

DESCRIPTION

Title of Invention

HOT-DIP ZN-ALLOY-PLATED STEEL SHEET

5 Technical Field

[0001] The present invention relates to a hot-dip Zn alloy-plated steel sheet excellent in blackening resistance.

Background Art

10 [0002] As plated steel sheet excellent in corrosion resistance, a hot-dip Zn alloy-plated steel sheet having a base steel sheet with a surface coated with a hot-dip Zn alloy plating layer including Al and Mg is known. The composition of the plating layer of a hot-dip Zn alloy-plated steel sheet includes, for example, 4.0 to 15.0% by mass of Al, 1.0 to 4.0% by mass of Mg, 0.002 to 0.1% by mass of Ti, 0.001 to 0.045% by mass of B, and the balance
15 of Zn and unavoidable impurities. The hot-dip Zn alloy-plated steel sheet includes a plating layer of mixed metal structure of [primary crystal Al] and [single phase Zn] in a matrix of [Al/Zn/Zn₂Mg ternary eutectic structure], having sufficient corrosion resistance and surface appearance as an industrial product.

[0003] The hot-dip Zn alloy-plated steel sheet described above can be continuously
20 produced by the following steps. First, a base steel sheet (steel strip) is passed through a furnace, dipped in a hot-dip Zn alloy plating bath, and then passed through, for example, a gas wiping apparatus, such that the amount of the molten metal adhered to the surface of the base steel sheet is adjusted to a specified amount. Subsequently, the steel strip with the specified amount of molten metal adhered thereto is passed through an air jet cooler
25 and a mist cooling zone, so that the molten metal is cooled to form a hot-dip Zn alloy plating layer. Further, the steel strip with the hot-dip Zn alloy plating layer is passed

through a water quenching zone, so as to come in contact with cooling water. A hot-dip Zn alloy-plated steel sheet is thus obtained.

[0004] The hot-dip Zn alloy-plated steel sheet thus produced, however, allows the surface of the plating layer to be blackened over time in some cases. Since the progress of blackening of a hot-dip Zn alloy-plated steel sheet spoils the appearance with a dark gray color without metallic luster, a method for suppressing the blackening has been needed.

[0005] As a method for preventing the blackening, adjusting of the temperature of the surface of a plating layer in the water quenching zone has been proposed (e.g. refer to PTL 1). In the invention described in PTL 1, the temperature of the surface of a plating layer is adjusted at lower than 105°C when contacted with cooling water in the water quenching zone so that blackening of the surface of a plating layer is prevented. Alternatively, instead of the temperature control of the surface of a plating layer at lower than 105°C, readily oxidizable elements (rare earth elements, Y, Zr or Si) are added into a plating bath and the temperature of the surface of a plating layer is adjusted at 105 to 300°C so that blackening of the surface of the plating layer is prevented.

Citation List

Patent Literature

[0006]

20 PTL 1

Japanese Patent Application Laid-Open No.2002-226958

Summary of Invention

Technical Problem

25 [0007] In the invention described in PTL 1, since the surface of a plating layer is required to be cooled to a specified temperature before passed through a water quenching zone, the

production of a hot-dip Zn alloy-plated steel sheet is restricted in some cases. For example, the feed rate of a plated steel sheet having a large thickness is required to be slow so that the plated steel sheet is cooled to a specified temperature, resulting in reduced productivity. In addition, in the case of adding readily oxidizable elements into a plating bath, the readily oxidizable elements tend to form a dross. Consequently, complicated concentration control of the readily oxidizable elements is required, resulting in a complicated production process, which has been a problem.

[0008] Embodiments of the present invention is to provide a hot-dip Zn alloy-plated steel sheet excellent in blackening resistance which can be produced without reduction in productivity and without complicated control of the components of a plating bath.

Solution to Problem

[0009] The present inventors have found that the problem can be solved by forming a composite oxide film containing the constituent components of a plating layer and vanadium on the surface of the plating layer and reducing the ratio of Zn hydroxide contained in the composite oxide film, and accomplished the present invention through further study.

[0010] Embodiments of the present invention relate to the following hot-dip Zn alloy-plated steel sheet.

[0011]

20

25

According to an aspect, there is provided a method of producing a hot-dip Zn alloy-plated steel sheet comprising: dipping a base steel sheet in a hot-dip Zn alloy plating bath to form a hot-dip Zn alloy plating layer on a surface of the base steel sheet; and contacting an aqueous solution containing a vanadium compound with a surface of the hot-dip Zn alloy plating layer to cool the base steel sheet and the hot-dip Zn alloy plating layer having a raised temperature through formation of the hot-dip Zn alloy plating layer and to form a composite oxide film on a surface of the hot-dip Zn alloy plating layer; wherein a temperature of the surface of the hot-dip Zn alloy plating layer when the aqueous solution is to be contacted with the surface of the hot-dip Zn alloy plating layer is equal to or more than 100°C and equal to or less than a solidifying point of the hot-dip Zn alloy plating layer; and the composite oxide film comprises constituent components of the hot-dip Zn alloy plating layer and vanadium, and the composite oxide film satisfies, at a whole of a surface of the composite oxide film, following Equation 1:

$$\frac{S[Hydroxide]}{S[Hydroxide] + S[Oxide]} \times 100 \leq 40 \quad (\text{Equation 1})$$

S[Oxide] is a peak area derived from Zn oxide and centered at approximately 1022 eV in an intensity profile of the XPS analysis of the surface of the composite oxide film; and S[Hydroxide] is a peak area derived from Zn hydroxide and centered at approximately 1023 eV in the intensity profile of the XPS analysis of the surface of the composite oxide

film.

