

[Document Type] Specification

[Title of the Invention]

Zn-Al-Mg-BASED HOT-DIP PLATED STEEL SHEET

[Technical Field]

5 [0001]

The present invention relates to a Zn-Al-Mg-based hot-dip plated steel sheet.

Priority is claimed on Japanese Patent Application No. 2019-216685 and Japanese Patent Application No. 2019-216686, filed in Japan on November 29, 2019, the content of which is incorporated herein by reference.

10 [Background Art]

[0002]

Zn-Al-Mg-based hot-dip plated steel sheets having higher corrosion resistance than hot-dip galvanized steel sheets are in wide use in a variety of manufacturing industries such as building materials, home appliances, and automobile fields, and the amount of Zn-Al-Mg-based hot-dip plated steel sheets used has been increasing in recent years.

[0003]

For the purpose of displaying letters, marks, design drawings or the like on the surface of a hot-dip plating layer of a hot-dip plated steel sheet, there are cases where a step such as printing or painting is carried out on the hot-dip plating layer to display the letters, the marks, the design drawings or the like on the surface of the hot-dip plating layer.

[0004]

However, the step such as printing or painting carried out on the hot-dip plating layer creates a problem of an increase in the cost or time for providing the letters, designs

or the like. Furthermore, in the case of displaying letters, designs or the like on the surface of a plating layer by printing or painting, there is a concern that a metal glossy external appearance, which is highly popular among consumers, may be lost and, due to a problem of deterioration of coating films themselves over time or deterioration of the
5 adhesion of the coating films over time, durability may be poor and the letters, the designs or the like may disappear over time. In addition, in the case of displaying letters, designs or the like on the surface of a plating layer with pre-inked stamps, the costs or time can be kept relatively low, but there is a concern that the corrosion resistance of the hot-dip plating layer may deteriorate due to ink. Moreover, in the case
10 of displaying a design or the like by grinding a hot-dip plating layer, the durability of the design or the like is excellent, but a significant decrease in the thickness of the hot-dip plating layer at a ground site inevitably degrades the corrosion resistance, and there is a concern of deterioration of plating characteristics.

[0005]

15 As described in the following patent documents, a variety of techniques for Zn-Al-Mg-based hot-dip plated steel sheets have been developed, but there is no known technique for improving the durability in the case of displaying letters, designs or the like on the surface of a plating layer.

[0006]

20 Regarding Zn-Al-Mg-based hot-dip plated steel sheets, there is related art intended to make the pear skin-like external appearance of plating shown on the Zn-Al-Mg-based hot-dip plated steel sheets more beautiful.

For example, Patent Document 1 describes a Zn-Al-Mg-based hot-dip plated steel sheet having a pear skin-like external appearance with a fine texture and a number
25 of smooth glossy portions, that is, a Zn-Al-Mg-based hot-dip plated steel sheet having a

favorable pear skin-like external appearance in which the number of white portions per unit area is large and the proportion of the area of the glossy portions is large. In addition, Patent Document 1 describes that an unfavorable pear skin state is a state in which a surface external appearance in which irregular white portions and circular glossy portions are present in a mixed manner and scattered on the surface is exhibited.

In addition, Patent Document 2 describes a Zn-Al-Mg-based plated steel sheet in which, in a cross section of a plating layer in the thickness direction, a portion where no Al crystals are present between the interface between the plating layer and a base metal and a plating surface layer occupies 10% to 50% of the length of the cross section in the width direction, whereby the external appearance of the plating is improved.

Furthermore, Patent Document 3 describes a hot-dip galvanized steel sheet having excellent formability in which a center line average roughness Ra of a surface of the plated steel sheet is 0.5 to 1.5 μm , the number of 1.27 μm or larger peaks per inch (2.54 cm) (PPI) is 150 to 300, and the number of 0.5 μm or larger peaks per centimeter (Pc) satisfies $Pc \geq PPI/2.54 + 10$.

Moreover, Patent Document 4 describes a highly corrosion-resistant hot-dip galvanized steel sheet in which a ternary eutectic structure of Al/MgZn₂/Zn is refined, whereby the glossiness of a plating layer increases as a whole and the external appearance evenness is improved.

However, no techniques for improving the durability and preventing the deterioration of corrosion resistance in the case of displaying letters or the like on the surface of a plating layer are thus far known in the related art.

[Citation List]

[Patent Document]

[0007]

[Patent Document 1]

Japanese Patent No. 5043234

[Patent Document 2]

Japanese Patent No. 5141899

5 [Patent Document 3]

Japanese Patent No. 3600804

[Patent Document 4]

PCT International Publication No. WO 2013/002358

[Summary of the Invention]

10 [Problems to be Solved by the Invention]

[0008]

The present invention has been made in consideration of the above-described circumstances, and an object of the present invention is to provide a hot-dip plated steel sheet capable of displaying letters, designs or the like on the surface of a plating layer and having excellent durability and excellent corrosion resistance.

15

[Means for Solving the Problem]

[0009]

The gist of the present invention is as described below.

[1] A Zn-Al-Mg-based hot-dip plated steel sheet including a steel sheet and a

20 hot-dip plating layer formed on a surface of the steel sheet,

in which the hot-dip plating layer contains,

in an average composition, 4 mass% or more and less than 25 mass% of Al and 0 mass% or more and less than 10 mass% of Mg with a remainder of Zn and impurities and

25 includes, as a metallographic structure, [Al phase] and [ternary eutectic structure

of Al/Zn/MgZn₂],

the hot-dip plating layer includes a first region and a second region,

the first region and the second region satisfy any one of the following (a) or (b),

and

5 the first region or the second region is disposed so as to form a predetermined shape.

(a) The first region is a region where an average length of the [Al phase] on a surface of the hot-dip plating layer is 200 μm or longer, and the second region is a region where the average length of the [Al phase] on the surface of the hot-dip plating layer is
10 shorter than 200 μm.

(b) The first region is a region where, in a boundary between the steel sheet and the hot-dip plating layer, a length Le of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is more than 0.3 of a length L of the boundary, and the second region is a region where, in the boundary between the steel sheet and the hot-dip plating
15 layer, the length Le of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is 0.3 or less of the length L of the boundary.

[2] The Zn-Al-Mg-based hot-dip plated steel sheet according to [1], in which, in a case where the first region and the second region satisfy (b), a ratio I(200)/I(111) of an X-ray diffraction intensity I(200) of a (200) plane to an X-ray diffraction intensity I(111)
20 of a (111) plane of the [Al phase] on the surface of the hot-dip plating layer is 0.8 or more.

[3] The Zn-Al-Mg-based hot-dip plated steel sheet according to [1] or [2], in which the first region or the second region is disposed so as to form a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a
25 letter or a shape of two or more thereof in combination.

[4] The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of [1] to [3], in which the first region or the second region is intentionally formed.

[5] The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of [1] to [4], in which the hot-dip plating layer further contains, in the average composition,
5 0.0001 to 2 mass% of Si.

[6] The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of [1] to [5], in which the hot-dip plating layer further contains, in the average composition, any one or more of Ni, Ti, Zr and Sr in a total of 0.0001 to 2 mass%.

[7] The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of [1] to
10 [6], in which the hot-dip plating layer further contains, in the average composition, any one or more of Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf and C in a total of 0.0001 to 2 mass%.

[8] The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of [1] to [7], in which a total amount of the hot-dip plating layer attached to both surfaces of the
15 steel sheet is 30 to 600 g/m².

[Effects of the Invention]

[0010]

According to the present invention, it is possible to provide a hot-dip plated steel sheet having excellent durability and also having excellent corrosion resistance in the
20 case of displaying letters, designs or the like on the surface of a hot-dip plating layer.

[Brief Description of Drawings]

[0011]

Fig. 1 is a view describing a method for measuring the size of an Al phase in a Zn-Al-Mg-based hot-dip plated steel sheet that is an example of the present embodiment.

25 Fig. 2 is a picture showing an observation result of a first region in No. 1-4 with

a scanning electron microscope.

Fig. 3 is a picture showing an observation result of a second region in No. 1-4 with the scanning electron microscope.

Fig. 4 is a picture showing an example of a Zn-Al-Mg-based hot-dip plated steel sheet of Example 1.

Fig. 5 is a cross-sectional picture of a first region in No. 2-1 with the scanning electron microscope.

Fig. 6 is a cross-sectional picture of a second region in No. 2-1 with the scanning electron microscope.

Fig. 7 is a picture showing an example of a surface of a hot-dip plating layer of a Zn-Al-Mg-based hot-dip plated steel sheet of Example 2 and is a picture showing a state in which a predetermined pattern is displayed by a second region.

[Embodiment for implementing the Invention]

[0012]

Hereinafter, an embodiment of the present invention will be described.

In the present specification, numerical ranges expressed using “to” include numerical values before and after “to” as the lower limit value and the upper limit value.

[0013]

A Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment includes a steel sheet and a hot-dip plating layer formed on a surface of the steel sheet, the hot-dip plating layer contains, in the average composition, 4 mass% or more and less than 25 mass% of Al and 0 mass% or more and less than 10 mass% of Mg with a remainder of Zn and impurities and includes, as the metallographic structure, [Al phase] and [ternary eutectic structure of Al/Zn/MgZn₂]. The hot-dip plating layer includes a first region and a second region, the first region and the second region satisfy any one of

the following (a) or (b), and the first region or the second region is disposed so as to form a predetermined shape.

(a) The first region is a region where the average length of the [Al phase] on a surface of the hot-dip plating layer is 200 μm or longer, and the second region is a region where the average length of the [Al phase] on the surface of the hot-dip plating layer is shorter than 200 μm .

(b) The first region is a region where, in the boundary between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is more than 0.3 of the length L of the boundary, and the second region is a region where, in the boundary between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is 0.3 or less of the length L of the boundary.

[0014]

In the Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment, the first region or the second region is preferably disposed so as to form a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a letter or a shape of two or more thereof in combination. The first region or the second region is intentionally formed.

[0015]

Here, the [Al phase] is a phase that looks like islands with clear boundaries in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂], corresponds to, for example, "Al" phase" (which is a solid solution of Al that forms a solid solution of Zn and contains a small amount of Mg) at a high temperature in the Al-Zn-Mg ternary equilibrium diagram, and is differentiated from Al in the ternary eutectic structure.

Hereinafter, such a phase will be expressed as [Al phase] in the present embodiment.

