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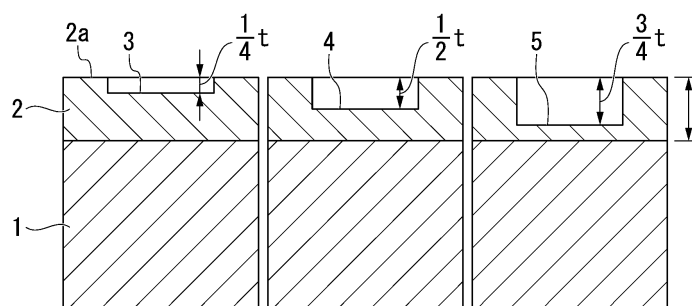
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(74) Representative: **Vossius & Partner****Patentanwälte Rechtsanwälte mbB****Siebertstrasse 3****81675 München (DE)**(54) **Zn-Al-Mg-BASED HOT-DIPPED STEEL SHEET**

(57) A Zn-Al-Mg-based hot-dip plated steel sheet includes a hot-dip plated layer formed on a surface of a steel sheet, in which the hot-dip plated layer contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with a remainder including Zn and impurities, and in a case where a 5 mm square cross section parallel to a surface of the hot-dip plated layer is

exposed at any position of a $3t/4$ position, a $t/2$ position, and a $t/4$ position from the surface with a thickness of the hot-dip plated layer represented by t , a ratio (B/A (%)) of an area fraction B of a [Zn phase] to a total area fraction A of a [Zn phase] and an [Al/MgZn₂/Zn ternary eutectic structure] of a plating microstructure in at least one cross section is 20% or more.

FIG. 1



Description

Technical Field

[0001] The present invention relates to a Zn-Al-Mg-based hot-dip plated steel sheet having an external appearance close to white.

[0002] Priority is claimed on Japanese Patent Application No. 2022-094356, filed June 10, 2022, the content of which is incorporated herein by reference.

Background Art

[0003] A hot-dip plated steel sheet is used as a steel sheet having good corrosion resistance. A hot-dip galvanized steel sheet, which is a representative example of the hot-dip plated steel sheet, is widely used in various manufacturing industries such as the fields of automobiles, home appliances, and building materials. In addition, a highly corrosion-resistant hot-dip galvanized steel sheet obtained by incorporating Al or Mg into a hot-dip galvanized layer has been proposed for the purpose of further improving the corrosion resistance of the hot-dip galvanized steel sheet. For example, Patent Documents 1 to 3 propose a Zn-Al-Mg-based hot-dip plated steel sheet.

[0004] The Zn-Al-Mg-based hot-dip plated steel sheet mainly contains four types of phases and microstructures of an [Al phase], a [Zn phase], a [MgZn₂ phase], and an [Al/MgZn₂/Zn ternary eutectic structure] in the hot-dip plated layer. When Si is contained in the hot-dip plated layer in addition to Zn, Al, and Mg, mainly five types of phases and microstructures including a [Mg₂Si phase] are contained in addition to the above four types of phases and microstructures. As described above, since various phases and microstructures are present in a mixed state in the hot-dip plated layer of the Zn-Al-Mg-based hot-dip plated steel sheet, the surface of the hot-dip plated layer has a satin-like external appearance.

Citation List

Patent Documents

[0005]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. H10-226865

Patent Document 2: Japanese Unexamined Patent Application, First Publication No. H10-306357

Patent Document 3: Japanese Unexamined Patent Application, First Publication No. 2004-68075

Summary of Invention

Technical Problem

[0006] Like a hot-dip galvanized steel sheet, a Zn-Al-Mg-based hot-dip plated steel sheet is widely used in various manufacturing industries such as the fields of automobiles, home appliances, and building materials. In recent years, there has been an increasing demand from consumers for the surface external appearance of a plated steel sheet, and a Zn-Al-Mg-based hot-dip plated steel sheet is required to have an external appearance that is not completely white but is closer to white. In the case of an external appearance close to white, there is an advantage that a defect on the surface of the plated layer is less noticeable.

[0007] The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a Zn-Al-Mg-based hot-dip plated steel sheet in which an external appearance of a surface of a hot-dip plated layer is closer to white than in the related art, a surface defect is less noticeable, and corrosion resistance is also excellent.

Solution to Problem

[0008] In order to solve the above problem, the present invention adopts the following configurations.

[1] A Zn-Al-Mg-based hot-dip plated steel sheet, including a steel sheet and a hot-dip plated layer formed on a surface of the steel sheet, wherein

the hot-dip plated layer contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with a remainder including Zn and impurities, and

in a case where a 5 mm square cross section parallel to a surface of the hot-dip plated layer is exposed at any

position of a $3t/4$ position, a $t/2$ position, and a $t/4$ position from the surface with a thickness of the hot-dip plated layer represented by t , a ratio (B/A (%)) of an area fraction B of a [Zn phase] to a total area fraction A of a [Zn phase] and an [Al/MgZn₂/Zn ternary eutectic structure] of a plating microstructure in at least one of the cross sections is 20% or more.

[2] A Zn-Al-Mg-based hot-dip plated steel sheet, including a steel sheet and a hot-dip plated layer formed on a surface of the steel sheet, wherein

the hot-dip plated layer contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with a remainder including Zn and impurities, and further contains one or two selected from the group consisting of group A and group B below, and in a case where a 5 mm square cross section parallel to a surface of the hot-dip plated layer is exposed at any position of a $3t/4$ position, a $t/2$ position, and a $t/4$ position from the surface with a thickness of the hot-dip plated layer represented by t , a ratio (B/A (%)) of an area fraction B of a [Zn phase] to a total area fraction A of a [Zn phase] and an [Al/MgZn₂/Zn ternary eutectic structure] of a plating microstructure in at least one of the cross sections is 20% or more.

[Group A] Si: 0.0001 to 2 mass%

[Group B] one or two or more of the group consisting of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C: 0.0001 to 2 mass% in total

[3] The Zn-Al-Mg-based hot-dip plated steel sheet according to [1] or [2], wherein the area fraction of the [Zn phase] of the plating microstructure in at least one of the cross sections is 10% or more.

[4] The Zn-Al-Mg-based hot-dip plated steel sheet according to [1] or [2], wherein an average grain size of the [Zn phase] of the plating microstructure in at least one of the cross sections is 2.5 to 10 μm .

[5] The Zn-Al-Mg-based hot-dip plated steel sheet according to [3], wherein an average grain size of the [Zn phase] of the plating microstructure in at least one of the cross sections is 2.5 to 10 μm .

[6] The Zn-Al-Mg-based hot-dip plated steel sheet according to [2], wherein the hot-dip plated layer has an average composition containing the group A in terms of mass%.

[7] The Zn-Al-Mg-based hot-dip plated steel sheet according to [2], wherein the hot-dip plated layer has an average composition containing the group B in terms of mass%.

Advantageous Effects of Invention

[0009] According to the present invention, it is possible to provide a Zn-Al-Mg-based hot-dip plated steel sheet in which an external appearance of a surface of a hot-dip plated layer is closer to white than in the related art, a surface defect is less noticeable, and corrosion resistance is also excellent.

Brief Description of Drawings

[0010]

[FIG. 1] FIG. 1 is a schematic cross-sectional view for explaining an exposed surface for measuring a plating microstructure of a hot-dip plated layer in a Zn-Al-Mg-based hot-dip plated steel sheet according to an embodiment of the present invention.