In an embodiment, the hot-dip Zn alloy plating layer comprises 1.0 to 22.0% by mass of Al, 0.1 to 10.0% by mass of Mg, and the balance of the hot-dip Zn alloy plating layer being Zn and unavoidable impurities.

5 In an embodiment, the hot-dip Zn alloy plating layer further comprises at least one selected from the group consisting of 0.001 to 2.0% by mass of Si, 0.001 to 0.1% by mass of Ti, and 0.001 to 0.045% by mass of B.

In an embodiment, the adhering amount of the vanadium contained in the composite oxide film is in the range of 0.01 to 10.0 mg/m².

10

Advantageous Effects of Invention

[0012] According to embodiments of the present invention, a hot-dip Zn alloy-plated steel sheet excellent in blackening resistance can be easily produced at high productivity.

15 Brief Description of Drawings

[0013]

FIGS. 1A to 1D illustrate the intensity profiles of the chemical binding energy

20

corresponding to the 2p orbitals of Zn at the surface of a composite oxide film.

FIG. 2A illustrates an exemplary method for contacting a cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer by a spraying process;

FIG. 2B illustrates an exemplary method for contacting a cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer by a dipping process; and

FIG. 3 is a schematic diagram illustrating the configuration of a part of the production line of a hot-dip Zn alloy-plated steel sheet.

Description of Embodiments

[0014] (Hot-dip Zn alloy-plated steel sheet of the present invention)

The hot-dip Zn alloy-plated steel sheet of the present invention includes a base steel sheet, a hot-dip Zn alloy plating layer, and a composite oxide film. The hot-dip Zn alloy-plated steel sheet of the present invention is excellent in blackening resistance, by virtue of a specified composite oxide film.

[0015] The type of the base steel sheet is not particularly limited. For example, a steel sheet made of low-carbon steel, medium-carbon steel, high-carbon steel, alloy steel or the like may be used as the base steel sheet. When excellent press formability is required, a steel sheet for deep drawing made of low-carbon Ti-alloyed steel, low-carbon Nb-alloyed steel or the like is preferably used as the base steel sheet. Alternatively, a high-strength steel sheet containing P, Si, Mn and the like may be used.

[0016] The hot-dip Zn alloy plating layer is disposed on the surface of a base steel sheet. The composition of the hot-dip Zn alloy plating layer may be appropriately selected depending on the purpose. For example, the plating layer includes 1.0 to 22.0% by mass of Al, 0.1 to 10.0% by mass of Mg, and the balance of Zn and unavoidable impurities. The plating layer may further include at least one selected from the group consisting of 0.001 to 2.0% by mass of Si, 0.001 to 0.1% by mass of Ti, and 0.001 to 0.045% by mass of

B. Examples of the hot-dip Zn alloy plating include a molten Zn-0.18% by mass of Al-0.09% by mass of Sb alloy plating, a molten Zn-0.18% by mass of Al-0.06% by mass of Sb alloy plating, a molten Zn-0.18% by mass Al alloy plating, a molten Zn-1% by mass of Al-1% by mass of Mg alloy plating, a molten Zn-1.5% by mass of Al-1.5% by mass of Mg alloy plating, a molten Zn-2.5% by mass of Al-3% by mass of Mg alloy plating, a molten Zn-2.5% by mass of Al-3% by mass of Mg-0.4% by mass of Si alloy plating, a molten Zn-3.5% by mass of Al-3% by mass of Mg alloy plating, a molten Zn-4% by mass of Al-0.75% by mass of Mg alloy plating, a molten Zn-6% by mass of Al-3% by mass of Mg-0.05% by mass of Ti-0.003% by mass of B alloy plating, a molten Zn-6% by mass of Al-3% by mass of Mg-0.02% by mass of Si-0.05% by mass of Ti-0.003% by mass of B alloy plating, a molten Zn-11% by mass of Al-3% by mass of Mg alloy plating, a molten Zn-11% by mass of Al-3% by mass of Mg-0.2% by mass of Si alloy plating, and a molten Zn-55% by mass of Al-1.6% by mass of Si alloy plating. Although blackening of a plating layer can be suppressed by addition of Si as described in PTL 1, in the case of the hot-dip Zn alloy-plated steel sheet of the present invention, blackening of a plating layer can be suppressed without addition of Si to the plating layer.

[0017] The amount of the hot-dip Zn alloy plating layer adhered is not specifically limited. The amount of the plating layer adhered may be, for example, approximately 60 to 500 g/m².