[0016]

<Steel sheet>

The material of the steel sheet that is used as the base material of the hot-dip plating layer is not particularly limited. While described below in detail, as the steel sheet, ordinary steel or the like can be used, and Al killed steel or some high alloy steel can also be used. In addition, the shape of the steel sheet is also not particularly limited. The hot-dip plating layer according to the present embodiment is formed by applying a hot-dip plating method described below to the steel sheet.

[0017]

10 <Hot-dip plating layer>

(Chemical components)

Next, the chemical components of the hot-dip plating layer will be described.

The hot-dip plating layer contains, in the average composition, 4 mass% or more and less than 25 mass% of Al and 0% by mass or more and less than 10 mass% of Mg with the remainder of Zn and impurities. The hot-dip plating layer preferably contains, in the average composition, 4 to 22 mass% of Al and 1 to 10 mass% of Mg with the remainder of Zn and impurities.

The hot-dip plating layer may contain, in the average composition, 0.0001 to 2 mass% of Si. The hot-dip plating layer may contain, in the average composition, any one or two of Ni, Ti, Zr and Sr in a total of 0.0001 to 2 mass%. The hot-dip plating layer may contain, in the average composition, any one or more of Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM and Hf in a total of 0.0001 to 2 mass%.

[0018]

[Al: 4 mass% or more and less than 25 mass%]

25 The Al content in the hot-dip plating layer is, in the average composition, 4

mass% or more and less than 25 mass% and preferably 4.0 mass% or more and less than 25.0 mass%. Al is an element necessary to ensure corrosion resistance. When the Al content in the hot-dip plating layer is less than 4 mass%, an effect on improvement in corrosion resistance is insufficient, and the [Al phase] is not sufficiently formed, which is not preferable in terms of ensuring designability. When the Al content is 25 mass% or more, the [Al phase] is excessively formed, which is not preferable in terms of ensuring designability. The Al content in the hot-dip plating layer may be 5 to 22 mass%, may be 5.0 to 22.0 mass%, may be 5 to 18 mass%, may be 5.0 to 18.0 mass% or may be 6 to 16 mass% from the viewpoint of corrosion resistance. The Al content may be 6.0 to 16.0 mass%.

[0019]

[Mg: 0 mass% or more and less than 10 mass%]

The Mg content in the hot-dip plating layer is, in the average composition, 0 mass% or more and less than 10 mass% and may be, in the average composition, 0 mass% or more and less than 10.0 mass%. The Mg content is preferably 1 mass% or more and less than 10 mass% and may be preferably 1 mass% or more and less than 10.0 mass%. Mg may be added to improve corrosion resistance. When the Mg content in the hot-dip plating layer is 1 mass% or more, an effect on improvement in corrosion resistance is more sufficient, which is preferable. In addition, when Mg is 10 mass% or more, a Mg compound crystallizes, which is not preferable in terms of ensuring designability. In addition, dross is significantly generated in a plating bath, and it is difficult to stably manufacture the hot-dip plated steel sheet, which is not preferable. From the viewpoint of the balance between corrosion resistance and suppression of the generation of dross, the Mg content in the hot-dip plating layer may be set to 1.5 to 6 mass%, may be set to 1.5 to 6.0 mass%, may be set to 2 to 5 mass% or may be set to 2.0

to 5.0 mass%.

[0020]

The hot-dip plating layer may contain Si in a range of 0.0001 to 2 mass%, and the Si content may be preferably set to 0.0001 to 2.000 mass%. Si is an element effective for improving the adhesion of the hot-dip plating layer.

When 0.0001 mass% or more of Si is contained in the hot-dip plating layer, since an effect on improvement in adhesion is developed, it is preferable to contain 0.0001 mass% or more of Si.

On the other hand, even when more than 2 mass% of Si is contained, since the effect on improvement in plating adhesion is saturated, the Si content is set to 2 mass% or less even in a case where Si is contained in the hot-dip plating layer.

From the viewpoint of plating adhesion, the Si content in the hot-dip plating layer may be set to 0.0010 to 1 mass%, may be set to 0.0010 to 1.000 mass%, may be set to 0.0100 to 0.8 mass% or may be set to 0.0100 to 0.800 mass%.

[0021]

The hot-dip plating layer may contain, in the average composition, any one or more of Ni, Ti, Zr and Sr in a total of 0.0001 to 2 mass% and preferably 0.0001 to 2.00 mass%. An intermetallic compound including these elements acts as a crystallization nucleus of the [Al phase] and makes the [ternary eutectic structure of Al/MgZn₂/Zn] finer and more uniform to improve the external appearance or smoothness of the hot-dip plating layer. When the amount of these elements in the hot-dip plating layer is less than 0.0001 mass%, an effect on making a solidification structure fine and uniform becomes insufficient, which is not preferable. In addition, when the amount of these elements in the hot-dip plating layer exceeds 2 mass%, the effect on refinement of the [ternary eutectic structure of Al/MgZn₂/Zn] is saturated, the surface roughness of the hot-

dip plating layer increases, and the external appearance becomes poor, which is not preferable.

In a case where the above-described elements are added particularly for the purpose of improving the external appearance of the hot-dip plating layer, the amount of the above-described elements is preferably 0.001 to 0.5 mass%, preferably 0.001 to 0.50 mass%, more preferably 0.001 to 0.05 mass%, and still more preferably 0.002 to 0.01 mass%.

[0022]

The hot-dip plating layer may contain, in the average composition, one or more of Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM and Hf in a total of 0.0001 to 2 mass% and preferably 0.0001 to 2.00 mass%. When the hot-dip plating layer contains these elements, it is possible to further improve corrosion resistance.

REM refers to one or more of rare earth elements having atomic numbers of 57 to 71 in the periodic table.

[0023]

The remainder of the chemical components of the hot-dip plating layer is zinc and impurities. Examples of the impurity include an impurity that is inevitably contained in ground metals other than zinc and an impurity that is contained due to the melting of steel in a plating bath. In addition, there is a case where Fe derived from an alloy layer that is formed in the interface between the plating layer and steel at the time of melting a plating is measured.

[0024]

The average composition of the hot-dip plating layer can be measured by the following method. First, a surface layer coating film is removed with a coating film-exfoliating agent that does not erode the plating (for example, NEO REVER SP-751

manufactured by Sansai Kako Co., Ltd.), then, the hot-dip plating layer is melted in hydrochloric acid containing an inhibitor (for example, HIBIRON manufactured by Sugimura Chemical Industrial Co., Ltd.), and an inductively coupled plasma (ICP) emission spectroscopic analysis is carried out on the obtained solution, whereby the average composition can be obtained. The concentration of the hydrochloric acid may be 10 mass%. In addition, in a case where no surface layer coating film is present, the operation for the removal of the surface layer coating film can be skipped.

[0025]

(Metallographic structure)

Next, the metallographic structure of the hot-dip plating layer will be described. The hot-dip plating layer according to the present embodiment includes [Al phase] and [ternary eutectic structure of Al/Zn/MgZn₂] as the metallographic structure.

Specifically, the hot-dip plating layer according to the present embodiment has a form in which the [Al phase] is included in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂].

Furthermore, [MgZn₂ phase] or [Zn phase] may be included in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂].

In addition, in a case where Si has been added, [Mg₂Si phase] may be included in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂].

[0026]

[Ternary eutectic structure of Al/Zn/MgZn₂]

Here, the [ternary eutectic structure of Al/Zn/MgZn₂] refers to a ternary eutectic structure of an Al phase, a Zn phase and an intermetallic compound MgZn₂ phase, and the Al phase that forms the [ternary eutectic structure of Al/Zn/MgZn₂] corresponds to, for example, an “Al” phase” (which is a solid solution of Al that forms a solid solution of

Zn and contains a small amount of Mg) at a high temperature in the Al-Zn-Mg ternary equilibrium diagram.

At normal temperature, the Al'' phase at a high temperature normally appears as a fine Al phase and a fine Zn phase separately. The Zn phase in the [ternary eutectic structure of Al/Zn/MgZn₂] is a solid solution of Zn that forms a solid solution of a small amount of Al and, in some cases, further forms a solid solution of a small amount of Mg. The MgZn₂ phase in the [ternary eutectic structure of Al/Zn/MgZn₂] is an intermetallic compound phase present in the vicinity of approximately 84 mass% of Zn in the Zn-Mg binary equilibrium diagram.

According to the phase diagram, it is considered that, in each phase, other elements added form no solid solutions or only an extremely small amount of solid solutions even when forming solid solutions. However, the amount thereof cannot be clearly differentiated by a normal analysis, and thus, in the present specification, a ternary eutectic structure including these three phases will be expressed as the [ternary eutectic structure of Al/Zn/MgZn₂].

[0027]

In the present embodiment, as described below, the first region is defined as a region where, in the boundary between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is more than 0.3 of the length L of the boundary, and the second region is defined as a region where the length is 0.3 or less of the length L of the boundary.

[0028]

[Al phase]

The [Al phase] is a phase that looks like islands with clear boundaries in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂] and corresponds to, for

example, “Al” phase” (which is a solid solution of Al that forms a solid solution of Zn and contains a small amount of Mg) at a high temperature in the Al-Zn-Mg ternary equilibrium diagram. In the Al” phase at a high temperature, the amount of Zn or Mg that forms a solid solution differs depending on the concentration of Al or Mg in a plating bath. This Al” phase at a high temperature is normally separated into a fine Al phase and a fine Zn phase at normal temperature, and the island-like shape shown at normal temperature is considered to be attributed to the shape of the Al” phase at a high temperature.

According to the phase diagram, it is considered that, in this phase, other elements added form no solid solutions or solid solutions only in an extremely small amount even when forming solid solutions. However, the [Al phase] cannot be clearly differentiated by a normal analysis, and thus, in the present specification, a phase derived from this Al” phase at a high temperature and having a shape attributed to the shape of the Al” phase will be referred to as the [Al phase].

The [Al phase] can be clearly differentiated from the Al phase that forms the [ternary eutectic structure of Al/Zn/MgZn₂] in microscopic observation.

In the present embodiment, as described below, in a case where the first region and the second region satisfy (a), the average length of the [Al phase] may be set to 200 μm or more in the first region and may be set to less than 200 μm in the second region.

[0029]

[Zn phase]

The [Zn phase] is a phase that looks like islands with clear boundaries in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂], and, in actual cases, there is a case where a solid solution of a small amount of Al or a small amount of Mg is formed. According to the phase diagram, it is considered that, in this phase, other

elements added form no solid solutions or solid solutions only in an extremely small amount even when forming solid solutions.

