.1	84	-	0.0	-	T1	340	320	320	⊗	○	Example
32	55	1.5	0.58	0.015	0.0002	Mn: 0.1	85	Ni-Al, Ni-Al-Fe	6.5	6.2	T1	180	180	180	×	○	Comparative Example
33	55	1.5	0.62	0.008	0.0003	Mg: 3.0	84	-	0.0	-	T1	640	640	620	⊗	△	Example
34	55	1.5	0.59	0.108	0.0002	Mg: 3.0	85	Ni-Al, Ni-Al-Fe	8.5	7.1	T1	200	200	180	×	△	Comparative Example
35	55	1.5	0.57	0.008	0.0002	Ca: 1.0	85	-	0.0	-	T1	300	300	300	⊗	△	Example
36	55	1.5	0.61	0.020	0.0001	Ca: 1.0	86	Ni-Al, Ni-Al-Fe	7.2	6.8	T1	200	180	180	×	△	Comparative Example
37	55	1.5	0.64	0.008	0.0002	Sr: 1.0	85	-	0.0	-	T1	300	320	300	⊗	△	Example
38	55	1.5	0.58	0.012	0.0002	Sr: 1.0	85	Ni-Al, Ni-Al-Fe	5.8	5.8	T1	180	160	180	×	△	Comparative Example
39	55	1.5	0.58	0.008	0.0002	Mg: 2.0, Ca: 0.1	84	-	0.0	-	T1	580	600	600	⊗	△	Example
40	55	1.5	0.61	0.048	0.0002	Mg: 2.0, Ca: 0.1	85	Ni-Al, Ni-Al-Fe	12.1	8.9	T1	180	200	180	×	△	Comparative Example
41	55	1.5	0.56	0.008	0.0002	Mg: 2.0, Cr: 0.2	85	-	0.0	-	T1	640	620	620	⊗	△	Example
42	55	1.5	0.59	0.075	0.0002	Mg: 2.0, Cr: 0.2	86	Ni-Al, Ni-Al-Fe	13.2	11.3	T1	160	180	180	×	△	Comparative Example
43	55	1.5	0.62	0.008	0.0001	Mg: 4.0, Sr: 0.1	86	-	0.0	-	T1	700	680	680	⊗	△	Example
44	55	1.5	0.63	0.105	0.0002	Mg: 4.0, Sr: 0.1	85	Ni-Al, Ni-Al-Fe	14.8	14.2	T1	180	200	180	×	△	Comparative Example
45	55	1.5	0.51	0.003	0.0002	-	46	-	0.0	-	T1	240	220	240	○	○	Example
46	55	1.5	0.51	0.003	0.0002	-	100	-	0.0	-	T1	360	360	360	⊗	○	Example
47	55	1.5	0.51	0.003	0.0003	-	126	-	0.0	-	T1	380	360	400	⊗	△	Example

[0174] The results in Table 7 demonstrate that each of the Samples of Examples of the present disclosure has superior and balanced corrosion resistance and workability after painting compared to the Samples of Comparative Examples.

5

INDUSTRIAL APPLICABILITY

[0175] The present disclosure provides a hot-dip Al-Zn coated steel sheet that reliably and stably has excellent corrosion resistance.

10 Further, the present disclosure provides a surface-treated steel sheet that reliably and stably has excellent corrosion resistance and anti-white rust property, and a prepainted steel sheet that reliably and stably has excellent corrosion resistance and worked portion corrosion resistance.

CLAIMS

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

5 the coating has a composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 4.0 mass%, with the balance being Zn and inevitable impurity, and

Ni content in the inevitable impurity is 0.010 mass% or less of the total mass of the coating.

10

[Claim 2] The hot-dip Al-Zn coated steel sheet according to claim 1, wherein the coating contains Ni compounds and the major axis length of the Ni compounds is 4.0 μm or less.

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

[Claim 4] The hot-dip Al-Zn coated steel sheet according to claim 1, 20 wherein the coating does not contain Ni compounds.

[Claim 5] The hot-dip Al-Zn coated steel sheet according to claim 1 or 2, wherein Al content in the coating is 50 mass% to 60 mass%.

25 [Claim 6] The hot-dip Al-Zn coated steel sheet according to claim 1 or 2, wherein Co content in the inevitable impurity in the coating is 0.080 mass% or less of the total mass of the coating.

[Claim 7] A method of producing a hot-dip Al-Zn coated steel sheet 30 including a coating, the method comprising:

a hot-dip coating treatment to form the coating, the hot dip coating treatment including immersing a base steel sheet in a coating bath having a composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 4.0 mass%, with the balance being Zn and inevitable impurity, and

35 controlling Ni content in the inevitable impurity in the coating bath to be 0.010 mass% or less of the total mass of the coating bath.

[Claim 8] A surface-treated steel sheet comprising the coating according to claim 1 or 2 and a chemical conversion layer formed on the coating, wherein the chemical conversion layer contains: at least one resin selected from the group consisting of an epoxy resin, a urethane resin, an acrylic resin, an acrylic silicon resin, an alkyd resin, a polyester resin, a polyalkylene resin, an amino resin, and a fluororesin; and at least one 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.

[Claim 9] A prepainted steel sheet comprising a paint layer formed either directly on the coating according to claim 1 or 2, or on a chemical conversion layer on top of the coating, 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 content ratio of (a) to (b), (a):(b), is in a range from 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 includes 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 a magnesium oxide.