[0018] The composite oxide film is disposed on the surface of a hot-dip Zn alloy plating layer, preferably on the entire surface. The composite oxide film mainly contains constituent components of the hot-dip Zn alloy plating layer (e.g. Zn, Al and Mg) and vanadium. The composite oxide film satisfies, at the entire surface, the following equation 2.

$$\frac{S[Hydroxide]}{S[Hydroxide] + S[Oxide]} \times 100 \leq 40 \quad (\text{Equation 2})$$

wherein S[Oxide] is a peak area derived from the Zn oxide and centered at approximately 1022 eV in the intensity profile of the XPS analysis of the surface of a composite oxide film; and S[Hydroxide] is a peak area derived from the Zn hydroxide and centered at approximately 1023 eV in the intensity profile of the XPS analysis of the surface of a composite oxide film.

[0019] The equation 2 indicates that the ratio of the peak area derived from the Zn hydroxide and centered at approximately 1023 eV (hereinafter referred to as "hydroxide ratio") is 40% or less relative to the total of the peak area derived from the Zn oxide and centered at approximately 1022 eV and a peak area derived from the Zn hydroxide and centered at approximately 1023 eV in the intensity profile measured in the XPS analysis.

[0020] FIGS. 1A to 1D illustrate the intensity profiles of the chemical bonding energy corresponding to the 2p orbitals of Zn at the surface of the composite oxide film of a hot-dip Zn alloy-plated steel sheet. FIG. 1A illustrates the intensity profile with a Zn hydroxide ratio of approximately 80%, FIG. 1B illustrates the intensity profile with a Zn hydroxide ratio of approximately 40%, FIG. 1C illustrates the intensity profile with a Zn hydroxide ratio of approximately 15%, and FIG. 1D illustrates the intensity profile with a Zn hydroxide ratio of approximately 10%. A dotted line is the base line, a broken line is the intensity profile derived from Zn oxide (a peak centered at approximately 1022 eV), and a dashed dotted line is the intensity profile derived from Zn hydroxide (a peak centered at approximately 1023 eV). In the hot-dip Zn alloy-plated steel sheet of the present invention, the Zn hydroxide ratio is 40% or less over the entire surface of the plating layer as shown in FIGS. 1B to 1D.

[0021] The XPS analysis of the surface of the composite oxide film of a hot-dip Zn alloy-plated steel sheet of the present invention is performed using an XPS analyzer (AXIS Nova, produced by Kratos Group PLC.). The peak area derived from Zn oxide and centered at approximately 1022 eV and the peak area derived from Zn hydroxide and

centered at approximately 1023 eV are calculated using software (Vision 2) attached to the XPS analyzer.

[0022] The position of the peak derived from Zn oxide is precisely at 1021.6 eV, and the position of the peak derived from Zn hydroxide is precisely at 1023.3 eV. These values may change in some cases due to characteristics of XPS analysis, contamination of a sample, and charging of a sample. Those skilled in the art, however, are capable of distinguishing the peak derived from Zn oxide from the peak derived from Zn hydroxide.

[0023] The adhering amount of the vanadium in the composite oxide film is not specifically limited, but preferably in the range of 0.01 to 10.0 mg/m². With an adhering amount of the vanadium of 0.01 mg/m² or more, the blackening resistance can be further improved. With an adhering amount of the vanadium of 10.0 mg/m² or less, the reactivity with a chemical conversion liquid for chemical conversion treatment can be improved. The adhering amount of vanadium in a composite oxide film can be measured using an ICP emission analyzer.

[0024] (Producing method of hot-dip Zn alloy-plated steel sheet of the present invention)

The producing method of a hot-dip Zn alloy-plated steel sheet of the present invention is not specifically limited. For example, the hot-dip Zn alloy-plated steel sheet of the present invention may be produced by: (1) a first step of forming a hot-dip Zn alloy plating layer (hereinafter, also referred to as "plating layer") on the surface of a base steel sheet; and (2) a second step of contacting a specified aqueous solution with the surface of the plating layer for cooling of the base steel sheet and the plating layer at a raised temperature through formation of the plating layer, and for forming a composite oxide film. Each of the steps is described as follows.

[0025] (1) First step

In the first step, a base steel sheet is dipped in a hot-dip Zn alloy plating bath, so that a hot-dip Zn alloy plating layer is formed on the surface of the base steel sheet.

[0026] First, a base steel sheet is dipped in a hot-dip Zn alloy plating bath, and a specified amount of molten metal is allowed to adhere to the surface of the base steel sheet by gas wiping or the like. As described above, the type of the base steel sheet is not specifically limited. The composition of the plating bath is appropriately selected depending on the composition of the hot-dip Zn alloy plating layer to be formed.

[0027] Subsequently, the molten metal adhered to the surface of a base steel sheet is cooled to a temperature equal to or more than 100°C and equal to or less than the solidifying point of the plating layer so as to be solidified. A plated steel sheet is thus formed, having a plating layer with a composition approximately the same as the composition of the plating bath, on the surface of the base steel sheet.

[0028] (2) Second step

In the second step, a specified cooling aqueous solution is contacted with the surface of the hot-dip Zn alloy plating layer, so that the base steel sheet and the plating layer at a raised temperature through formation of the hot-dip Zn alloy plating layer are cooled. In this step, a composite oxide film is formed on the surface of the plating layer. From the viewpoint of productivity, the second step is performed preferably by water quenching (water cooling). In this case, the temperature of the surface of the hot-dip Zn alloy plating layer when the cooling aqueous solution is to be contacted with the surface of the hot-dip Zn alloy plating layer is equal to or more than 100°C and approximately equal to or less than the solidifying point of the plating layer.