The [Zn phase] can be clearly differentiated from the Zn phase that forms the [ternary eutectic structure of Al/Zn/MgZn₂] in microscopic observation. There is a case where the [Zn phase] is included in the hot-dip plating layer according to the present embodiment depending on manufacturing conditions, but the influence of the [Zn phase] on corrosion resistance is rarely observed. Therefore, even when the [Zn phase] is included in the hot-dip plating layer, there is no particular problem.

[0030]

10 [MgZn₂ phase]

The [MgZn₂ phase] is a phase that looks like islands with clear boundaries in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂], and, in actual cases, there is a case where a solid solution of a small amount of Al is formed. According to the phase diagram, it is considered that, in this phase, other elements added form no solid solutions or solid solutions only in an extremely small amount even when forming solid solutions.

The [MgZn₂ phase] can be clearly differentiated from the MgZn₂ phase that forms the [ternary eutectic structure of Al/Zn/MgZn₂] in microscopic observation. There is a case where the [MgZn₂ phase] is not included in the hot-dip plating layer according to the present embodiment depending on manufacturing conditions, but the [MgZn₂ phase] is included in the hot-dip plating layer under almost all manufacturing conditions.

[0031]

[Mg₂Si phase]

25 The [Mg₂Si phase] is a phase that looks like islands with clear boundaries in the

solidification structure of the plating layer to which Si has been added. According to the phase diagram, it is considered that, in the [Mg₂Si phase], Zn, Al and other elements added form no solid solutions or solid solutions only in an extremely small amount even when forming solid solutions. The [Mg₂Si phase] can be clearly differentiated from
5 other phases in the hot-dip plating layer in microscopic observation.
[0032]

The hot-dip plating layer of the present embodiment is formed by immersing the steel sheet in a plating bath, then, lifting the steel sheet, and then solidifying the molten metal attached to the surface of the steel sheet. At this time, first, the [Al phase] is
10 formed, and then the [ternary eutectic structure of Al/Zn/MgZn₂] is formed as the temperature of the molten metal decreases.

Depending on the chemical components of the hot-dip plating layer (that is, the chemical components of the plating bath), there is a case where the [Mg₂Si phase], the [MgZn₂ phase] or the [Zn phase] is formed in the parent material of the [ternary eutectic
15 structure of Al/Zn/MgZn₂].
[0033]

(First region and second region)

Next, the first region and the second region of the hot-dip plating layer will be described. In the hot-dip plating layer (on the surface of the hot-dip plating layer)
20 according to the present embodiment, the first region and the second region are present. While described below, the first region and the second region can be distinguished from each other with the naked eye, under a magnifying glass or under a microscope.
[0034]

The first region may be a region where a straight line portion, a curved line
25 portion or the like is displayed, and, the second region may be a region where a straight

line portion, a curved line portion or the like is displayed. In a case where the first region is a region where a straight line portion, a curved line portion or the like is displayed, it is possible to dispose the first region so as to form a predetermined shape and use the other regions as the second region. In addition, in a case where the second
5 region is a region where a straight line portion, a curved line portion or the like is displayed, it is possible to dispose the second region so as to form a predetermined shape and use the other regions as the first region.

The boundary between the first region and the second region can be perceived with the naked eye, under a magnifying glass or under a microscope.

10 [0035]

In a case where the first region is disposed so as to form a predetermined shape, the first region needs to be formed large enough for the presence of the first region to be discriminated with the naked eye, under a magnifying glass or under a microscope. The second region in this case becomes a region that occupies portions other than the first
15 region in the hot-dip plating layer (on the surface of the hot-dip plating layer) and may occupy the majority of the hot-dip plating layer. In addition, the first region may be disposed in the second region. Specifically, the first region may be disposed in the second region so as to form a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a letter or a shape of two or more thereof
20 in combination. A shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a letter or a shape of two or more thereof in combination is displayed on the surface of the hot-dip plating layer by adjusting the shape of the first region. This shape is an artificially-formed shape and is not a naturally-formed shape.

25 [0036]

On the other hand, in a case where the second region is disposed so as to form a predetermined shape, the second region needs to be formed large enough for the presence of the second region to be discriminated with the naked eye, under a magnifying glass or under a microscope. The first region in this case becomes a region that occupies

5 portions other than the second region in the hot-dip plating layer (on the surface of the hot-dip plating layer) and may occupy the majority of the hot-dip plating layer. In addition, the second region may be disposed in the first region. Specifically, the second region may be disposed in the first region so as to form a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a letter or a
10 shape of two or more thereof in combination. A shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a letter or a shape of two or more thereof in combination is displayed on the surface of the hot-dip plating layer by adjusting the shape of the second region. This shape is an artificially-formed shape and is not a naturally-formed shape.

15 [0037]

The first region and the second region may be distinguishable not only with the naked eye but also under a magnifying glass or under a microscope. Specifically, the shape such as a straight line portion that is formed by the first region or the second region needs to be distinguishable in a visual field of 50 times or less. In visual fields of 50
20 times or less, the predetermined shape that is formed by the first region or the second region can be distinguished due to the difference in surface state.

The first region or the second region can be distinguished at a magnification of preferably 20 times or less, more preferably 10 times or less, and still more preferably 5 times or less.

25 [0038]

The first region and the second region satisfy any one of the following (a) or (b).

(a) The first region is a region where the average length of the [Al phase] on the surface of the hot-dip plating layer is 200 μm or longer, and the second region is a region where the average length of the [Al phase] on the surface of the hot-dip plating layer is
5 shorter than 200 μm .

(b) The first region is a region where, in the boundary between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is more than 0.3 of the length L of the boundary, and the second region is a region where, in the boundary between the steel sheet and the hot-
10 dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is 0.3 or less of the length L of the boundary.

Hereinafter, case (a) and case (b) will be sequentially described.

[0039]

(In case where first region and second region satisfy (a))

15 In the first region in the case of satisfying (a), metallic gloss attributed to the Al phase having a long average length is observed. Therefore, the gloss can be recognized as lines compared with the second region. On the other hand, in the second region, metallic gloss is recognized as dots compared with the first region, which is attributed to the Al phase having a short average length. Therefore, the first region and the second
20 region can be distinguished from each other with the naked eye, under a magnifying glass or under a microscope.

[0040]

In the hot-dip plating layer, at least the [Al phase] and the [ternary eutectic structure of Al/Zn/MgZn₂] are present. The hot-dip plating layer has a form in which
25 the [Al phase] is included in the parent material of the [ternary eutectic structure of

Al/Zn/MgZn₂]. In addition, the [Al phase] is a phase that is precipitated relatively early during the solidification of the hot-dip plating layer, and the form of the [Al phase] at that time is a dendritic shape.

[0041]

- 5 In a case where (a) is satisfied, the average length of the [Al phase] present in the first region is 200 μm or longer.

 When the average length of the [Al phase] becomes 200 μm or longer, relatively large dendritic crystals of the [Al phase] are exposed on the surface of the hot-dip plating layer, and the [Al phase] exhibiting metallic gloss is long compared with the [ternary
10 eutectic structure of Al/Zn/MgZn₂] or the like present around the [Al phase] and has clear borders, and thus the [Al phase] becomes visible as lines as a whole.

[0042]

- On the other hand, the average length of the [Al phase] present in the second region is shorter than 200 μm. When the average length of the [Al phase] becomes
15 shorter than 200 μm, relatively short dendritic crystals of the [Al phase] are exposed on the surface of the hot-dip plating layer, and the [Al phase] exhibiting metallic gloss is short compared with the [ternary eutectic structure of Al/Zn/MgZn₂] or the like present around the [Al phase] and has unclear borders, and thus the [Al phase] becomes visible as dots as a whole. The second region is preferably a region where the average length
20 of the [Al phase] is 180 μm or shorter and more preferably a region where the average length of the [Al phase] is shorter than 150 μm. As the difference between the average length of the [Al phase] in the first region and the average length of the [Al phase] in the second region becomes larger, it becomes easier to distinguish the first region and the second region, which is preferable.

25 [0043]

The first region is assumed to be formed by the fact that, in the early stage of the solidification of the hot-dip plating layer, the [Al phase] is formed at a relatively low number density and the [Al phase] itself coarsens. In addition, the second region is assumed to be formed by the fact that, in the early stage of the solidification of the hot-dip plating layer, the [Al phase] is formed at a relatively high number density and the [Al phase] itself does not coarsen and remains as fine grains.

[0044]

In order to control the size of the [Al phase], the cooling rate of molten metal needs to be controlled during the solidification of the hot-dip plating layer. Specifically, in a case where the [Al phase] is coarsened, the cooling rate during the solidification needs to be decreased, and, in a case where the [Al phase] is refined, the cooling rate during the solidification needs to be increased. A shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a mark or a letter or a shape of two or more thereof in combination is intentionally or artificially displayed by a manufacturing method described below by partially increasing or decreasing the cooling rate of the molten metal on the surface of the steel sheet at the time of immersing the steel sheet in a hot-dip plating bath and then lifting the steel sheet.

[0045]

The average length of the [Al phase] is measured by the following method. First, reflected electron images of regions at three arbitrary visual fields in each of the first region and the second region on the surface of the hot-dip plating layer are captured with a scanning electron microscope. Each region is a rectangular region having sizes of $500\ \mu\text{m} \times 360\ \mu\text{m}$. On the captured pictures, dendritic grains of the Al phase are confirmed. Approximately, the dendritic grain of the Al phase has a shape with a main axis portion and secondary arm portions elongating from the main axis portion as shown

in Fig. 1. For the grains of the Al phase in the pictures, the lengths A in the longitudinal direction are measured. The lengths A of all of the grains of the Al phase in the three visual fields are obtained, and the average value thereof is regarded as the average length of the Al phase in the first region or the second region. The dendritic grains of the Al phase radially grow from solidification nuclei in many cases, but are not always arrayed on the same plane, which creates cases where only a part, for example, only the tip of the secondary arm or only the main axis portion, is observed at the time of observing a dendritic grain of the Al phase on the surface. Such grains of the Al phase are excluded from the measurement of the lengths. On the other hand, dendritic grains in which the main axis and the secondary arms are covered with a separate phase present therebetween and thus can be observed to be not connected with each other are included in the measurement of the lengths.