[FIG. 2] FIG. 2 is a perspective view for explaining an exposed surface for measuring a plating microstructure of a hot-dip plated layer in a Zn-Al-Mg-based hot-dip plated steel sheet according to an embodiment of the present invention.

Description of Embodiments

[0011] The present inventors investigated in detail a plated layer of a conventional Zn-Al-Mg-based hot-dip plated steel sheet having a satin-like external appearance. The satin-like external appearance appears due to coexistence of a fine glossy portion exhibiting metallic gloss and a fine white portion exhibiting white in a mixed state. Among them, when the microstructure of the hot-dip plated layer in the white portion was examined, it was found that the ratio of the [Zn phase] to the total of the [Zn phase] and the [Al/MgZn₂/Zn ternary eutectic structure] is higher than that in the glossy portion. In addition, it was found that the proportion of the [Zn phase] in the hot-dip plated layer is also relatively high.

[0012] Therefore, the present inventors intensively studied in order to obtain a white external appearance as a whole by increasing the white portion and decreasing the glossy portion in the hot-dip plated layer, and found that the surface external appearance of the hot-dip plated layer exhibits white as a whole by adjusting the chemical composition of the hot-

dip plated layer and increasing the proportion of the [Zn phase]. In particular, the present inventors found that it is effective to increase the ratio of the [Zn phase] to the total of the [Al/MgZn₂/Zn ternary eutectic structure] and the [Zn phase] in the entire hot-dip plated layer.

[0013] Hereinafter, a Zn-Al-Mg-based hot-dip plated steel sheet according to an embodiment of the present invention will be described.

[0014] The Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment includes a steel sheet and a hot-dip plated layer formed on a surface of the steel sheet, and the hot-dip plated layer contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with a remainder including Zn and impurities, and in a case where a 5 mm square cross section parallel to a surface of the hot-dip plated layer is exposed at any position of a 3t/4 position, a t/2 position, and a t/4 position from the surface of the hot-dip plated layer with a thickness of the hot-dip plated layer represented by t, a ratio (B/A (%)) of an area fraction B of a [Zn phase] to a total area fraction A of a [Zn phase] and an [Al/MgZn₂/Zn ternary eutectic structure] of a plating microstructure in at least one of the cross sections is 20% or more. Here, the "5 mm square cross section parallel to a surface of the hot-dip plated layer" refers to a square-shaped exposed surface that is parallel to the surface of the hot-dip plated layer and has a 5 mm square size in plane view.

[0015] The material of the steel material as a base of the hot-dip plated layer is not particularly limited. As the material, it can be applied to general steel, Al-killed steel, and some high-alloy steels, and the shape is not particularly limited. The steel material may be subjected to Ni pre-plating. The hot-dip plated layer according to the present embodiment is formed by applying a hot-dip plating method described later to a steel material.

[0016] Next, the chemical composition of the hot-dip plated layer will be described.

[0017] The hot-dip plated layer according to the present embodiment contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with the remainder including Zn and impurities.

[0018] Further, the hot-dip plated layer may contain one or two selected from the group consisting of group A and group B below.

[Group A] Si: 0.0001 to 2 mass%

[Group B] one or two or more of the group consisting of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C: 0.0001 to 2 mass% in total

[0019] The amount of Al is in the range of 5 to 22 mass% as an average composition. Al is an element necessary for ensuring corrosion resistance. When the amount of Al in the hot-dip plated layer is less than 5 mass%, the effect of improving corrosion resistance is insufficient. When the amount of Al in the hot-dip plated layer exceeds 22 mass%, corrosion resistance may be deteriorated although the cause is unknown. From the viewpoint of corrosion resistance, the lower limit of the Al content in the hot-dip plated layer is preferably 6 mass% or more, and more preferably 11 mass% or more. The upper limit of the Al content in the hot-dip plated layer is preferably 20 mass% or less, and more preferably 19 mass% or less.

[0020] The amount of Mg is in the range of 1.0 to 10 mass% as an average composition. Mg is an element necessary for improving the corrosion resistance of the hot-dip plated layer. When the amount of Mg in the hot-dip plated layer is less than 1.0 mass%, the effect of improving the corrosion resistance is insufficient, and when the amount of Mg in the hot-dip plated layer exceeds 10 mass%, the occurrence of dross in a plating bath becomes significant, and it becomes difficult to stably manufacture a plated steel material. From the viewpoint of the balance between the corrosion resistance and the occurrence of dross, the lower limit of the Mg content in the hot-dip plated layer is preferably 1.5 mass% or more, and more preferably 2 mass% or more. The upper limit of the Mg content in the hot-dip plated layer is preferably in the range of 8 mass% or less, and more preferably 6 mass% or less.

[0021] The hot-dip plated layer may contain Si in the range of 0.0001 to 2 mass%. Si is an element effective for improving the adhesion of the hot-dip plated layer. When Si is incorporated in an amount of 0.0001 mass% or more, an effect of improving adhesion is exhibited, and therefore Si is preferably incorporated in an amount of 0.0001 mass% or more. On the other hand, when the amount of Si in the hot-dip plated layer exceeds 2 mass%, the effect of improving plating adhesion is saturated, so that the amount of Si is set to 2 mass% or less. From the viewpoint of plating adhesion, the lower limit of the Si content in the hot-dip plated layer is more preferably 0.01 mass% or more, still more preferably 0.03% or more. The upper limit of the Si content in the hot-dip plated layer is more preferably 1 mass% or less, and still more preferably 0.8 mass% or less.

[0022] In addition, the hot-dip plated layer may contain, as an average composition, any one or two or more of the group consisting of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C in a total amount of 0.0001 to 2 mass%. The total amount is preferably 0.001 mass% or more, or 0.01 mass% or more. In addition, the total amount is up to 2 mass%. By the incorporation of any one or two or more of the group consisting of these elements, corrosion resistance can be further improved. "REM" is one or two or more of the group consisting of rare earth elements having atomic numbers 57 to 71 in the periodic table.

[0023] The remainder of the chemical composition of the hot-dip plated layer includes zinc and impurities.

[0024] The composition of the hot-dip plated layer can be measured by the following method. First, the surface layer coating film is removed with a coating film remover (for example, NEOREVER SP-751 manufactured by SANSAIKAKO) that does not erode plating, then the hot-dip plated layer is dissolved with hydrochloric acid containing an inhibitor (for example, HIBIRON manufactured by Sugimura Chemical Industry Co., Ltd.), and the obtained solution is subjected to inductively coupled plasma (ICP) optical emission spectroscopy, whereby the composition can be determined.

[0025] Next, the microstructure of the hot-dip plated layer will be described. The microstructure of the hot-dip plated layer of the present embodiment may have, for example, the following microstructure.

[0026] The hot-dip plated layer containing Al, Mg, and Zn contains an [Al phase], a [MgZn₂ phase], and a [Zn phase], and an [Al/Zn/MgZn₂ ternary eutectic structure]. Specifically, it has a form in which an [Al phase], a [MgZn₂ phase], and a [Zn phase] are contained in the matrix of an [Al/Zn/MgZn₂ ternary eutectic structure]. When Si is incorporated, a [Mg₂Si phase] may be contained in the matrix of an [Al/Zn/MgZn₂ ternary eutectic structure].

[Al/Zn/MgZn₂ ternary eutectic structure]

[0027] The [Al/Zn/MgZn₂ ternary eutectic structure] is a ternary eutectic structure of an Al phase, a Zn phase, and an intermetallic compound MgZn₂ phase, and the Al phase forming the ternary eutectic structure corresponds to, for example, an "Al" phase" (which is an Al solid solution in which Zn is solid-dissolved and contains a small amount of Mg) at a high temperature in an Al-Zn-Mg ternary equilibrium phase diagram.