[0029] The cooling aqueous solution is formed of an aqueous solution containing a vanadium compound. The concentration of the vanadium compound in the cooling aqueous solution is preferably 0.01 g/L or more in terms of V element. When a concentration of the vanadium compound is less than 0.01 g/L in terms of V element, blackening of the surface of a composite oxide film may not be sufficiently prevented.

[0030] The method for preparing the aqueous solution (cooling aqueous solution)

containing a vanadium compound is not specifically limited. For example, a vanadium compound and a dissolution promoter on an as needed basis, may be dissolved in water (solvent). Preferable examples of the vanadium compound include acetylacetone vanadyl, vanadium acetylacetonate, vanadium oxysulfate, vanadium pentoxide, and ammonium
5 vanadate. These vanadium compounds may be used singly or in combination.

[0031] In the case of adding a dissolution promoter, the amount of the dissolution promoter added is not specifically limited. For example, 90 to 130 parts by mass of the dissolution promoter may be added to 100 parts by mass of the vanadium compound. With an excessively small amount of the dissolution promoter added, the vanadium
10 compound cannot be sufficiently dissolved in some cases. On the other hand, with an excessively large amount of the dissolution promoter added, the effect is saturated, resulting in a cost disadvantage.

[0032] Examples of the dissolution promoter include 2-aminoethanol, tetraethylammonium hydroxide, ethylene diamine, 2,2'-iminodiethanol, and
15 1-amino-2-propanol.

[0033] The method for contacting the cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer is not specifically limited. Examples of the method for contacting the cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer include a spraying process and a dipping process.

20 [0034] FIGS. 2A and 2B illustrate exemplary methods for contacting a cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer. FIG. 2A illustrates an exemplary method for contacting a cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer by a spraying process. FIG. 2B illustrates an exemplary method for contacting a cooling aqueous solution with the surface of a hot-dip Zn alloy plating layer
25 by a dipping process.

[0035] As shown in FIG. 2A, cooling apparatus 100 for spraying process includes a

plurality of spray nozzles 110, squeeze rollers 120 disposed downstream of spray nozzles 110 in the feed direction of a steel strip S, and housing 130 which covers the nozzles and the rollers. Spray nozzles 110 are disposed on both sides of the steel strip S. The steel strip S is cooled by a cooling aqueous solution supplied from spray nozzles 110 such that a water film is temporarily formed on the surface of the plating layer, inside housing 130. The cooling aqueous solution is then removed with squeeze roller 120. The adhering amount of vanadium in the composite oxide film can be adjusted by controlling the opening of squeeze rollers 120.

[0036] As shown in FIG. 2B, cooling apparatus 200 for dipping process includes dip tank 210 in which a cooling aqueous solution is stored, dip roller 220 disposed inside dip tank 210, and squeeze rollers 230 disposed downstream of dip roller 220 in the feed direction of the steel strip S so as to remove the extra cooling aqueous solution adhered to the steel strip S. The steel strip S fed into dip tank 210 is then contacted with the cooling aqueous solution so as to be cooled. The steel strip S is then subjected to a turn of direction by the rotating dip roller 220, and pulled upward. The cooling aqueous solution is removed with squeeze roller 230. The adhering amount of vanadium in the composite oxide film can be adjusted by controlling the opening of squeeze rollers 230.

[0037] According to the procedure described above, a hot-dip Zn alloy-plated steel sheet of the present invention can be produced.

[0038] Although the composite oxide film was formed through contact with an aqueous solution containing a vanadium compound in the water quenching step, it is conceivable that a composite oxide film can be also formed by applying an aqueous solution containing a vanadium compound to a cooled hot-dip Zn alloy-plated steel sheet and drying the applied aqueous solution (post-treatment method). Accordingly, the present inventors tried to form a composite oxide film by applying an aqueous solution containing a vanadium compound (the same aqueous solution as that used in the producing method

described above) to a hot-dip Zn alloy-plated steel sheet cooled to normal temperature with a general industrial water, and drying the applied aqueous solution. Although a composite oxide film containing constituent components of a plating layer and vanadium was also formed on the surface of the plating layer through such a post-treatment method, the composite oxide film had a Zn hydroxide ratio of more than 40%. The hot-dip Zn alloy-plated steel sheet thus produced had no outstanding difference in blackening resistance compared with a hot-dip Zn alloy-plated steel plate having no composite oxide film.