[0046]

(In case where first region and second region satisfy (b))

The first region in the case of satisfying (b) is a region that exhibits low metallic gloss on the surface and looks relatively white or gray compared with the second region. On the other hand, the second region is a region where the metallic gloss on the surface is relatively high compared with the first region. Therefore, the first region and the second region can be distinguished from each other with the naked eye, under a magnifying glass or under a microscope.

[0047]

In the hot-dip plating layer, at least the [Al phase] and the [ternary eutectic structure of Al/Zn/MgZn₂] are present. The hot-dip plating layer has a form in which the [Al phase] is included in the parent material of the [ternary eutectic structure of Al/Zn/MgZn₂]. In addition, the [Al phase] is a phase that is precipitated relatively early

during the solidification of the hot-dip plating layer, and the form of the [Al phase] at that time is a dendritic shape.

[0048]

In a case where (b) is satisfied, the first region is a region where, in the boundary
5 between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is more than 0.3, preferably more than 0.30, of the length L of the boundary. In such a case, on the steel sheet side of the hot-dip plating layer in the thickness direction in the first region, a relatively large amount of the [ternary eutectic structure of Al/Zn/MgZn₂] is present, and the amount of the [Al
10 phase] or other phases or structures becomes relatively small. Therefore, on the surface side of the hot-dip plating layer in the thickness direction, a relatively large amount of the dendritic [Al phase] is present. Therefore, it is assumed that the surface in the first region has a relatively large surface roughness R_a , diffuses or reflects light that has been incident on the first region and looks relatively white or gray compared with the second
15 region.

[0049]

In the first region, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is preferably more than 0.30 of the length L of the boundary in the boundary between the steel sheet and the hot-dip plating layer. That is,
20 L_e/L in the first region is preferably more than 0.30.

[0050]

On the other hand, the second region is a region where, in the boundary between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is 0.3 or less, preferably 0.30 or less, of the length L of the boundary. In such a case, on the steel sheet side of the hot-dip
25

plating layer in the thickness direction in the second region, a relatively small amount of the [ternary eutectic structure of Al/Zn/MgZn₂] is present, and the amount of the [Al phase] or other phases or structures becomes relatively large. Therefore, on the surface side of the hot-dip plating layer in the thickness direction, a relatively small amount of the dendritic [Al phase] is present. Therefore, it is assumed that the surface in the second region has a relatively small surface roughness Ra and exhibits relatively metallic gloss compared with the second region.

[0051]

The second region is a region where, in the boundary between the steel sheet and the hot-dip plating layer, the length Le of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet is preferably 0.30 or less, more preferably 0.15 or less, still more preferably 0.1 or less and particularly preferably 0.10 or less of the length L of the boundary. As the difference between Le/L in the first region and Le/L in the second region becomes larger, it becomes relatively easier to distinguish the first region and the second region, which is preferable.

[0052]

The [Al phase] that is formed during the solidification of the hot-dip plating layer is normally precipitated as a whole in the thickness direction of the hot-dip plating layer. However, the abundance of the [Al phase] on the surface of the hot-dip plating layer can be controlled by intentionally or artificially controlling the length Le of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the boundary between the steel sheet and the hot-dip plating layer. In addition, since the [Al phase] has a dendritic form, when the abundance of the [Al phase] on the surface of the hot-dip plating layer increases, the surface roughness of the hot-dip plating layer increases. On the other hand, when the abundance of the [Al phase] on the surface of the hot-dip

plating layer decreases, the surface roughness of the hot-dip plating layer decreases. As described above, the first region and the second region can be formed on the surface of the hot-dip plating layer by controlling the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the boundary between the steel sheet and the hot-dip plating layer.

[0053]

In the case of including an interfacial alloy layer containing Fe and Zn formed in the boundary between the steel sheet and the hot-dip plating layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet through the interfacial alloy layer needs to be set within the above-described range. However, since the interfacial alloy layer is extremely thin compared to the thickness of the hot-dip plating layer, as described below, at the time of measuring the length L_e with a microscope, there is a case where the interface between the steel sheet and the hot-dip plating layer can be confirmed without being capable of confirming the interfacial alloy layer while also depending on the magnification at the time of measurement.

In this case, the first region needs to be a region where the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the interface between the steel sheet and the hot-dip plating layer is more than 0.3 of the length L of the interface. In addition, the second region needs to be a region where the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the interface between the steel sheet and the hot-dip plating layer is 0.3 or less of the length L of the interface.

[0054]

The proportion of the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the length L of the boundary (interface) in the boundary (interface) between the steel sheet and the hot-dip plating layer can be

measured by the following method. First, cross sections of the Zn-Al-Mg-based hot-dip plated steel sheet in the sheet thickness direction are exposed. The cross sections are exposed at five sites in each of the first region and the second region. Each cross section is captured with a scanning electron microscope. In each cross section, a region having a length of 150 μm is arbitrarily selected from the boundary (interface) between the steel sheet and the hot-dip plating layer. This length is defined as the boundary length L (interface length L). In addition, the [ternary eutectic structure of Al/Zn/MgZn₂] is confirmed in the range of the selected boundary (interface) length, the total length L_e of all of the [ternary eutectic structure of Al/Zn/MgZn₂] in the boundary (interface) between the steel sheet and the hot-dip plating layer is measured, and L_e/L is obtained. L_e/L 's are obtained from the five cross sections in each of the first region and the second region, and the average thereof is defined as the proportion of the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the length L of the boundary (interface) in the boundary (interface) between the steel sheet and the hot-dip plating layer.

[0055]

The [Al phase] that is formed during the solidification of the hot-dip plating layer is normally precipitated as a whole in the thickness direction of the hot-dip plating layer. However, when a substance that serves as a solidification nucleus is disposed in advance on the surface of the steel sheet, a large amount of the [Al phase] is precipitated from the solidification nucleus on the surface of the steel sheet as a nucleus during the solidification of the molten metal attached to the surface of the steel sheet in the region where the solidification nucleus is disposed. The formed [Al phase] segregates on a side relatively close to the steel sheet.

In addition, in the region where the solidification nucleus is disposed, since the

[Al phase] is formed in a relatively high density, the [Al phase] itself does not coarsen and remains as fine grains. Therefore, in the region where the solidification nucleus is disposed, the [Al phase] does not grow up to the surface side of the hot-dip plating layer, and a large amount of the [Al phase] is precipitated in the vicinity of the boundary (interface) between the steel sheet and the hot-dip plating layer. Therefore, the amount of the [ternary eutectic structure of Al/Zn/MgZn₂] precipitated in the region where the solidification nucleus is disposed decreases, and the proportion of the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the length L of the boundary (interface) decreases.

[0056]

In case (b), the region where the solidification nucleus is present on the surface of the steel sheet becomes the second region of the hot-dip plating layer, and the region where the solidification nucleus is not present becomes the first region of the hot-dip plating layer. In addition, since the second region is formed by the above-described mechanism, there is a case where a solidification nucleus is present in the boundary (interface) between the steel sheet and the hot-dip plating layer in the second region. More specifically, in the boundary (interface) between the steel sheet and the hot-dip plating layer in the second region, there is a case where any one or more elements selected from the group consisting of carbon (C), nickel (Ni), calcium (Ca), boron (B), phosphorus (P), titanium (Ti), manganese (Mn), iron (Fe), cobalt (Co), zirconium (Zr), molybdenum (Mo) and tungsten (W) or a compound containing any one or more of the above-described elements is present.

[0057]

The presence of the above-described element or compound in the boundary (interface) between the steel sheet and the hot-dip plating layer can be confirmed by

carrying out an elemental analysis on the boundary between the steel sheet and the hot-dip plating layer in the second region while digging a sample by sputtering using a glow-discharge optical emission spectroscopic analyzer (GDS).

[0058]

5 As described above, the second region having a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol or a letter or a shape of two or more thereof in combination can be formed on the hot-dip plating layer by disposing the solidification nucleus in the above-described shape on the surface of the steel sheet before the steel sheet is immersed in the hot-dip plating bath.

10 [0059]

 In addition, the first region having a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol or a letter or a shape of two or more thereof in combination can be formed on the hot-dip plating layer by disposing the solidification nucleus in a region excluding the above-described shape on the surface of the steel sheet before the steel sheet is immersed in the hot-dip plating bath.

[0060]

 In addition, in case (b), furthermore, the ratio $I(200)/I(111)$ of the X-ray diffraction intensity $I(200)$ of the (200) plane to the X-ray diffraction intensity $I(111)$ of the (111) plane of the Al phase on the surface of the hot-dip plating layer is preferably 0.8 or more and more preferably 0.80 or more. In both the first region and the second region, the ratio $I(200)/I(111)$ is preferably 0.8 or more and more preferably 0.80 or more.

[0061]

 When the ratio $I(200)/I(111)$ increases, in the [Al phase], the amount of an [Al phase] in which the (200) plane becomes parallel to the surface of the hot-dip plating

layer increases, and the amount of an [Al phase] in which the (111) plane becomes parallel to the surface of the hot-dip plating layer decreases. Therefore, in the case of being viewed from the surface of the hot-dip plating layer, the number of dendritic crystals that each looks like a cross increases, and the number of dendritic crystals that each looks like a hexagon decreases. When the dendritic crystals of the [Al phase] that is precipitated as primary crystals grow in a cross shape from crystal nuclei when viewed from the plating surface side in the process where the hot-dip plating layer solidifies from a molten state, the angle between the branches becomes wide, it becomes easy for a flow path of the melt to be formed in a direction perpendicular to the plating surface, and it becomes easy for the [Al phase] on the plating surface to be covered with the [ternary eutectic structure of Al/Zn/MgZn₂] that solidifies in the end. Therefore, when the ratio I(200)/I(111) becomes high, the surface becomes metallic glossy. This makes it possible to improve the overall external appearance of the hot-dip plating layer. In addition, in the first region, there is a tendency that a large amount of the [ternary eutectic structure of Al/Zn/MgZn₂] is present on the side near the boundary (interface) in the sheet thickness direction and thus a large amount of the [Al phase] is present near the surface. On the other hand, the reverse is true in the second region. At a site where a large amount of the [Al phase] is present on the surface, since the metallic gloss is further highlighted for the above-described reason, it becomes possible to more clearly distinguish the first region and the second region.

[0062]

The ratio I(200)/I(111) on the surface of the hot-dip plating layer can be controlled by adjusting the cooling rate after the formation of the plating layer.