[0028] The Al" phase at a high temperature usually appears separated into a fine Al phase and a fine Zn phase at normal temperature. The Zn phase in the ternary eutectic structure is a Zn solid solution in which a small amount of Al is solid-dissolved, and in some cases, further a small amount of Mg is solid-dissolved. The MgZn₂ phase in the ternary eutectic structure is an intermetallic compound phase present in the vicinity of Zn: about 84 mass% in a Zn-Mg binary equilibrium phase diagram.

[0029] As seen in the phase diagram, it is considered that another additive element is not solid-dissolved in each phase, or even if an additive element is solid-dissolved, the amount of the additive element is extremely small. However, since the amount thereof cannot be clearly distinguished by an ordinary analysis, the ternary eutectic structure formed of these three phases is represented by an [Al/Zn/MgZn₂ ternary eutectic structure] in the present specification.

[Al phase]

[0030] The [Al phase] is a phase that looks like an island with a clear boundary in the matrix of the [Al/Zn/MgZn₂ ternary eutectic structure], and this corresponds to, for example, an "Al" phase" (which is an Al solid solution in which Zn is solid-dissolved and contains a small amount of Mg) at a high temperature in an Al-Zn-Mg ternary equilibrium phase diagram. In the Al" phase at a high temperature, the amount of Zn and the amount of Mg to be solid-dissolved differ depending on the Al and Mg concentrations in the plating bath. The Al" phase at a high temperature is usually separated into a fine Al phase and a fine Zn phase at normal temperature, but the islandlike shape observed at normal temperature is considered to be attributed to the shape of the Al" phase at a high temperature.

[0031] As seen in the phase diagram, it is considered that another additive element is not solid-dissolved in this phase, or even if an additive element is solid-dissolved, the amount of the additive element is extremely small. However, since it cannot be clearly distinguished by an ordinary analysis, a phase, which is derived from the Al" phase at a high temperature and whose shape is attributed to the shape of the Al" phase is referred to as [Al phase] in the present specification.

[0032] The [Al phase] can be clearly distinguished from the Al phase forming the [Al/Zn/MgZn₂ ternary eutectic structure] by microscopic observation.

[Zn phase]

[0033] The [Zn phase] is a phase that looks like an island with a clear boundary in the matrix of the [Al/Zn/MgZn₂ ternary eutectic structure], and in practice, a small amount of Al or a small amount of Mg may be solid-dissolved. As seen in the phase diagram, it is considered that another additive element is not solid-dissolved in this phase, or even if an additive element is solid-dissolved, the amount of the additive element is extremely small.

[0034] The [Zn phase] is a region having a circle equivalent diameter of 2.5 μm or more, and can be clearly distinguished from the Zn phase forming the [Al/Zn/MgZn₂ ternary eutectic structure] by microscopic observation. The circle equivalent diameter of the [Zn phase] may be 10 μm or less.

[MgZn₂ phase]

[0035] The [MgZn₂ phase] is a phase that looks like an island with a clear boundary in the matrix of the [Al/Zn/MgZn₂ ternary eutectic structure], and in practice, a small amount of Al may be solid-dissolved. As seen in the phase diagram, it is

considered that another additive element is not solid-dissolved in this phase, or even if an additive element is solid-dissolved, the amount of the additive element is extremely small.

[0036] The $[\text{MgZn}_2 \text{ phase}]$ and the MgZn_2 phase forming the $[\text{Al}/\text{Zn}/\text{MgZn}_2 \text{ ternary eutectic structure}]$ can be clearly distinguished from each other by microscopic observation. The hot-dip plated layer according to the present embodiment may not contain $[\text{MgZn}_2 \text{ phase}]$ depending on the manufacturing conditions, but it is contained in the hot-dip plated layer under most manufacturing conditions.

$[\text{Mg}_2\text{Si phase}]$

[0037] The $[\text{Mg}_2\text{Si phase}]$ is a phase that looks like an island with a clear boundary in a solidified microstructure of the hot-dip plated layer to which Si is added. As seen in the phase diagram, it is considered that Zn, Al, or another additive element is not solid-dissolved in the $[\text{Mg}_2\text{Si phase}]$, or even if it is solid-dissolved, the amount of thereof is extremely small. The $[\text{Mg}_2\text{Si phase}]$ can be clearly distinguished from other phases in the hot-dip plated layer by microscopic observation.

[0038] Next, the amount of the $[\text{Zn phase}]$ will be described. In the present embodiment, as shown in FIGS. 1 and 2, in a case where a hot-dip plated layer 2 is cut out at any position of a $3t/4$ position, a $t/2$ position, and a $t/4$ position from the surface 2a of the hot-dip plated layer 2 with the thickness of the hot-dip plated layer 2 formed on a steel sheet 1 represented by t , so that exposed surfaces 3, 4, and 5 that are parallel to the surface 2a and have a square shape with a 5 mm square size in plane view appear, a ratio $(B/A (\%))$ of an area fraction B of the $[\text{Zn phase}]$ to the total area fraction A of the $[\text{Zn phase}]$ and the $[\text{Al}/\text{MgZn}_2/\text{Zn ternary eutectic structure}]$ of the plating microstructure in at least one of the exposed surfaces 3 to 5 is 20% or more. The ratio $(B/A (\%))$ may be 25% or more, or 30% or more. When the ratio of the $[\text{Zn phase}]$ to the total of the $[\text{Zn phase}]$ and the $[\text{Al}/\text{MgZn}_2/\text{Zn ternary eutectic structure}]$ is 20% or more, the occupancy ratio of a fine white portion exhibiting white increases on the surface of the hot-dip plated layer, so that the entire external appearance of the hot-dip plated layer exhibits white. The upper limit of the ratio $(B/A (\%))$ does not need to be particularly limited, but may be 70% or less, 60% or less, or 55% or less. The schematic cross-sectional view shown in FIG. 1 is a cross-sectional view taken along plane A-A' of FIG. 2.

[0039] In at least one of the exposed surfaces 3 to 5, the area fraction of the $[\text{Zn phase}]$ of the plating microstructure is preferably 20% or more. The area fraction of the $[\text{Zn phase}]$ may be 25% or more or 30% or more. When the area fraction of the $[\text{Zn phase}]$ is 20% or more, the occupancy ratio of a fine white portion exhibiting white increases on the surface of the hot-dip plated layer, so that the entire external appearance of the hot-dip plated layer is closer to white. The upper limit of the area fraction of the $[\text{Zn phase}]$ does not need to be particularly limited, but may be 60% or less, 50% or less, or 40% or less.

[0040] In at least one of the exposed surfaces 3 to 5, the average grain size of the $[\text{Zn phase}]$ of the plating microstructure is preferably 2.5 to 10 μm . When the average grain size of the $[\text{Zn phase}]$ is 2.5 to 10 μm , the surface external appearance can be made closer to white.

[0041] In addition, the area fraction of the $[\text{Al phase}]$ in the exposed surface for which the area fraction of the $[\text{Zn phase}]$ has been measured may be, for example, 10 to 80 area% or 20 to 65 area%.

[0042] Further, the area fraction of the $[\text{Al}/\text{MgZn}_2/\text{Zn ternary eutectic structure}]$ in the exposed surface for which the area fraction of the $[\text{Zn phase}]$ has been measured may be, for example, 10 to 80 area% or 20 to 65 area%.