[0039] The reason is not clear why the hot-dip Zn alloy-plated steel sheet of the present invention has higher blackening resistance than a hot-dip Zn alloy-plated steel sheet having no composite oxide film. As described above, the hot-dip Zn alloy-plated steel sheet produced by the post-treatment method has a Zn hydroxide ratio of more than 40% in the composite oxide film, which is different from that of the hot-dip Zn alloy-plated steel sheet of the present invention. Furthermore, the blackening resistance is notably different between the hot-dip Zn alloy-plated steel sheet of the present invention and the hot-dip Zn alloy-plated steel sheet produced by the post-treatment method. It is therefore conceivable that the stability of Zn contained in the composite oxide film is different between the hot-dip Zn alloy-plated steel sheet of the present invention and the hot-dip Zn alloy-plated steel sheet produced by the post-treatment method, and the Zn contained in the composite oxide film of the hot-dip Zn alloy-plated steel sheet of the present invention is more difficult to transform into an oxygen-deficient zinc oxide as the source of blackening. This may be the reason why the hot-dip Zn alloy-plated steel sheet of the present invention has higher blackening resistance.

[0040] (Production line)

The hot-dip Zn alloy-plated steel sheet of the present invention may be produced, for example, in the following production line.

[0041] FIG. 3 is a schematic diagram illustrating a part of production line 300 of a hot-dip Zn alloy-plated steel sheet. Production line 300 forms a plating layer and a composite oxide film on the surface of a base steel sheet (steel strip), and can continuously produce hot-dip Zn alloy-plated steel sheets of the present invention. Production line 300 may further form a chemical conversion coating on the surface of the composite oxide film on an as needed basis, and can continuously produce plated steel sheets with chemical conversion treatment.

[0042] As shown in FIG. 3, production line 300 includes furnace 310, plating bath 320, air jet cooler 340, mist cooling zone 350, water quenching zone 360, skin pass mill 370, and tension leveler 380.

[0043] The steel strip S fed from a feeding reel not shown in drawing through a predetermined step is heated in furnace 310. The heated steel strip S is dipped in plating bath 320, so that molten metal is adhered to both sides of the steel strip S. An excess amount of molten metal is then removed with a wiping apparatus having wiping nozzle 330, allowing a specified amount of molten metal to be adhered to the surface of the steel strip S.

[0044] The steel strip S with a specified amount of molten metal adhered thereto is cooled to the solidifying point of the molten metal or lower by air jet cooler 340 or in mist cooling zone 350. Air jet cooler 340 is a facility for cooling the steel strip S by spraying a gas. Mist cooling zone 350 is a facility for cooling the steel strip S by spraying atomized fluid (e.g. cooling water) and a gas. The molten metal is thereby solidified, so that a hot-dip Zn alloy plating layer is formed on the surface of the steel strip S. When the steel strip s is cooled in mist cooling zone 350, no water film is formed on the surface of the plating layer. The temperature after cooling is not specifically limited, and may be, for example, 100 to 250°C.

[0045] The hot-dip Zn alloy-plated steel sheet cooled to a specified temperature is further

cooled in water quenching zone 360. Water quenching zone 360 is a facility for cooling the steel strip S through contact with a large amount of cooling water in comparison with mist cooling zone 350, supplying an amount of water to form a temporary water film on the surface of the plating layer. For example, water quenching zone 360 includes headers having 10 flat spray nozzles disposed at intervals of 150 mm in the width direction of the steel strip S, which are disposed in 7 rows in the feeding direction of the base steel sheet S. In water quenching zone 360, an aqueous solution containing a vanadium compound is used as cooling aqueous solution. The steel strip S is cooled in water quenching zone 360, with the cooling aqueous solution in an amount to temporarily form a water film on the surface of the plating layer being supplied. For example, the cooling aqueous solution has a water temperature of approximately 20°C, a water pressure of approximately 2.5 kgf/cm², and a water quantity of approximately 150 m³/h. The phrase "a water film is temporarily formed" means a state allowing a water film in contact with a hot-dip Zn alloy-plated steel sheet to be visually observed for approximately one second or more. Through cooling using an aqueous solution of a vanadium compound in water quenching zone 360, a composite oxide film containing the constituent components of a plating layer and vanadium with a Zn hydroxide of 40% or less is formed on the surface of the plating layer. [0046] The water-cooled hot-dip Zn alloy-plated steel sheet is rolled for thermal refining by skin pass mill 370, corrected to flat by tension leveler 380, and then wound onto tension reel 390.

[0047] When a chemical conversion coating is further formed on the surface of a plating layer, a specified chemical conversion treatment liquid is applied to the surface of the hot-dip Zn alloy-plated steel sheet corrected by tension leveler 380, with roll coater 400. The hot-dip Zn alloy-plated steel sheet through the chemical conversion treatment is dried and cooled in drying zone 410 and air cooling zone 420, and then wound onto tension reel

390.

[0048] As described above, the hot-dip Zn alloy-plated steel sheet of the present invention has excellent blackening resistance and can be easily produced at high productivity.

5 [0049] The present invention is described in detail with reference to Examples as follows. The present invention is, however, not limited to the Examples.

Examples

[0050] (Experiment 1)

10 In Experiment 1, the blackening resistance of a hot-dip Zn alloy-plated steel sheet was examined for the hot-dip Zn alloy-plated steel sheet cooled using a cooling water containing a metal compound after plating.

[0051] 1. Production of hot-dip Zn alloy-plated steel sheet

Using production line 300 shown in FIG. 3, hot-dip Zn alloy-plated steel sheets were
15 produced. A hot-rolled steel strip with a sheet thickness of 2.3 mm was prepared as base steel sheet (steel strip) S. Plating was applied to the base steel sheet using the plating bath compositions and conditions described in Table 1, so that 14 types of hot-dip Zn alloy-plated steel sheets having different plating layer compositions from each other were produced. The composition of the plating bath and the composition of the plating layer
20 are approximately the same.