[0063]

<Chemical conversion film layer and coating film layer>

The Zn-Al-Mg-based hot-dip plated steel sheet according to the present embodiment may have a chemical conversion film layer or a coating film layer on the surface of the hot-dip plating layer. Here, the type of the chemical conversion film layer or coating film layer is not particularly limited, and a well-known chemical conversion
5 film layer or coating film layer can be used.

[0064]

[Method for manufacturing Zn-Al-Mg-based hot-dip plated steel sheet]

Hereinafter, a method for manufacturing the Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment will be described. In the following description,
10 cases where the first region and the second region satisfy (a) or (b) will be sequentially described.

[0065]

(Manufacturing method in case where first region and second region satisfy (a))

In the manufacturing method in a case where the first region and the second
15 region satisfy (a), first, a hot-rolled steel sheet is manufactured, and hot-rolled sheet annealing is carried out as necessary. After pickling, cold rolling is carried out to produce a cold-rolled sheet. The cold-rolled sheet is degreased, washed with water, and then annealed (cold-rolled sheet annealing), and the annealed cold-rolled sheet is immersed in a hot-dip plating bath to form a hot-dip plating layer. Hot-dip plating may
20 be a continuous hot-dip plating method in which the steel sheet is continuously passed through a hot-dip plating bath or may be a hot-dip galvanizing method in which a steel material obtained by working the steel sheet into a predetermined shape or the steel sheet itself is immersed in a hot-dip plating bath and then lifted.

[0066]

25 The hot-dip plating bath preferably contains 4 mass% or more and less than 25

mass% of Al and 0 mass% or more and less than 10 mass% of Mg with the remainder of Zn and impurities. In addition, the hot-dip plating bath may contain 4 to 22 mass% of Al and 1 to 10 mass% of Mg with the remainder of Zn and impurities. Furthermore, the hot-dip plating bath may contain 0.0001 to 2 mass% of Si. Still furthermore, the hot-dip plating bath may contain any one or more of Ni, Ti, Zr, Sr, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM and Hf in a total of 0.001 to 2 mass%. The average composition of the hot-dip plating layer of the present embodiment is almost the same as the composition of the hot-dip plating bath.

[0067]

10 The temperature of the hot-dip plating bath differs depending on the composition, but is preferably, for example, within a range of 400°C to 500°C. This is because, when the temperature of the hot-dip plating bath is within this range, a desired hot-dip plating layer can be formed.

 In addition, the amount of the hot-dip plating layer attached needs to be adjusted
15 with a method such as gas wiping carried out on the steel sheet lifted from the hot-dip plating bath. The total amount of the hot-dip plating layer attached to both surfaces of the steel sheet is preferably adjusted so as to be within a range of 30 to 600 g/m². In a case where the amount attached is less than 30 g/m², the corrosion resistance of the hot-dip plated steel sheet deteriorates, which is not preferable. In a case where the amount
20 attached is more than 600 g/m², the molten metal attached to the steel sheet sags, which makes it impossible to smoothen the surface of the hot-dip plating layer, which is not preferable.

[0068]

 In order to form the first region and the second region that satisfy (a), after the
25 amount of the hot-dip plating layer attached is adjusted, a non-oxidizing gas is locally

sprayed to the metal in a molten state with a gas nozzle while cooling the entire steel sheet. As the non-oxidizing gas, a non-oxidizing gas such as nitrogen or argon is preferably used.

[0069]

5 In order to form the first region in a predetermined shape, almost all of the hot-dip plating layer is cooled from the bath temperature to 345°C at an average cooling rate of 10°C/second or faster to form the second region. In addition, in order to form the first region, a part of the hot-dip plating layer is cooled from the bath temperature to 345°C at an average cooling rate of slower than 8°C/second, which is a slower rate than
10 that for the second region.

[0070]

More preferably, almost all of the hot-dip plating layer is cooled by forced draft cooling or mist cooling from the bath temperature to 345°C at an average cooling rate of 15°C/second or faster to form the second region, and a part of the hot-dip plating layer is
15 not cooled but left to stand or cooled by spraying a non-oxidizing gas having a relatively high temperature from the bath temperature to 345°C at an average cooling rate of 5°C/second or slower to form the first region. The temperature of the non-oxidizing gas in this case is preferably set, for example, within a range of 100°C to 300°C. However, as long as the above-described average cooling rate can be satisfied, there is no need to
20 limit the temperature of the non-oxidizing gas.

[0071]

In addition, in order to form the second region in a predetermined shape, almost all of the hot-dip plating layer is cooled from the bath temperature to 345°C at an average cooling rate of 8°C/second or slower to form the first region. In addition, in order to
25 form the second region, a part of the hot-dip plating layer is cooled from the bath

temperature to 345°C at an average cooling rate of 10°C/second or faster, which is a faster rate than that for the first region.

[0072]

More preferably, almost all of the hot-dip plating layer is left to stand from the bath temperature to 345°C at an average cooling rate of 5°C/second or slower to form the first region, and a part of the hot-dip plating layer is cooled by spraying a non-oxidizing gas having a relatively low temperature from the bath temperature to 345°C at an average cooling rate of 15°C/second or faster to form the second region. The first region may be cooled in an atmosphere of 50°C to 150°C in order to decrease the cooling rate. In addition, the temperature of the non-oxidizing gas at the time of cooling the second region may be set, for example, within a range of 10°C to 30°C or a mist gas containing water droplets may be used. However, as long as the above-described average cooling rate can be satisfied, there is no need to limit the atmospheric temperature or the temperature of the non-oxidizing gas during the cooling of the first region.

[0073]

(Manufacturing method in case where first region and second region satisfy (b))

In the manufacturing method in a case where the first region and the second region satisfy (b), solidification nuclei are disposed in the steel sheet so as to form a predetermined pattern, then, the steel sheet is immersed in a hot-dip plating bath and then lifted, and then cooled to solidify the hot-dip plating layer, thereby manufacturing the Zn-Al-Mg-based hot-dip plated steel sheet.

[0074]

First, a hot-rolled steel sheet is manufactured, and hot-rolled sheet annealing is carried out as necessary. After pickling, cold rolling is carried out to produce a cold-rolled sheet. The cold-rolled sheet is degreased, washed with water, and then annealed

(cold-rolled sheet annealing), and the annealed cold-rolled sheet is immersed in a hot-dip plating bath to form a hot-dip plating layer.

[0075]

Here, while the steel sheet is cold-rolled and then immersed in the hot-dip plating bath, solidification nuclei are attached to the surface of the steel sheet to form a pattern portion having a shape of any one of a straight line portion, a curved line portion, a figure, a number, a symbol or a letter or a shape of two or more thereof in combination. The solidification nuclei need to be attached in any stage of between the cold rolling and the cold-rolled sheet annealing, between the cold-rolled sheet annealing and the immersion in the hot-dip plating bath, or immediately before the final annealing of the cold-rolled sheet annealing.

[0076]

Components that form the solidification nucleus (hereinafter, referred to as the solidification nucleus-forming components in some cases) are not particularly limited as long as the components form the solidification nucleus in the process where the plating layer solidifies. Examples of the solidification nucleus-forming components include any one or more elements selected from the group consisting of carbon (C), nickel (Ni), calcium (Ca), boron (B), phosphorus (P), titanium (Ti), manganese (Mn), iron (Fe), cobalt (Co), zirconium (Zr), molybdenum (Mo) and tungsten (W), compounds containing any one or more of the above-described elements, and the like. One of the above-described components may be used or two or more thereof may be used in combination. An example of a method for attaching the solidification nuclei to the surface of the steel sheet is a method in which not only the solidification nucleus-forming components themselves but also an alloy foil, a resin, a surfactant, ink, oil or the like containing the solidification nucleus-forming components are attached to the surface of the steel sheet.

These solidification nucleus-forming components may remain as solid or may be contained in water or an organic solvent in a dissolved or dispersed state. Alternatively, the solidification nucleus-forming components may be contained in ink as a pigment or a dye.

5 [0077]

Examples of a method for attaching the solidification nuclei to the surface of the steel sheet include methods in which a material containing the solidification nucleus-forming components is transferred, applied, sprayed or the like to the surface of the steel sheet. For example, an ordinary printing method such as a foil transfer method in which
10 hot stamping, cold stamping or the like is used, a printing method in which a variety of sheets are used (gravure printing, flexographic printing, offset printing, silk printing or the like), an inkjet method, or a thermal transfer method in which an ink ribbon or the like is used can be used.

[0078]

15 An example of the transfer method in which an alloy foil is used is a method in which an alloy foil containing the solidification nucleus-forming components is attached to the surface of the steel sheet and a heated silicon roll is pressed against the alloy foil to transfer the solidification nucleus-forming components to the surface of the steel sheet.

[0079]

20 An example of the printing method in which a sheet is used is a method in which ink or surfactant containing a component that serves as the solidification nuclei is attached to a rubber roll or rubber stamp having a printing pattern formed on the circumferential surface and the rubber roll or the rubber stamp is pressed against the surface of the steel sheet to transfer the ink or the surfactant. This method makes it
25 possible to efficiently attach the solidification nucleus-forming components to the surface

of the steel sheet that is continuously passed

[0080]

The amount of the solidification nuclei attached is preferably, for example, within a range of 50 mg/m² or more and 5000 mg/m² or less. In a case where the amount attached is less than 50 mg/m², there is a possibility that the first region may not be formed large enough to be distinguished with the naked eye, under a magnifying glass or under a microscope, which is not preferable. On the other hand, in a case where the amount attached is more than 5000 mg/m², there is a concern that the adhesion of the hot-dip plating layer may deteriorate, which is not preferable.

10 [0081]

Next, the steel sheet on which the pattern portion is formed from the solidification nuclei is immersed in the hot-dip plating bath. Hot-dip plating may be a continuous hot-dip plating method in which the steel sheet is continuously passed through a hot-dip plating bath or may be a hot-dip galvanizing method in which a steel material obtained by working the steel sheet into a predetermined shape or the steel sheet itself is immersed in a hot-dip plating bath and then lifted.

[0082]

The composition of the hot-dip plating bath, the temperature of the hot-dip plating bath, the amount of the hot-dip plating layer attached, and the method for controlling the amount attached may be the same as those in the manufacturing method in a case where the first region and the second region satisfy (a).