[0043] Still further, the area fraction of the $[\text{MgZn}_2 \text{ phase}]$ in the exposed surface for which the area fraction of the $[\text{Zn phase}]$ has been measured may be, for example, 0 to 60 area% or 10 to 40 area%.

[0044] Still further, the area fraction of the $[\text{Mg}_2\text{Si phase}]$ in the exposed surface for which the area fraction of the $[\text{Zn phase}]$ has been measured may be, for example, 0 to 5 area% or 0 to 1 area%.

[0045] When the exposed surfaces 3, 4, and 5 of 5 mm square parallel to the surface are exposed at any position of the $3t/4$ position, the $t/2$ position, and the $t/4$ position from the surface 2a of the hot-dip plated layer 2, the hot-dip plated layer is scraped off by a method such as grinding or argon sputtering. In addition, the exposed surface is desirably a mirror surface, and for example, the maximum height R_z of the exposed surface is desirably 0.2 μm or less. The exposed surface to be observed may be an exposed surface at any depth of the $3t/4$ position, the $t/2$ position, and the $t/4$ position from the surface of the hot-dip plated layer. It is preferable to select the exposed surface at the $t/2$ position. If the B/A ratio or the area fraction of the $[\text{Zn phase}]$ satisfies the range of the present invention in the exposed surface at the $t/2$ position, there is a high possibility that the B/A ratio or the area fraction of the $[\text{Zn phase}]$ satisfies the range of the present invention also at the other positions. More preferably, the B/A ratio of the $[\text{Zn phase}]$ or the area fraction of the $[\text{Zn phase}]$ may satisfy the range of the present invention in the exposed surfaces at any two depths of the $3t/4$ position, the $t/2$ position, and the $t/4$ position from the surface of the hot-dip plated layer. More preferably, the B/A ratio of the $[\text{Zn phase}]$ or the area fraction of the $[\text{Zn phase}]$ may satisfy the range of the present invention in the exposed surfaces at all depths of the $3t/4$ position, the $t/2$ position, and the $t/4$ position from the surface of the hot-dip plated layer.

[0046] The plating microstructure is observed in a secondary electron image of a scanning electron microscope (SEM) on an exposed surface having a size of 5 mm $\times$ 5 mm to identify the $[\text{Zn phase}]$ and the $[\text{Al}/\text{MgZn}_2/\text{Zn ternary eutectic structure}]$. When each phase and a microstructure are identified, an elemental analysis by an energy dispersive X-ray

elemental analyzer attached to the SEM is used in combination, and each phase and a microstructure are identified while the distributions of Zn, Al, and Mg are checked. That is, among Zn, Al, and Mg, a region where Zn is mainly detected is defined as a Zn phase, a region where Al is mainly detected is defined as an Al phase, and a region where Zn and Mg are mainly detected is defined as a MgZn_2 phase. From the distribution of each phase detected, the phases are classified into [Al phase], [MgZn_2 phase], and [Zn phase], and [Al/Zn/ MgZn_2 ternary eutectic structure] according to the above-described method. Then, the area fraction of the [Zn phase] in the exposed surface is determined, and the ratio (B/A (%)) of the area fraction B of the [Zn phase] to the total area fraction A of the [Zn phase] and the [Al/ MgZn_2 /Zn ternary eutectic structure] is further determined.

[0047] In addition, the average grain size of the [Zn phase] of the plating microstructure is measured in the exposed surfaces 3 to 5. The average grain size is an average equivalent circle diameter. The number of [Zn phases] in each of the exposed surfaces 3 to 5 is counted, and the total area of the [Zn phases] in each of the exposed surfaces 3 to 5 is determined. Subsequently, the total area of the [Zn phases] is divided by the number to determine the area per [Zn phase], and the average equivalent circle diameter is determined from this area.

[0048] Next, a method for manufacturing the Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment will be described.

[0049] When the Zn-Al-Mg-based hot-dip plated steel sheet of the present embodiment is manufactured, it is necessary to control the microstructure of the hot-dip plated layer so that the area fraction of the [Zn phase] in the exposed surface parallel to the surface of the hot-dip plated layer at any position of the 3t/4 position, the t/2 position, and the t/4 position from the surface is small.

[0050] In order to manufacture the Zn-Al-Mg-based hot-dip plated steel sheet by a hot-dip plating method, the steel sheet is immersed in a hot-dip plating bath in which chemical composition is adjusted, thereby adhering a molten metal to the sheet surface. Subsequently, the steel sheet is pulled up from the plating bath, and the molten metal is solidified after the adhesion amount is controlled by gas wiping. During solidification, depending on the composition, an [Al phase] is first formed, and then an [Al/Zn/ MgZn_2 ternary eutectic structure] is formed as the temperature of the molten metal decreases. In addition, a [MgZn_2 phase] and a [Zn phase] are formed in the matrix of the [Al/Zn/ MgZn_2 ternary eutectic structure]. Further, when Si is contained in the hot-dip plated layer, a [Mg_2Si phase] is formed in the matrix of the [Al/Zn/ MgZn_2 ternary eutectic structure].

[0051] It has been found that when a coarse [Zn phase] is formed, the proportion of the [Al phase] or the [MgZn_2 phase] in the hot-dip plated layer relatively increases, and these phases are exposed on the plated surface, so that the external appearance of the surface of the hot-dip plated layer is close to white. It is presumed that the formation of the [Zn phase] is affected by the number of nucleation points for Zn. That is, the present inventors have found that when the number of nucleation points for Zn is small, Zn in the liquid phase immediately before final solidification does not crystallize as a fine Zn phase in the [Al/Zn/ MgZn_2 ternary eutectic structure] but crystallizes as a coarse [Zn phase]. As a method for reducing the number of nucleation points for Zn, it is conceivable to increase the surface cleanliness of the steel sheet, which is an original sheet, and to reduce substances that can become nucleation points for Zn as much as possible.

[0052] Hereinafter, the manufacturing method will be described in detail.

[0053] A hot-rolled steel sheet is manufactured, and hot-band annealing is performed as necessary. After pickling, cold rolling is performed as necessary to obtain a cold-rolled sheet. The hot-rolled sheet or the cold-rolled sheet is degreased and washed with water, then annealed, and the hot-rolled sheet or the cold-rolled sheet after annealing is immersed in a hot-dip plating bath to form a hot-dip plated layer.

[0054] Here, before annealing, in order to increase the surface cleanliness, the steel sheet is subjected to alkaline electrolytic cleaning, washed with pure water, and then dried in an inert atmosphere to remove moisture from the sheet surface, and the process proceeds to an annealing step.

[0055] As the cleaning liquid used for the alkaline electrolytic cleaning, for example, an alkaline cleaning liquid containing sodium hydroxide or potassium hydroxide is preferable. As a procedure of the alkaline electrolytic cleaning, the steel sheet is immersed in the cleaning liquid for immersion cleaning, and then the steel sheet is electrolytically cleaned in the cleaning liquid. The electrolytic cleaning is preferably alternating electrolytic cleaning. Subsequently, pure water is sprayed onto the sheet surface to wash away the cleaning liquid adhered thereto. In the spray water washing, a plurality of spray nozzles may be arranged along the traveling direction of the steel sheet, and pure water may be sprayed from each nozzle. The pure water is preferably water having an electric resistivity of $1 \text{ M}\Omega \cdot \text{cm}$ or more.