[0052]

[Table 1]

Plating No.	Plating bath composition (balance: Zn) (% by mass)						Plating conditions		
	Al	Mg	Si	Ti	B	Sb	Bath temperature (°C)	Adhering amount (g/m ²)	Sheet passing speed (m/min)
1	0.18	—	—	—	—	0.09	430	90	80
2	0.18	—	—	—	—	0.06	430	90	80
3	0.18	—	—	—	—	—	430	90	80
4	1	1	—	—	—	—	430	90	80
5	1.5	1.5	—	—	—	—	430	90	80
6	2.5	3	—	—	—	—	430	90	80
7	2.5	3	0.4	—	—	—	430	90	80
8	3.5	3	—	—	—	—	430	90	80
9	4	0.75	—	—	—	—	430	90	80
10	6	3	—	0.05	0.003	—	430	90	80
11	6	3	0.02	0.05	0.003	—	430	90	80
12	11	3	—	—	—	—	450	90	80
13	11	3	0.2	—	—	—	450	90	80
14	55	—	1.6	—	—	—	600	90	80

[0053] In production of a hot-dip Zn alloy-plated steel sheet, the cooling conditions in air jet cooler 340 were changed, such that the temperature of the steel sheet (the surface of plating layer) is adjusted at 200°C immediately before passing through water quenching zone 360. In water quenching zone 360, any one of the aqueous solution described in Table 2 was used as cooling aqueous solution for formation of the composite oxide film. Each of the cooling aqueous solutions was prepared by dissolving the metal compound described in Table 2 and a dissolution promotor on an as needed basis at a specified ratio in a water having a pH of 7.6, and adjusting the water temperature to 20°C. The concentration of the metal compound in each of the cooling aqueous solutions was 250 mg/L in terms of metal element in any case. The spray apparatus in water quenching zone 360 for use includes headers having 10 flat spray nozzles disposed at intervals of 150 mm in the width direction, which are disposed in 7 rows in the feeding direction of the base steel sheet S. Each of the cooling aqueous solutions supplied from water quenching zone 360 was under conditions with a water pressure of 2.5 kgf/cm² and a water quantity of 150 m³/h.

[0054] As Comparative Example, a composite oxide film was formed by using a water containing no metal compound instead of using any one of the aqueous solutions described in Table 2 in water quenching zone 360, then applying any of the aqueous solutions described in Table 2 by a roll coat method or a spray ringer roll method, and drying the applied aqueous solution (post-treatment method).

[0055]

[Table 2]

Category	Cooling water No.	Metal compound (A)		Dissolution promoter (B)	
		Name	Amount added (mg/L)	Name	Ratio of amount added (B/A)
Example	1	Vanadium acetylacetonate	1709	Tetraethylammonium hydroxide	1.1
	2	Acetylacetonate vanadyl	1301	Ethylene diamine	1.3
	3	Ammonium metavanadate	574	—	—
	4	Sodium metavanadate	598	—	—
	5	Divanadium tetroxide	407	2,2'-Iminodiethanol	0.9
Comparative Example	6	Vanadium pentoxide	446	1-Amino-2-propanol	1.1
	7	Ammonium chromate	606	—	—
	8	Potassium chromate	467	—	—
	9	Sodium silicate	1087	—	—

[0056] 2. Evaluation of hot-dip Zn alloy-plated steel sheet

(1) Measurement of Zn (OH)₂ ratio on surface of composite oxide film

For each of the hot-dip Zn alloy-plated steel sheets, the Zn hydroxide ratio on the surface of the composite oxide film was measured using an XPS analyzer (AXIS Nova, produced by Kratos Group PLC.). The Zn hydroxide ratio was calculated using software (Vision 2) attached to the XPS analyzer.

[0057] (2) Measurement of adhering amount of V on surface of composite oxide film

For each of the hot-dip Zn alloy-plated steel sheets, the adhering amount of vanadium on the surface of the composite oxide film was measured using an ICP emission analyzer (ICPS-8100, produced by Shimadzu Corporation).

[0058] (3) Treatment for accelerating deterioration of gloss

A test piece was cut out from each of the produced hot-dip Zn alloy-plated steel sheets. Each of the test pieces was placed in a thermo-hygrostat (LHU-113, produced by Espec Corp.), and subjected to a treatment for accelerating deterioration of the gloss at a temperature 70°C, with a relative humidity of 90%, for 72 hours.

[0059] (4) Measurement of degree of blackening

The brightness (L* value) at the surface of the plating layer for each of the hot-dip Zn alloy-plated steel sheets was measured before and after the treatment for accelerating deterioration of the gloss. The brightness (L* value) at the surface of the plating layer was measured using a spectroscopic color difference meter (TC-1800, produced by Tokyo Denshoku Co., Ltd), by spectral reflectance measurement in accordance with JIS K 5600.