[0083]

In the manufacturing method in a case where the first region and the second region satisfy (b), after the amount of the hot-dip plating layer attached is adjusted, there is a need to adjust the temperature during wiping so that the hot-dip plating layer remains

in a molten state. Furthermore, there is a need to rapidly cool the hot-dip plating layer in order to form a number of fine crystals of the Al phase in the plating after the wiping. Meanwhile, in order to align the solidification direction, it is necessary to hold a solidified state for a certain period of time. Therefore, after the wiping, the hot-dip plating layer is cooled to a temperature that is lower than a temperature at which solidification begins (liquidus temperature) and equal to or higher than a temperature at which the plating completely solidifies (solidus temperature) within one second. In order to sufficiently precipitate fine crystals, the hot-dip plating layer is desirably cooled to a temperature that is lower than the liquidus temperature by 20°C or more within one second.

[0084]

In addition, since it is also required to preferentially precipitate Al, the rapid cooling is more desirably stopped at a temperature that is higher than a temperature at which not only Al present on the solidus line but also a $MgZn_2$ phase is precipitated (defined as the $MgZn_2$ phase precipitation temperature line). When the hot-dip plating layer is cooled to a temperature of ($MgZn_2$ phase precipitation temperature + 5)°C or higher, only fine Al crystals are generated, and it becomes easy to align Al crystal orientations. After that, the hot-dip plating layer is cooled to 300°C or lower by slow cooling at an average cooling rate of slower than 10°C/second in order to grow crystals.

[0085]

In a case where a chemical conversion layer is formed on the surface of the hot-dip plating layer after the formation of the hot-dip plating layer, a chemical conversion treatment is carried out on the hot-dip plated steel sheet in which the hot-dip plating layer has been formed. The type of the chemical conversion treatment is not particularly limited, and a well-known chemical conversion treatment can be used.

In addition, in a case where a coating film layer is formed on the surface of the hot-dip plating layer or on the surface of the chemical conversion layer, a painting treatment is carried out on the hot-dip plated steel sheet in which the hot-dip plating layer has been formed or the chemical conversion layer has been formed. The type of the painting treatment is not particularly limited, and a well-known painting treatment can be used.

[0086]

As described above, in the Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment, the first region and the second region are included in the hot-dip plating layer, and the first region and the second region satisfy any one of the following (a) or (b), whereby it becomes possible to distinguish the first region and the second region. The first region and the second region are not formed by printing or painting and thus have high durability. In addition, the first region and the second region are not formed by printing or painting and thus have no influence on the corrosion resistance of the hot-dip plating layer. Furthermore, the first region and the second region are not formed by the grinding or the like of the surface of the hot-dip plating layer. Therefore, the hot-dip plated steel sheet of the present embodiment becomes excellent in terms of corrosion resistance.

[0087]

In addition, according to the present embodiment, it is possible to provide a Zn-Al-Mg-based hot-dip plated steel sheet having high durability in the first region or the second region formed in a predetermined shape and having favorable plating characteristics such as corrosion resistance. In particular, it is possible to form the first region or the second region in an intentional or artificial shape and to dispose the first region or the second region so as to form a shape of any one of a straight line portion, a

curved line portion, a dot portion, a figure, a number, a symbol, a mark or a letter or a shape of two or more thereof in combination.

[0088]

In addition, in the Zn-Al-Mg-based hot-dip plated steel sheet of the present
5 embodiment, it is possible to display a variety of designs, trademarks and other
identification marks on the surface of the hot-dip plating layer without carrying out
printing or painting and to enhance the distinguishability, design properties or the like of
the origin of the steel sheet. In addition, it is also possible to impart information
necessary for process control, inventory control or the like or any information required
10 by consumers to the Zn-Al-Mg-based hot-dip plated steel sheet with the first region or
the second region. This also makes it possible to contribute to improvement in the
productivity of the Zn-Al-Mg-based hot-dip plated steel sheet.

[Examples]

[0089]

15 Next, examples of the present invention will be described.

[0090]

(Example 1)

Steel sheets were degreased and washed with water, and then reduction
annealing, immersion in a plating bath, control of the amount attached and cooling were
20 carried out, thereby manufacturing hot-dip plated steel sheets Nos. 1-1 to 1-21 shown in
Table 2A and Table 2B. For the cooling following the control of the amount attached,
after the steel sheets were lifted from the plating bath and then the amounts attached were
adjusted by gas wiping, nitrogen gas was locally sprayed to the metal in a molten state
with a gas nozzle while cooling the entire steel sheets. After that, the steel sheets were
25 cooled to completely solidify the molten metal. The nitrogen gas-spraying ranges were

controlled so as to form 50 mm-interval grid patterns. The cooling conditions are shown in Table 1. The average cooling rates shown in Table 1 are all the average cooling rates from the bath temperature to 345°C.

[0091]

- 5 Grid patterns were expressed in second regions under cooling conditions A to C, and a grid pattern was expressed in a first region under a cooling condition D. In addition, patterns of comparative examples were formed under cooling conditions E and F.

[0092]

- 10 Under the cooling condition A, nitrogen gas (30°C) was sprayed as a non-oxidizing gas while the entire steel sheet was slowly cooled in an atmosphere (120°C).

 Under the cooling condition B, nitrogen gas (20°C) was sprayed as a non-oxidizing gas while the entire steel sheet was left to stand.

- 15 Under the cooling condition C, nitrogen gas containing mist was sprayed as a non-oxidizing gas while the entire steel sheet was left to stand.

 Under the cooling condition D, nitrogen gas (250°C) was sprayed as a non-oxidizing gas while the entire steel sheet was cooled with nitrogen gas containing mist.

 In addition, under the cooling condition E, nitrogen gas (30°C) was sprayed as a non-oxidizing gas while the entire steel sheet was left to stand in nitrogen gas (30°C).

- 20 Under the cooling condition F, the entire steel sheet was left to stand.

[0093]

[Table 1]

Cooling condition pattern	First region		Second region		Note
	Average cooling rate (°C/second)	Cooling gas temperature (°C)	Average cooling rate (°C/second)	Cooling gas temperature (°C)	
A	8	120	12	30	Grid pattern is in second region
B	5	Left to stand	15	20	Grid pattern is in second region
C	5	Left to stand	30	Mist	Grid pattern is in second region
D	3	250	30	Mist	Grid pattern is in first region
E	12	30	12	30	Comparative conditions
F	5	Left to stand	5	Left to stand	Comparative conditions

[0094]

[Table 2A]

No.	Manufacturing condition	Hot-dip plating layer					Amount of plating attached (g/m ²)
		Average composition (mass%) remainder: Zn and impurities					
		Al	Mg	Si	Others		
1-1	Cooling pattern A	11.0	3.0	-	-		135
1-2	Cooling pattern B	11.0	3.0	-	-		135
1-3	Cooling pattern C	11.0	3.0	-	-		135
1-4	Cooling pattern B	11.0	3.4	0.200	-		135

1-5	Cooling pattern C	11.0	3.4	0.200	-	135
1-6	Cooling pattern B	11.0	3.4	0.500	-	135
1-7	Cooling pattern C	11.0	3.4	0.500	-	135
1-8	Cooling pattern B	11.0	3.4	0.200	Ti = 0.1	135
1-9	Cooling pattern B	11.0	3.4	0.200	Ni = 0.2	135
1-10	Cooling pattern B	11.0	3.4	0.200	Sn = 0.1	135
1-11	Cooling pattern B	11.0	3.4	0.200	Sr = 0.05	135
1-12	Cooling pattern B	6.0	3.4	0.200	-	135
1-13	Cooling pattern B	8.0	3.4	0.200	-	135
1-14	Cooling pattern B	15.0	3.4	0.200	-	135
1-15	Cooling pattern B	25.0	3.4	1.000	Cr = 0.05	135
1-16	Cooling pattern B	11.0	1.0	0.200	-	135
1-17	Cooling pattern B	12.0	5.0	1.200	-	135
1-18	Cooling pattern B	11.0	8.0	0.200	-	135
1-19	Cooling pattern D	11.0	3.4	0.200	-	135
1-20	Cooling pattern E	11.0	3.4	0.200	-	135
1-21	Cooling pattern F	11.0	3.4	0.200	-	135
1-22	Printing after plating (cooling after plating is under pattern E)	11.0	3.4	0.200	-	135
1-23	Printing after plating (cooling after plating is under pattern F)	11.0	3.4	0.200	-	135

[0095]

[Table 2B]

No.	Hot-dip plating layer			Grid pattern-forming range	Evaluation			Note
	First region Length of Al phase (μm)	Second region			Distinguishability		Corrosion resistance	
		Length of Al phase (μm)			Initial state	Aged state		
1-1	300	195		Second region	A	A	A	Invention Example
1-2	350	180		Second region	A	A	A	Invention Example
1-3	350	150		Second region	A	A	A	Invention Example
1-4	350	180		Second region	A	A	A	Invention Example
1-5	350	150		Second region	A	A	A	Invention Example
1-6	350	180		Second region	A	A	A	Invention Example
1-7	350	150		Second region	A	A	A	Invention Example
1-8	350	180		Second region	A	A	A	Invention Example
1-9	350	180		Second region	A	A	A	Invention Example
1-10	350	180		Second region	A	A	A	Invention Example
1-11	350	180		Second region	A	A	A	Invention Example
1-12	350	180		Second region	B	B	B	Invention Example
1-13	350	180		Second region	A	A	A	Invention Example
1-14	350	180		Second region	A	A	A	Invention Example
1-15	350	180		Second region	B	B	A	Invention Example
1-16	350	180		Second region	A	A	B	Invention Example
1-17	350	180		Second region	A	A	A	Invention Example
1-18	350	180		Second region	B	B	A	Invention Example
1-19	400	150		First region	A	A	A	Invention Example

1-20	200	<u>200</u>	<u>Not confirmed</u>	D	D	A	Comparative Example
1-21	350	<u>350</u>	<u>Not confirmed</u>	D	D	A	Comparative Example
1-22	-	-	Printed site	A	D	B	Comparative Example
1-23	-	-	Ground site	B	C	D	Comparative Example

Underlines indicate that values are not in the scope of the present invention.

[0096]

In addition, a Zn-Al-Mg-based hot-dip plated steel sheet was manufactured in the same manner as described above. After that, a 50 mm-interval grid pattern was printed on the surface of a hot-dip plating layer by an inkjet method. This result is shown in Table 2A and Table 2B as No. 1-22.