[0056] The annealing after the alkaline electrolytic cleaning may be performed within 10 seconds from the end of the alkaline electrolytic cleaning. The end of the alkaline electrolytic cleaning is preferably at the time of extraction by spray washing with pure water at the end of the alkaline electrolytic cleaning. The annealing conditions are not particularly limited.

[0057] Further, it is preferable to remove moisture adhered to the sheet surface as much as possible by performing drying in an inert atmosphere after extraction by spray water washing and until annealing from the viewpoint of being able to prevent adhesion of fine floating particles in the air. Drying can be performed by blowing off moisture by spraying an inert gas and subsequent evaporation.

[0058] By removing organic contaminants adhered to the sheet surface by alkaline electrolytic cleaning and further performing annealing within 10 seconds after the end of final spray washing with pure water, it is possible to prevent adhesion of fine floating particles in the air onto the cold-rolled sheet. If the annealing start time exceeds 10 seconds after the final spray water washing, the surface cleanliness of the steel sheet may decrease.

[0059] Subsequently, the steel sheet is immersed in a hot-dip plating bath. The hot-dip plating bath preferably contains Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with the remainder including Zn and impurities. The hot-dip plating bath may contain Si: 0.0001 to 2 mass%. In addition, the hot-dip plating bath may contain any one or two or more of the group consisting of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C in a total amount of 0.0001 to 2 mass%.

[0060] The temperature of the hot-dip plating bath is preferably in the range of 400 to 500°C. When the temperature of the hot-dip plating bath is in this range, a desired hot-dip plated layer can be formed.

[0061] The adhesion amount of the hot-dip plated layer may be adjusted by a method such as gas wiping for the steel sheet pulled up from the hot-dip plating bath. The adhesion amount of the hot-dip plated layer is preferably adjusted so that the total adhesion amount on both surfaces of the steel sheet falls within the range of 30 to 600 g/m². It is not preferable that the adhesion amount is less than 30 g/m² because the corrosion resistance of the Zn-Al-Mg-based hot-dip plated steel sheet is deteriorated. It is not preferable that the adhesion amount exceeds 600 g/m² because a molten metal adhered to the steel sheet drips, and the surface of the hot-dip plated layer cannot be made smooth.

[0062] After the adhesion amount of the hot-dip plated layer is adjusted, the steel sheet is cooled. Cooling of the molten metal adhered to the steel sheet is started after the steel sheet is pulled up from the hot-dip plating bath. Depending on the composition of the hot-dip plating bath, for example, the [Al phase] starts to crystallize around 430°C. Subsequently, [MgZn₂] starts to crystallize at around 370°C, and an [Al/Zn/MgZn₂ ternary eutectic structure] starts to crystallize at around 340°C, and further a [Zn phase] starts to crystallize, and solidification is completed.

[0063] At this time, since the nucleation points for Zn are reduced on the surface of the steel sheet, Zn or MgZn₂ as a eutectic structure is less likely to crystallize, [Al/Zn/MgZn₂ ternary eutectic structures] are reduced, and meanwhile, Zn in the liquid phase is increased, and many [Zn phases] are formed.

[0064] When a chemical conversion treatment layer is formed on the surface of the hot-dip plated layer, the hot-dip plated steel sheet after the hot-dip plated layer is formed is subjected to a chemical conversion treatment. The type of the chemical conversion treatment is not particularly limited, and a known chemical conversion treatment can be used.

[0065] When a coating film layer is formed on the surface of the hot-dip plated layer or the surface of the chemical conversion treatment layer, the hot-dip plated steel sheet after the hot-dip plated layer is formed or after the chemical conversion treatment layer is formed is subjected to a coating treatment. The type of the coating treatment is not particularly limited, and a known coating treatment can be used.

[0066] As described above, according to the present embodiment, the metallic glossiness of the surface of the hot-dip plated layer can be enhanced as compared with the related art.

Examples

[0067] Next, Examples of the present invention will be described. After alkaline electrolytic cleaning was performed for the steel sheet after cold rolling, cold-rolled annealing was performed after elapse of the time shown in Tables 1A and 1B.

[0068] As the cleaning liquid used for the alkaline electrolytic cleaning, an alkaline cleaning liquid containing sodium hydroxide was used. As a procedure of the alkaline electrolytic cleaning, the steel sheet was immersed in the cleaning liquid for immersion cleaning, and then the steel sheet was electrolytically cleaned in the cleaning liquid. As the electrolytic cleaning, alternating electrolytic cleaning was adopted. Subsequently, the cleaning liquid adhered was washed away by spray washing with pure water. As the pure water, water having an electric resistivity of 1 MΩ·cm or more was used. Thereafter, cold-rolled annealing was performed after elapse of the time shown in Tables 1A and 1B from the final spray water washing while drying in an inert atmosphere. As the annealing conditions, the soaking temperature was 800°C and the soaking time was 1 minute.

[0069] Subsequently, the steel sheet after the cold-rolled annealing was immersed in a hot-dip plating bath and then pulled up. Thereafter, the adhesion amount was adjusted by gas wiping, and further cooling was performed. In No. 66, spray washing with ultrapure water and drying were performed without performing alkaline electrolytic cleaning, and in No. 67, annealing was started 15 seconds after spray water washing. In this way, hot-dip plated steel sheets of Nos. 1 to 67 shown in Tables 1A to 2B were manufactured.

[0070] As shown in FIGS. 1 and 2, 5 mm square exposed surfaces parallel to the surface of the hot-dip plated layer were formed at the t/4 position, the t/2 position, and the 3t/4 position from the surface in the obtained hot-dip plated steel sheet. The exposed surfaces were formed by scraping the hot-dip plated layer by grinding and then performing mirror polishing.

[0071] The plating microstructure was observed in a secondary electron image of a scanning electron microscope (SEM) on the exposed surface having a size of 5 mm × 5 mm to identify the [Zn phase] and the [Al/MgZn₂/Zn ternary eutectic structure]. When each phase and a microstructure were identified, an elemental analysis by an energy dispersive

EP 4 538 409 A1

X-ray elemental analyzer attached to the SEM was used in combination, and each phase and a microstructure were identified while the distributions of Zn, Al, and Mg were checked. Then, the area fraction of the [Zn phase] in each exposed surface was determined, and the ratio (B/A (%)) of the area fraction B of the [Zn phase] to the total area fraction A of the [Zn phase] and the [Al/MgZn₂/Zn ternary eutectic structure] was further determined. As for the [Zn phase], a region having a circle equivalent diameter of 2.5 μm or more was measured as the [Zn phase]. Thus, the Zn phase in the [Al/MgZn₂/Zn ternary eutectic structure] and the [Zn phase] were distinguished.

[0072] The results are shown in Tables 2A and 2B.

[0073] In addition, the area fraction of the [Al phase] was in the range of 30 to 80 area% in the exposed surface for which the area fraction of the [Zn phase] was measured in Nos. 1 to 61. In the same exposed surface, the area fraction of the [Al/MgZn₂/Zn ternary eutectic structure] was in the range of 10 to 75 area%. In the same exposed surface, the area fraction of the [MgZn₂ phase] was in the range of 0 to 60 area%. In the same exposed surface, the area fraction of the [Mg₂Si phase] was in the range of 0 to 5 area%.

[0074] In addition, the surface of the hot-dip plated layer of the obtained hot-dip plated steel sheet was observed and visually evaluated based on the following determination criteria. A and B were evaluated as acceptable. The results are shown in Tables 2A and 2B.

[0075]

A: No handling defect is observed even from 0.5 m ahead.