The measurement conditions are as follows:

Optical condition: d/8° method (double beam optical system)

Field of view: 2-degree field of view

Measurement method: reflectometry

Standard illuminant: C

Color system: CIELAB

Measurement wavelength: 380 to 780 nm

Measurement wavelength interval: 5 nm

Spectroscope: 1,200/mm diffraction grating

5 Lighting: halogen lamp (voltage: 12 V, power: 50 W, rating life: 2,000 hours)

Measurement area: 7.25 mm diameter

Detection element: photomultiplier tube (R928 produced by Hamamatsu Photonics K.K.)

Reflectance: 0 to 150%

10 Measurement temperature: 23°C

Standard plate: white

[0060] For each of the plated steel sheets, the evaluation was ranked as "A" for a difference in L^* values (ΔL^*) between before and after the treatment for accelerating deterioration of the gloss of less than 1, "B" for a difference of 1 or more and less than 3, 15 "C" for a difference of 3 or more and less than 7, and "D" for a difference of 7 or more. It can be determined that a plated steel sheet evaluated as "A" or "B" has blackening resistance.

[0061] (4) Evaluation results

For each of the plated steel sheets, the relation between the type of the cooling aqueous solution for use and the method for forming the composite oxide film (a water 20 quenching method (WQ), a roll coat method (RC), or a spray ringer roll method (SP)), and the Zn hydroxide ratio, the adhering amount of V and the evaluation results of the degree of blackening is described in Table 3 to Table 6.

[0062]

[Table 3]

Category	Test piece No.	Plating No.	Cooling water No.	Treatment method	Hydroxide Ratio (%)	Adhering Amount of V (mg/m ²)	Blackening test result
Ex.	1	11	1	WQ	7	0.004	B
Ex.	2	11	2	WQ	11	0.004	B
Ex.	3	11	3	WQ	7	0.005	B
Ex.	4	11	4	WQ	13	0.004	B
Ex.	5	11	5	WQ	7	0.005	B
Ex.	6	11	6	WQ	25	0.005	B
Ex.	7	11	1	WQ	6	0.01	A
Ex.	8	11	2	WQ	11	0.017	A
Ex.	9	11	3	WQ	16	0.013	A
Ex.	10	11	4	WQ	19	0.022	A
Ex.	11	11	5	WQ	23	0.029	A
Ex.	12	11	6	WQ	24	0.027	A
Ex.	13	11	1	WQ	8	0.13	A
Ex.	14	11	2	WQ	18	0.18	A
Ex.	15	11	3	WQ	21	0.17	A
Ex.	16	11	4	WQ	14	0.12	A
Ex.	17	11	5	WQ	25	0.16	A
Ex.	18	11	6	WQ	18	0.18	A
Ex.	19	11	1	WQ	22	1.02	A
Ex.	20	11	2	WQ	7	1.01	A
Ex.	21	11	3	WQ	23	0.96	A
Ex.	22	11	4	WQ	7	0.96	A
Ex.	23	11	5	WQ	5	0.98	A
Ex.	24	11	6	WQ	19	1.01	A
Ex.	25	11	1	WQ	20	7.95	A
Ex.	26	11	2	WQ	16	7.98	A
Ex.	27	11	3	WQ	6	8.02	A
Ex.	28	11	4	WQ	21	8.05	A
Ex.	29	11	5	WQ	6	8.01	A
Ex.	30	11	6	WQ	18	8.04	A

[0063]

[Table 4]

Category	Test piece No.	Plating No.	Cooling water No.	Treatment method	Hydroxide Ratio (%)	Adhering Amount of V (mg/m ²)	Blackening test result
Ex.	31	11	1	WQ	13	15.04	A
Ex.	32	11	2	WQ	8	14.97	A
Ex.	33	11	3	WQ	17	14.98	A
Ex.	34	11	4	WQ	5	14.99	A
Ex.	35	11	5	WQ	14	14.97	A
Ex.	36	11	6	WQ	17	14.96	A
Comp. Ex.	37	11	7	WQ	19	0	C
Comp. Ex.	38	11	8	WQ	9	0	C
Comp. Ex.	39	11	9	WQ	24	0	D
Comp. Ex.	40	11	1	RC	76	1.03	D
Comp. Ex.	41	11	2	RC	76	0.96	D
Comp. Ex.	42	11	3	RC	65	0.99	D
Comp. Ex.	43	11	4	RC	71	7.96	D
Comp. Ex.	44	11	5	RC	83	7.96	D
Comp. Ex.	45	11	6	RC	76	8.01	D
Comp. Ex.	46	11	1	SP	76	1.06	D
Comp. Ex.	47	11	2	SP	76	1.05	D
Comp. Ex.	48	11	3	SP	65	1.01	D
Comp. Ex.	49	11	4	SP	71	8.03	D
Comp. Ex.	50	11	5	SP	83	8.03	D
Comp. Ex.	51	11	6	SP	76	8.03	D

[0064]

[Table 5]