[0097]

Furthermore, a Zn-Al-Mg-based hot-dip plated steel sheet was manufactured in the same manner as described above. After that, a 50 mm-interval grid pattern was formed by grinding the surface of a hot-dip plating layer. This result is shown in Table 2A and Table 2B as No. 1-23.

[0098]

For the obtained hot-dip plated steel sheets, the average lengths of Al phases in the first regions and the second regions were obtained. First, the boundary between the first region and the second region was specified by observing the surface of the hot-dip plating layer with the naked eye. In examples where the discrimination of the boundary was difficult, the nitrogen gas-spraying ranges were regarded as the first regions or the second regions.

[0099]

The average length of the [Al phase] was measured by the following method. First, reflected electron images of regions at three arbitrary visual fields in each of the first region and the second region on the surface of the hot-dip plating layer were captured with a scanning electron microscope. Each region was a rectangular region having sizes of $500\ \mu\text{m} \times 360\ \mu\text{m}$. On the captured pictures, dendritic grains of the [Al phase] were confirmed. Approximately, the dendritic grain of the [Al phase] had a shape with a main axis portion and primary arm portions elongating from the main axis

portion as shown in Fig. 1. For the grains of the [Al phase] in the pictures, the lengths A in the longitudinal direction were measured. The lengths A of all of the grains of the [Al phase] in the three visual fields were obtained, and the average value thereof was regarded as the average length of the [Al phase] in the first region or the second region.

- 5 The dendritic grains of the [Al phase] radially grow from solidification nuclei in many cases, but are not always arrayed on the same plane, which creates cases where only a part, for example, only the tip of the arm or only the main axis portion, is observed at the time of observing a dendritic grain of the Al phase on the surface. Such grains of the [Al phase] were excluded from the measurement of the lengths. On the other hand,
- 10 dendritic grains in which the main axis and the arms were covered with a separate phase present therebetween and thus could be observed to be not connected with each other were included in the measurement of the lengths.

[0100]

[Distinguishability]

- 15 On test sheets provided with the grid pattern in an initial state where the test sheet was just manufactured and in an aged state where the test sheet had been exposed outdoors for six months, visual evaluation was carried out based on the following determination criteria. A to C were regarded as pass for both the initial state and the aged state.

20 [0101]

A: The grid pattern is visible at a distance of 5 meters.

B: The grid pattern is not visible at a distance of 5 meters, but is highly visible at a distance of 3 meters.

- C: The grid pattern is not visible at a distance of 3 meters, but is highly visible at
- 25 a distance of 1 meter.

D: The grid pattern is not visible at a distance of one meter.

[0102]

[Corrosion resistance]

The test sheet was cut to 150 × 70 mm, 30 cycles of a copper corrosion test CCT
5 according to JASO-M609 were carried out, and then a rust generation status was
investigated and evaluated based on the following determination criteria. A to C were
regarded as pass.

A: No rust is generated, and both the grid pattern and the other regions maintain
a beautiful design external appearance.

10 B: No rust is generated, but an extremely slight change in the design external
appearance change is admitted in both the grid pattern and the other regions.

C: The design external appearance is slightly impaired, but the grid pattern and
the other regions can be visually differentiated.

D: Both the grid pattern and the other regions significantly deteriorate in the
15 external appearance quality and cannot be visually differentiated.

[0103]

As shown in Table 2A and Table 2B, the Zn-Al-Mg-based hot-dip plated steel
sheets of Present Invention Examples No. 1-1 to No. 1-19 were excellent in terms of both
the distinguishability and the corrosion resistance. Fig. 2 shows the observation result
20 of the first region in No. 1-4 with a scanning electron microscope, and Fig. 3 shows the
observation result of the second region in No. 1-4 with the scanning electron microscope.
It was found that the average length of the [Al phase] became large in the [Al phase] in
the first region shown in Fig. 2 compared with the [Al phase] in the second region shown
in Fig. 3 and the first region and the second region exhibit mutually different external
25 appearances and can be distinguished from each other.

[0104]

In No. 1-20 and No. 1-21, since the cooling conditions were not appropriate, no grid patterns were confirmed.

[0105]

5 In addition, in No. 1-22 where the grid pattern was printed by the inkjet method, the pattern was thinned by the outdoor exposure for six months, and the distinguishability deteriorated.

In addition, in No. 1-23 where the grid pattern was formed by grinding, the thickness of the plating layer at the ground site decreased, and the corrosion resistance in
10 the ground site deteriorated.

[0106]

The plating layers in No. 1-1 to No. 1-23 included the [Al phase] and the [ternary eutectic structure of Al/Zn/MgZn₂].

[0107]

15 Fig. 4 shows the surface of a hot-dip plated steel sheet displaying a letter string (alphabet) formed by spraying nitrogen gas to a Zn-Al-Mg-based hot-dip plating layer. According to the present invention, it becomes possible to intentionally display a letter or a mark on the surface of a hot-dip plated steel sheet.

[0108]

20 (Example 2)

Cold-rolled steel sheets were degreased and washed with water. Next, inks containing a solidification nucleus-forming component shown in Table 3 (fine particles of C or Ni) were attached to rubber sheets having a shape to which a 50 mm-interval grid pattern had been transferred. These rubber sheets were pressurized against the water-
25 washed steel sheets, thereby attaching the inks to the surfaces of the steel sheets. After

that, cold-rolled sheet annealing was carried out on the steel sheets. The steel sheets after the cold-rolled sheet annealing were immersed in a hot-dip plating bath and then lifted. After that, the amounts attached were adjusted by gas wiping, and the steel sheets were further cooled. As the cooling after the control of the amounts attached, the steel sheets were cooled under cooling conditions where the temperatures of hot-dip plating layers one second after the gas wiping became temperatures shown in Table 4 and then left to stand. Zn-Al-Mg-based hot-dip plated steel sheets Nos. 2-1 to 2-20 shown in Table 5A and Table 5B were manufactured as described above. The steel sheet temperatures in Table 4 were all equal to or lower than a temperature at which solidification began (liquidus temperature) and equal to or higher than a temperature at which a plating completely solidified (solidus temperature) and were desirably within a range of (a temperature at which the precipitation of $MgZn_2$ began + 5)°C or higher and less than (the liquidus temperature - 20)°C.

[0109]

In addition, a Zn-Al-Mg-based hot-dip plated steel sheet was manufactured in the same manner as described above except that a plating treatment using a hot-dip plating bath was carried out on a steel sheet to which no solidification nuclei had been attached. This is shown in Table 5A and Table 5B as No. 2-21.

[0110]

In addition, a Zn-Al-Mg-based hot-dip plated steel sheet was manufactured in the same manner as described above except that a plating treatment using a hot-dip plating bath was carried out on a steel sheet to which no solidification nuclei had been attached. A 50 mm-interval grid pattern was printed on the surface of a hot-dip plating layer in this steel sheet by an inkjet method. A Zn-Al-Mg-based hot-dip plated steel sheet No. 2-22 was manufactured as described above.

[0111]

In addition, a Zn-Al-Mg-based hot-dip plated steel sheet was manufactured in the same manner as described above except that a plating treatment using a hot-dip plating bath was carried out on a steel sheet to which no solidification nuclei had been attached. After that, a 50 mm-interval grid pattern was formed by grinding the surface of a hot-dip plating layer. A Zn-Al-Mg-based hot-dip plated steel sheet No. 2-23 was manufactured as described above.

[0112]

For the obtained hot-dip plated steel sheets, the ratios of the length L_e of the ternary eutectic structure facing the steel sheet to the length L of the boundary in the boundary between the steel sheet and the hot-dip plating layer in the first region and the second region were obtained. First, the boundary between the first region and the second region was specified by observing the surface of the hot-dip plating layer with the naked eye. In examples where the discrimination of the boundary was difficult, the solidification nucleus attachment ranges were regarded as the second regions.

[0113]

The proportion of the length L_e of the ternary eutectic structure facing the steel sheet in the length L of the boundary in the boundary between the steel sheet and the hot-dip plating layer was measured by the following method. First, cross sections of the Zn-Al-Mg-based hot-dip plated steel sheet in the sheet thickness direction were exposed. The cross sections were exposed at five sites in each of the first region and the second region. Each cross section was captured with a scanning electron microscope. In each cross section, a region having a length of 150 μm was arbitrarily selected from the boundary between the steel sheet and the hot-dip plating layer. This length was regarded as the boundary length L . In addition, the [ternary eutectic structure of

Al/Zn/MgZn₂] is confirmed in the range of the selected boundary length, the total length Le of all of the [ternary eutectic structure of Al/Zn/MgZn₂] in the boundary between the steel sheet and the hot-dip plating layer is measured, and Le/L is obtained. Le/L's were obtained from the five cross sections in each of the first region and the second region, and the average thereof was regarded as the proportion of the length Le of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel sheet in the length L of the boundary in the boundary between the steel sheet and the hot-dip plating layer.

[0114]

In addition, at an arbitrary position on the surface of the hot-dip plating layer, the ratio I(200)/I(111) of the X-ray diffraction intensity I(200) of the (200) plane to the X-ray diffraction intensity I(111) of the (111) plane of the [Al phase] was obtained. The X-ray diffraction intensity I(200) of the (200) plane and the X-ray diffraction intensity I(111) of the (111) plane of the [Al phase] were measured on the surface of the hot-dip plating layer by the X-ray diffraction method in which CuK α 1 rays were used and the ratio I(200)/I(111) was obtained. The intensity of the diffraction peak of the (200) plane of Al that appeared at 44.74° in the 2 θ range was regarded as the peak intensity of the (200) plane of the Al phase. The intensity of the diffraction peak of the (111) plane of Al that appeared within a range of 38.47° in the 2 θ range was regarded as the peak intensity of the (111) plane of the Al phase. For X-ray diffraction measurement, an X-ray diffractometer for micro region measurement was used. The step was set to 0.02°, the scanning speed was set to 5°/min, and a high-speed semiconductor two-dimensional detector was used as the detector. X-rays that were emitted from the X-ray light source were focused with a polycapillary. The irradiation range with the focused X-rays was set to a circle having a diameter of 1 mm.

[0115]

[Distinguishability]

On test sheets provided with the grid pattern in an initial state where the test sheet was just manufactured and in an aged state where the test sheet had been exposed outdoors for six months, visual evaluation was carried out based on the following determination criteria. A to C were regarded as pass for both the initial state and the aged state.