B: A handling defect is observed from 0.5 m ahead, but no handling defect is observed from 2 m ahead.

C: A handling defect is observed also from 2 m ahead.

[0076] The corrosion resistance of the hot-dip plated steel sheet was evaluated by the corrosion loss after a CCT test. The plated steel sheet was cut into 150 × 70 mm, and the corrosion loss after 30 cycles of CCT was investigated using CCT in accordance with JASO-M609. In the evaluation, a corrosion loss of less than 30 g/m² was evaluated as F, a corrosion loss of 30 g/m² or more and less than 50 g/m² was evaluated as G, a corrosion loss of 50 g/m² or more was evaluated as P, and F and G were evaluated as acceptable.

[Table 1A]

No.	Manufacturing method		Hot-dip plated layer				
	Alkaline electrolytic cleaning	Time required from end of cleaning to start of annealing (sec)	Average composition (mass%) remainder: Zn and impurities				Plating adhesion amount (total amount on both surfaces) (g/m ²)
			Al	Mg	Si	Others	
1	○	3	5	3.0	-	-	40
2	○	5	6	3.0	0.2	-	280
3	○	3	11	3.0	0.2	-	300
4	○	4	19	6.0	0.2	-	280
5	○	10	22	6.0	0.2	-	30
6	○	2	11	1.0	0.2	-	280
7	○	4	11	1.5	0.2	-	310
8	○	3	11	2.0	0.2	-	280
9	○	2	11	6.0	0.2	-	320
10	○	1	11	8.0	0.2	-	290
11	○	6	11	10	0.2	-	290
12	○	6	11	3.0	0.0001	-	320
13	○	8	11	3.0	0.01	-	280
14	○	8	11	3.0	0.03	-	300
15	○	3	11	3.0	0.08	-	280
16	○	4	11	3.0	1	-	320

EP 4 538 409 A1

(continued)

5	No.	Manufacturing method		Hot-dip plated layer				
		Alkaline electrolytic cleaning	Time required from end of cleaning to start of annealing (sec)	Average composition (mass%) remainder: Zn and impurities				Plating adhesion amount (total amount on both surfaces) (g/m ²)
				Al	Mg	Si	Others	
10	17	○	7	11	3.0	2	-	600
	18	○	2	11	3.0	0.2	Ti 0.01%	300
	19	○	8	11	3.0	0.2	Ni 0.01%	310
15	20	○	7	11	3.0	0.2	Zr 0.01%	310
	21	○	4	11	3.0	0.2	Ni 0.01%	310
	22	○	8	11	3.0	0.2	Sr 0.01%	280
20	23	○	9	11	3.0	0.2	Fe 0.01%	320
	24	○	9	11	3.0	0.2	Sb 0.01%	280
	25	○	5	11	3.0	0.2	Pb 0.01%	300
25	26	○	6	11	3.0	0.2	Sn 0.01%	280
	27	○	6	11	3.0	0.2	Ca 0.01%	300
	28	○	4	11	3.0	0.2	Co 0.01%	300
30	29	○	8	11	3.0	0.2	Mn 0.01%	290
	30	○	3	11	3.0	0.2	P 0.01%	310
	31	○	8	11	3.0	0.2	B 0.01%	300
35	32	○	5	11	3.0	0.2	Bi 0.01%	320
	33	○	6	11	3.0	0.2	Cr 0.01%	320

[Table 1B]

35	No.	Manufacturing method		Hot-dip plated layer				
40		Alkaline electrolytic cleaning	Time required from end of cleaning to start of annealing (sec)	Average composition (mass%) remainder: Zn and impurities				Plating adhesion amount (total amount on both surfaces) (g/m ²)
				Al	Mg	Si	Others	
45	34	○	8	11	3.0	0.2	Sc 0.01%	290
	35	○	6	11	3.0	0.2	Y 0.01%	310
	36	○	3	11	3.0	0.2	REM 0.01%	280
	37	○	6	11	3.0	0.2	Hf 0.01%	280
50	38	○	1	11	3.0	0.2	C 0.01%	320
	39	○	4	11	3.0	0.2	-	280
	40	○	8	11	3.0	-	Ti 0.01%	290
55	41	○	9	11	3.0	-	Ni 0.01%	310
	42	○	4	11	3.0	-	Zr 0.01%	280
	43	○	8	11	3.0	-	Ni 0.01%	310
	44	○	7	11	3.0	-	Sr 0.01%	280

EP 4 538 409 A1

(continued)

No.	Manufacturing method		Hot-dip plated layer				
	Alkaline electrolytic cleaning	Time required from end of cleaning to start of annealing (sec)	Average composition (mass%) remainder: Zn and impurities				Plating adhesion amount (total amount on both surfaces) (g/m ²)
			Al	Mg	Si	Others	
45	○	9	11	3.0	-	Fe 0.01%	320
46	○	6	11	3.0	-	Sb 0.01%	310
47	○	5	11	3.0	-	Pb 0.01%	310
48	○	9	11	3.0	-	Sn 0.01%	320
49	○	3	11	3.0	-	Ca 0.01%	320
50	○	7	11	3.0	-	Co 0.01%	300
51	○	5	11	3.0	-	Mn 0.01%	300
52	○	4	11	3.0	-	P 0.01%	310
53	○	9	11	3.0	-	B 0.01%	280
54	○	5	11	3.0	-	Bi 0.01%	280
55	○	3	11	3.0	-	Cr 0.01%	280
56	○	6	11	3.0	-	Sc 0.01%	280
57	○	5	11	3.0	-	Y 0.01%	320
58	○	6	11	3.0	-	REM 0.01%	320
59	○	5	11	3.0	-	Hf 0.01%	300
60	○	5	11	3.0	-	C 0.01%	310
61	○	6	11	3.0	-	Ti 0.01% + Ca0.01%	300
62	○	7	<u>4</u>	3.0	0.2	-	280
63	○	2	<u>23</u>	3.0	0.2	-	290
64	○	4	11	<u>0.5</u>	0.2	-	320
65	○	7	11	<u>11</u>	0.2	-	280
66	×	9	8	3.0	0.2	-	300
67	○	<u>15</u>	7	3.0	0.2	-	280
Underlined values indicate values outside the scope of the present invention or outside the range of preferred manufacturing conditions.							

[Table 2A]

No.	Hot-dip plated layer						Evaluation		Remarks
	t/4 position		t/2 position		3t/4 position		Visual evaluation	Corrosion resistance	
	[Zn phase] (area%)	B/A (%)	[Zn phase] (area%)	B/A (%)	[Zn phase] (area%)	B/A (%)			
1	30	40	35	40	30	40	A	G	
2	35	50	40	55	35	55	A	F	
3	25	50	30	55	25	50	A	F	
4	20	40	20	45	25	40	A	F	

(continued)

5	No.	Hot-dip plated layer						Evaluation		Remarks
		t/4 position		t/2 position		3t/4 position		Visual evaluation	Corrosion resistance	
		[Zn phase] (area%)	B/A (%)	[Zn phase] (area%)	B/A (%)	[Zn phase] (area%)	B/A (%)			
10	5	20	45	20	40	25	40	A	G	Inventive Example
	6	30	40	25	35	30	40	A	G	
	7	25	40	20	40	25	40	A	F	
15	8	20	45	25	45	25	40	A	F	
	9	20	40	20	35	20	35	A	F	
	10	20	30	25	35	20	30	A	F	
20	11	20	35	20	35	20	40	A	G	
	12	20	35	20	40	25	45	A	F	
	13	25	40	25	40	20	35	A	F	
25	14	20	35	25	40	20	40	A	F	
	15	20	30	20	30	20	35	A	F	
	16	20	45	30	50	25	45	A	F	
30	17	25	50	20	55	30	50	A	F	
	18	30	50	25	45	25	50	A	F	
	19	25	40	25	40	25	45	A	F	
35	20	20	30	25	35	20	30	A	F	
	21	25	40	20	35	20	35	A	F	
	22	25	45	30	50	20	45	A	F	
40	23	25	45	25	45	25	40	A	F	
	24	25	45	25	40	25	40	A	F	
	25	25	40	25	40	25	45	A	F	
45	26	20	35	20	35	20	30	A	F	
	27	20	40	20	40	20	35	A	F	
	28	20	35	20	35	20	35	A	F	
50	29	20	35	20	35	25	40	A	F	
	30	20	45	30	50	20	50	A	F	
	31	25	45	20	40	20	40	A	F	
	32	20	30	20	25	20	25	A	F	
	33	20	35	20	35	20	35	A	F	

EP 4 538 409 A1

[Table 2B]

5	No.	Hot-dip plated laver						Evaluation		Remarks
		t/4 position		t/2 position		3t/4 position		Visual evaluation	Corrosion resistance	
		[Zn phase] (area%)	B/A (%)	[Zn phase] (area%)	B/A (%)	[Zn phase] (area%)	B/A (%)			
10	34	25	40	20	40	20	35	A	F	Inventive Example
	35	20	35	20	35	25	40	A	F	
	36	25	45	20	40	25	40	A	F	
	37	20	30	20	30	20	35	A	F	
	38	20	40	25	45	25	45	A	F	
15	39	20	25	20	25	20	25	B	F	
	40	30	40	20	35	30	45	A	F	
	41	30	45	25	50	30	40	A	F	
20	42	25	40	25	40	30	30	A	F	
	43	20	45	20	40	30	35	A	F	
	44	30	45	25	45	20	40	A	F	
	45	25	35	20	40	25	40	A	F	
25	46	30	30	20	40	25	35	A	F	
	47	20	35	20	35	30	40	A	F	
	48	30	45	30	35	25	45	A	F	
	49	25	40	20	35	20	45	A	F	
30	50	30	35	20	35	20	40	A	F	
	51	20	45	20	45	20	45	A	F	
	52	25	40	25	30	20	40	A	F	
	53	25	30	30	35	25	30	A	F	
35	54	20	45	25	40	30	45	A	F	
	55	30	45	30	40	30	40	A	F	
	56	30	40	20	35	25	40	A	F	
	57	20	35	20	40	20	40	A	F	
40	58	30	35	30	30	25	40	A	F	
	59	20	40	30	45	25	50	A	F	
	60	30	30	20	30	30	40	A	F	
	61	25	35	30	35	25	40	A	F	
50	62	15	<u>15</u>	10	<u>10</u>	10	<u>10</u>	C	P	Comparative Example
	63	5	15	5	15	5	20	B	P	
	64	5	<u>10</u>	0	<u>5</u>	5	<u>10</u>	C	P	
	65	10	25	5	20	10	25	B	P	
66	0	5	0	0	0	5	C	F		
55	67	5	<u>10</u>	10	<u>15</u>	5	<u>10</u>	C	F	
Underlined values indicate values outside the scope of the present invention.										

[0077] In the hot-dip plated steel sheets of No. 1 to No. 61, the chemical composition of the hot-dip plated layer fell within the range of the present invention, and hot-dip plating was performed after alkaline electrolytic cleaning, spray washing with pure water, drying, and annealing. Therefore, the number of generation sites for Zn on the sheet surface decreased, and when a 5 mm square exposed surface was formed at the 3t/4 position, the t/2 position, or the t/4 position from the surface of the hot-dip plated layer, the ratio (B/A (%)) of the plating microstructure in at least one exposed surface was 20% or more. Therefore, the external appearance of the hot-dip plated layer was white, and defects were less noticeable. In addition, corrosion resistance was also good. In No. 1 to No. 61, the average grain size of the [Zn phase] was in the range of 2.5 to 10 μm in each of the exposed surfaces at the 3t/4 position, the t/2 position, and the t/4 position.

[0078] In the hot-dip plated steel sheet of No. 62, since the Al content of the hot-dip plated layer was small, the ratio (B/A (%)) was less than 20% in each of the exposed surfaces at the 3t/4 position, the t/2 position, and the t/4 position, and defects were easily noticeable. In addition, since the Al content of the hot-dip plated layer was small, corrosion resistance was deteriorated.

[0079] In the hot-dip plated steel sheet of No. 63, since the Al content of the hot-dip plated layer was excessive, the corrosion resistance was deteriorated.

[0080] In the hot-dip plated steel sheet of No. 64, since the Mg content of the hot-dip plated layer was small, the ratio (B/A (%)) was less than 20% in each of the exposed surfaces at the 3t/4 position, the t/2 position, and the t/4 position, and defects were easily noticeable. In addition, since the Mg content of the hot-dip plated layer was small, corrosion resistance was deteriorated.

[0081] In the hot-dip plated steel sheet of No. 65, since the Mg content of the hot-dip plated layer was excessive, the corrosion resistance was deteriorated.

[0082] In the hot-dip plated steel sheet of No. 66, since alkaline electrolytic cleaning was not performed, and only spray washing with pure water and drying were performed, the synergistic effect of alkaline electrolytic cleaning and spray water washing was not obtained, the nucleation sites for Zn increased, the ratio (B/A (%)) at the 3t/4 position, the t/2 position, or the t/4 position from the surface of the hot-dip plated layer was less than 20%, and defects were easily noticeable.

[0083] In the hot-dip plated steel sheet of No. 67, since annealing was started 15 seconds after spray water washing, the nucleation sites for Zn increased, the ratio (B/A (%)) at the 3t/4 position, the t/2 position, or the t/4 position from the surface of the hot-dip plated layer was less than 20%, and defects were easily noticeable.

Industrial Applicability

[0084] The Zn-Al-Mg-based hot-dip plated steel sheet of the present disclosure has high industrial applicability because the external appearance of the surface of the hot-dip plated layer is close to white, a surface defect is less noticeable, and the corrosion resistance is also excellent.

Reference Signs List

[0085]

- 1 Steel sheet
- 2 Hot-dip plated layer
- 2a Surface of hot-dip plated layer
- 3 Cross section (exposed surface) at t/4 position
- 4 Cross section (exposed surface) at t/2 position
- 5 Cross section (exposed surface) at 3t/4 position.

Claims

1. A Zn-Al-Mg-based hot-dip plated steel sheet, comprising a steel sheet and a hot-dip plated layer formed on a surface of the steel sheet, wherein

the hot-dip plated layer contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with a remainder including Zn and impurities, and

in a case where a 5 mm square cross section parallel to a surface of the hot-dip plated layer is exposed at any position of a 3t/4 position, a t/2 position, and a t/4 position from the surface with a thickness of the hot-dip plated layer represented by t, a ratio (B/A (%)) of an area fraction B of a [Zn phase] to a total area fraction A of a [Zn phase] and an [Al/MgZn₂/Zn ternary eutectic structure] of a plating microstructure in at least one of the cross sections is 20% or more.