[0116]

A: The grid pattern is visible at a distance of 8 meters.

B: The grid pattern is not visible at a distance of 8 meters, but is highly visible at a distance of 4 meters.

C: The grid pattern is not visible at a distance of 4 meters, but is highly visible at a distance of 1 meter.

D: The grid pattern is not visible at a distance of 1 meter.

[0117]

[Corrosion resistance]

The test sheet was cut to 150 × 70 mm, 30 cycles of a copper corrosion test CCT according to JASO-M609 were carried out, and then a rust generation status was investigated and evaluated based on the following determination criteria. A to C were regarded as pass.

A: No rust is generated, and both the grid pattern and the other regions maintain a beautiful design external appearance.

B: No rust is generated, but an extremely slight change in the design external appearance change is admitted in both the grid pattern and the other regions.

C: The design external appearance is slightly impaired, but the grid pattern and the other regions can be visually differentiated.

D: Both the grid pattern and the other regions significantly deteriorate in the external appearance quality and cannot be visually differentiated.

[0118]

[Table 3]

Treatment method	Solidification nucleus element
1	C
2	Ni
3	None

5 [0119]

[Table 4]

Cooling condition pattern	Bath temperature (°C)	Steel sheet temperature one second after wiping (°C)
A	435	400
B	435	385
C	400	350
D	480	440
E	515	480
F	435	420
G	435	350

[0120]

[Table 5A]

No.	Manufacturing method		Hot-dip plating layer				
	Imparting of solidification nucleus	Cooling method	Average composition (mass%) remainder: Zn and impurities				Amount of plating attached (g/m ²)
			Al	Mg	Si	Others	
2-1	1	Cooling A	11.0	3.0	0.000	-	135
2-2	1	Cooling B	11.0	3.0	0.000	-	135
2-3	1	Cooling F	11.0	3.0	0.000	-	135
2-4	1	Cooling A	11.0	3.4	0.200	-	135
2-5	1	Cooling B	11.0	3.4	0.200	-	135
2-6	1	Cooling A	11.0	3.4	0.500	-	135
2-7	2	Cooling A	11.0	3.4	0.500	-	135
2-8	1	Cooling A	11.0	3.4	0.200	Ti = 0.1	135
2-9	1	Cooling B	11.0	3.4	0.200	Ti = 0.1	135
2-10	1	Cooling B	11.0	3.4	0.200	Ni = 0.2	135
2-11	1	Cooling B	11.0	3.4	0.200	Sn = 0.1	135
2-12	1	Cooling B	11.0	3.4	0.200	Sr = 0.05	135
2-13	1	Cooling C	6.0	3.4	0.200	-	135
2-14	1	Cooling A	9.0	3.4	0.200	-	135
2-15	1	Cooling D	15.0	3.4	0.200	-	135
2-16	1	Cooling E	22.0	3.4	1.000	Cr = 0.05	135
2-17	1	Cooling A	11.0	1.0	0.200	-	135

2-18	1	Cooling A	11.0	5.0	1.200	-	135
2-19	1	Cooling A	11.0	8.0	0.200	-	135
2-20	1	Cooling A	11.0	3.4	0.200	-	135
2-21	<u>3</u>	Cooling A	11.0	3.4	0.200	-	135
2-22	<u>3</u>	Printing after plating (cooling A during plating)	11.0	3.4	0.200	-	135
2-23	<u>3</u>	Grinding after plating (cooling A during plating)	11.0	3.4	0.200	-	135

Underlines mean that values are apart from preferable manufacturing conditions.

[0121]

[Table 5B]

No.	Plating structure			Evaluation			Note
	First region Le/L	Second region Le/L	Surface XRD I(200)/I(111)	Distinguishability		Corrosion resistance	
				Initial state	Aged state		
2-1	0.55	0.13	1.85	A	A	A	Invention Example
2-2	0.65	0.08	2.35	A	A	A	Invention Example
2-3	0.72	0.12	0.62	B	B	A	Invention Example
2-4	0.64	0.05	1.80	A	A	A	Invention Example
2-5	0.61	0.07	2.45	A	A	A	Invention Example
2-6	0.58	0.09	1.90	A	A	A	Invention Example
2-7	0.45	0.18	1.85	A	A	A	Invention Example
2-8	0.60	0.10	1.88	A	A	A	Invention Example

2-9	0.64	0.08		2.17	A	A	A	Invention Example
2-10	0.59	0.10		2.05	A	A	A	Invention Example
2-11	0.67	0.11		2.03	A	A	A	Invention Example
2-12	0.61	0.15		2.10	A	A	A	Invention Example
2-13	0.53	0.17		0.90	B	B	B	Invention Example
2-14	0.48	0.09		1.30	A	A	A	Invention Example
2-15	0.63	0.07		2.50	A	A	A	Invention Example
2-16	0.57	0.12		2.60	B	B	A	Invention Example
2-17	0.54	0.15		1.80	A	A	B	Invention Example
2-18	0.62	0.10		1.83	A	A	A	Invention Example
2-19	0.71	0.13		1.90	B	B	A	Invention Example
2-20	0.60	0.11		1.79	A	A	A	Invention Example
2-21	0.64	=		1.87	D	D	A	Comparative Example
2-22	0.55	=		1.75	A	D	B	Comparative Example
2-23	0.58	=		1.81	B	C	D	Comparative Example

Underlines mean that values are not in the scope of the present invention.

[0122]

As shown in Table 5A and Table 5B, the Zn-Al-Mg-based hot-dip plated steel sheets of Present Invention Examples No. 2-1 to No. 2-20 were excellent in terms of both the distinguishability and the corrosion resistance. Fig. 5 shows the cross-sectional observation result of the first region in No. 2-1 with a scanning electron microscope, and Fig. 6 shows the cross-sectional observation result of the second region in No. 2-1 with the scanning electron microscope. It was found that the first region and the second region exhibit different external appearances and can be distinguished from each other.

[0123]

In No. 2-21, since no solidification nuclei were attached, no second region was formed, and no grid pattern was formed.

[0124]

In addition, in No. 2-22 where the grid pattern was printed by the inkjet method, the pattern was thinned by the outdoor exposure for six months, and the designability deteriorated. In addition, since no solidification nuclei were attached, no second region was formed.

Furthermore, in No. 2-23 where the grid pattern was formed by grinding, the thickness of the plating layer at the ground site decreased, and the corrosion resistance in the ground site deteriorated. In addition, since no solidification nuclei were attached, no second region was formed.

[0125]

The hot-dip plating layers in No. 2-1 to No. 2-23 included the [Al phase] and the [ternary eutectic structure of Al/Zn/MgZn₂].

[0126]

Fig. 7 shows the surface of a hot-dip plated steel sheet displaying a letter string

(alphabet) with a second region in a Zn-Al-Mg-based hot-dip plating layer.

According to the present invention, it becomes possible to intentionally display a letter or a mark on the surface of a hot-dip plated steel sheet.

[Industrial Applicability]

5 [0127]

According to the present invention, it is possible to display a variety of designs, trademarks and other identification marks on the surface of the Zn-Al-Mg-based hot-dip plating layer without carrying out printing or painting and to enhance the distinguishability, design properties or the like of the origin of the steel sheet. In

10 addition, it is also possible to impart information necessary for process control, inventory control or the like or any information required by consumers to the Zn-Al-Mg-based hot-dip plated steel sheet with the first region or the second region. This also makes it possible to contribute to improvement in the productivity of the Zn-Al-Mg-based hot-dip plated steel sheet. Therefore, the present invention has sufficient industrial
15 applicability.

[CLAIMS]

1. A Zn-Al-Mg-based hot-dip plated steel sheet, comprising:

a steel sheet; and

5 a hot-dip plating layer formed on a surface of the steel sheet,

wherein the hot-dip plating layer contains,

in an average composition, 4 mass% or more and less than 25 mass% of Al and
0 mass% or more and less than 10 mass% of Mg with a remainder of Zn and impurities
and

10 includes, as a metallographic structure, [Al phase] and [ternary eutectic structure
of Al/Zn/MgZn₂],

the hot-dip plating layer includes a first region and a second region,

the first region and the second region satisfy any one of the following (a) or (b),

and

15 the first region or the second region is disposed so as to form a predetermined
shape,

(a) the first region is a region where an average length of the [Al phase] on a
surface of the hot-dip plating layer is 200 μm or longer, and the second region is a region
where the average length of the [Al phase] on the surface of the hot-dip plating layer is
20 shorter than 200 μm, and

(b) the first region is a region where, in a boundary between the steel sheet and
the hot-dip plating layer, a length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂]
facing the steel sheet is more than 0.3 of a length L of the boundary, and the second
region is a region where, in the boundary between the steel sheet and the hot-dip plating
25 layer, the length L_e of the [ternary eutectic structure of Al/Zn/MgZn₂] facing the steel

sheet is 0.3 or less of the length L of the boundary.

2. The Zn-Al-Mg-based hot-dip plated steel sheet according to Claim 1,

wherein, in a case where the first region and the second region satisfy (b), a ratio
5 $I(200)/I(111)$ of an X-ray diffraction intensity $I(200)$ of a (200) plane to an X-ray
diffraction intensity $I(111)$ of a (111) plane of the [Al phase] on the surface of the hot-dip
plating layer is 0.8 or more.

3. The Zn-Al-Mg-based hot-dip plated steel sheet according to Claim 1 or 2,

10 wherein the first region or the second region is disposed so as to form a shape of
any one of a straight line portion, a curved line portion, a figure, a number, a symbol, a
mark or a letter or a shape of two or more thereof in combination.

4. The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of Claims 1 to

15 3,

wherein the first region or the second region is intentionally formed.

5. The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of Claims 1 to

4,

20 wherein the hot-dip plating layer further contains, in the average composition,
0.0001 to 2 mass% of Si.

6. The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of Claims 1 to

5,

25 wherein the hot-dip plating layer further contains, in the average composition,

any one or more of Ni, Ti, Zr and Sr in a total of 0.0001 to 2 mass%.

7. The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of Claims 1 to 6,

5 wherein the hot-dip plating layer further contains, in the average composition, any one or more of Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf and C in a total of 0.0001 to 2 mass%.

8. The Zn-Al-Mg-based hot-dip plated steel sheet according to any one of Claims 1 to

10 7,

 wherein a total amount of the hot-dip plating layer attached to both surfaces of the steel sheet is 30 to 600 g/m².