2. A Zn-Al-Mg-based hot-dip plated steel sheet comprising a steel sheet and a hot-dip plated layer formed on a surface of the steel sheet, wherein

the hot-dip plated layer contains, as an average composition, Al: 5 to 22 mass% and Mg: 1.0 to 10 mass%, with a remainder including Zn and impurities, and

further contains one or two selected from the group consisting of group A and group B below, and in a case where a 5 mm square cross section parallel to a surface of the hot-dip plated layer is exposed at any position of a 3t/4 position, a t/2 position, and a t/4 position from the surface with a thickness of the hot-dip plated layer represented by t, a ratio (B/A (%)) of an area fraction B of a [Zn phase] to a total area fraction A of a [Zn phase] and an [Al/MgZn₂/Zn ternary eutectic structure] of a plating microstructure in at least one of the cross sections is 20% or more:

[group A] Si: 0.0001 to 2 mass%

[group B] one or two or more of the group consisting of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C: 0.0001 to 2 mass% in total.

3. The Zn-Al-Mg-based hot-dip plated steel sheet according to claim 1 or 2, wherein the area fraction of the [Zn phase] of the plating microstructure in at least one of the cross sections is 10% or more.
4. The Zn-Al-Mg-based hot-dip plated steel sheet according to claim 1 or 2, wherein an average grain size of the [Zn phase] of the plating microstructure in at least one of the cross sections is 2.5 to 10 μm .
5. The Zn-Al-Mg-based hot-dip plated steel sheet according to claim 3, wherein an average grain size of the [Zn phase] of the plating microstructure in at least one of the cross sections is 2.5 to 10 μm .
6. The Zn-Al-Mg-based hot-dip plated steel sheet according to claim 2, wherein the hot-dip plated layer has an average composition containing the group A in terms of mass%.
7. The Zn-Al-Mg-based hot-dip plated steel sheet according to claim 2, wherein the hot-dip plated layer has an average composition containing the group B in terms of mass%.

FIG. 1

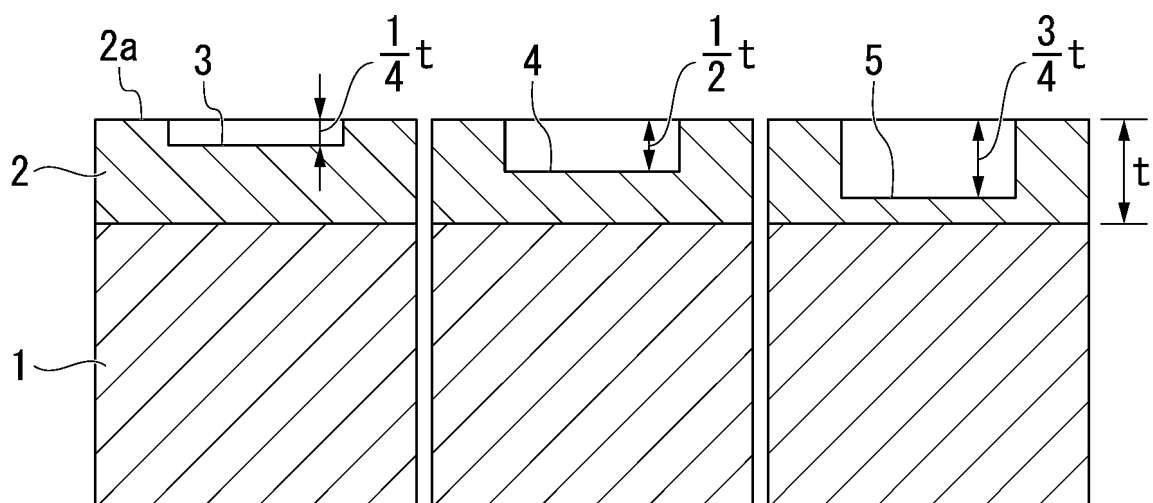
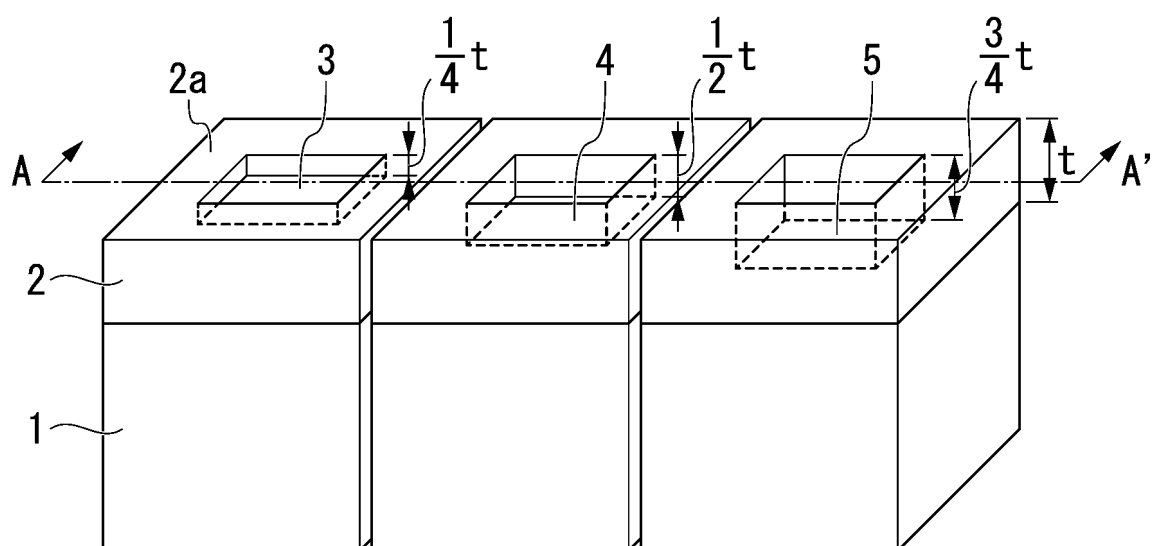


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/021573

A. CLASSIFICATION OF SUBJECT MATTER

C23C 2/06(2006.01)i; **C22C 18/00**(2006.01)i; **C22C 18/04**(2006.01)i; **C23C 2/02**(2006.01)i; **C23C 2/40**(2006.01)i
 FI: C23C2/06; C23C2/40; C23C2/02; C22C18/04; C22C18/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C2/06; C22C18/00; C22C18/04; C23C2/02; C23C2/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2018-532889 A (POSCO) 08 November 2018 (2018-11-08) claims, paragraph [0058], table 3, no. 10	1, 3
A		2, 4-7
X	JP 2021-508779 A (POSCO) 11 March 2021 (2021-03-11) claims 1, 2, paragraph [0041], table 1, invention examples 1-6	1-3, 7
Y	paragraph [0013]	4-6
X	WO 2018/169085 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 20 September 2018 (2018-09-20) claims, paragraphs [0081]-[0092], [0101]-[0112], tables 1-1, 1-3, no. 22	2, 4, 6-7
Y	paragraph [0063]	4-6
A		1, 3
X	WO 2018/169084 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 20 September 2018 (2018-09-20) claims, paragraphs [0076]-[0088], [0101]-[0112], tables 1-1, 1-3, no. 24	2, 4, 6-7
A		1, 3, 5

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 August 2023

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Name and mailing address of the ISA/IP

Japan Patent Office (ISA/IP)
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/021573

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 8-060324 A (KAWASAKI SEITETSU K.K.) 05 March 1996 (1996-03-05) entire text	1-7
A	CN 109897990 A (PANZHIHUA IRON & STEEL RESEARCH INSTITUTE, PANGANG GROUP) 18 June 2019 (2019-06-18) entire text	1-7

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/021573

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