Category	Test piece No.	Plating No.	Cooling water No.	Treatment method	Hydroxide Ratio (%)	Adhering Amount of V (mg/m ²)	Blackening test result
Ex.	52	9	1	WQ	11	0.005	B
Ex.	53	14	2	WQ	12	0.004	B
Ex.	54	2	3	WQ	7	0.007	B
Ex.	55	10	4	WQ	12	0.005	B
Ex.	56	1	5	WQ	15	0.003	B
Ex.	57	12	6	WQ	22	0.005	B
Ex.	58	5	1	WQ	14	0.024	A
Ex.	59	8	2	WQ	8	0.019	A
Ex.	60	13	3	WQ	11	0.022	A
Ex.	61	3	4	WQ	14	0.017	A
Ex.	62	10	5	WQ	8	0.021	A
Ex.	63	4	6	WQ	24	0.023	A
Ex.	64	13	1	WQ	20	0.221	A
Ex.	65	7	2	WQ	21	0.239	A
Ex.	66	12	3	WQ	6	0.217	A
Ex.	67	9	4	WQ	5	0.224	A
Ex.	68	7	5	WQ	16	0.189	A
Ex.	69	5	6	WQ	12	0.24	A
Ex.	70	12	1	WQ	15	1.08	A
Ex.	71	9	2	WQ	6	1.05	A
Ex.	72	4	3	WQ	9	0.98	A
Ex.	73	1	4	WQ	14	0.97	A
Ex.	74	14	5	WQ	8	0.95	A
Ex.	75	3	6	WQ	10	1.04	A
Ex.	76	10	1	WQ	10	7.85	A
Ex.	77	8	2	WQ	6	7.81	A
Ex.	78	13	3	WQ	19	8.19	A
Ex.	79	10	4	WQ	22	7.81	A
Ex.	80	6	5	WQ	8	8.12	A
Ex.	81	12	6	WQ	15	8.09	A

[0065]

[Table 6]

Category	Test piece No.	Plating No.	Cooling water No.	Treatment method	Hydroxide Ratio (%)	Adhering Amount of V (mg/m ²)	Blackening test result
Ex.	82	5	1	WQ	24	15.16	A
Ex.	83	9	2	WQ	24	15.01	A
Ex.	84	1	3	WQ	18	15.08	A
Ex.	85	2	4	WQ	6	14.96	A
Ex.	86	13	5	WQ	12	15.05	A
Ex.	87	6	6	WQ	11	15.04	A
Comp. Ex.	88	13	7	WQ	20	0	C
Comp. Ex.	89	12	8	WQ	5	0	C
Comp. Ex.	90	10	9	WQ	12	0	D
Comp. Ex.	91	9	1	RC	72	1.02	D
Comp. Ex.	92	14	2	RC	70	0.96	D
Comp. Ex.	93	12	3	RC	88	0.91	D
Comp. Ex.	94	8	4	RC	74	0.97	D
Comp. Ex.	95	9	5	RC	67	0.91	D
Comp. Ex.	96	5	6	RC	65	1.08	D
Comp. Ex.	97	9	1	SP	72	0.99	D
Comp. Ex.	98	14	2	SP	70	0.96	D
Comp. Ex.	99	12	3	SP	88	0.83	D
Comp. Ex.	100	8	4	SP	74	0.88	D
Comp. Ex.	101	9	5	SP	67	0.81	D
Comp. Ex.	102	5	6	SP	65	1.07	D

[0066] As shown in Table 3 to Table 6, in the case of cooling using an aqueous solution containing vanadium in water quenching zone 360, a composite oxide film containing vanadium was formed having the surface with a Zn hydroxide ratio of 40% or less, and excellent blackening resistance. In contrast, in the case of cooling using an aqueous solution containing no vanadium in water quenching zone 360, a composite oxide film containing no vanadium was formed, and blackening was insufficiently suppressed. In

the case of application of an aqueous solution containing vanadium by a roll coat method or a spray ringer roll method, a composite oxide film was formed, having the surface with a Zn hydroxide ratio of more than 40%, and blackening was insufficiently suppressed.

[0067] From the comparison of the blackening resistance of the test pieces Nos. 1 to 6 and Nos. 52 to 57 with the blackening resistance of the test pieces Nos. 7 to 36 and Nos. 58 to 87, it is found that the blackening resistance is particularly excellent in the case of an adhering amount of vanadium in the composite oxide film of 0.01 mg/m^2 or more.

[0068] From the results described above, it is found that the cooling using an aqueous solution containing vanadium in water quenching zone 360 allows a composite oxide film to be formed, which contains vanadium and has the surface with a Zn hydroxide ratio of 40% or less. The plated steel sheet having such a composite oxide film is excellent in blackening resistance.

[0069] (Experiment 2)

In Experiment 2, the 102 types of hot-dip Zn alloy-plated steel sheets produced in Experiment 1 were subjected to a chemical conversion treatment under the following chemical conversion treatment conditions A to C. Blackening resistance was measured when the treatment for accelerating deterioration of the gloss was carried out in the same manner as in Experiment 1. The appearance after the chemical conversion treatment was also evaluated.

[0070] In chemical conversion treatment conditions A, ZINCHROME 3387N (chrome concentration: 10 g/L , produced by Nihon Parkerizing Co., Ltd.) was used as chemical conversion treatment liquid. The chemical conversion treatment liquid was applied to have an adhering amount of chromium of 10 mg/m^2 by a spray ringer roll method.

[0071] In chemical conversion treatment conditions B, an aqueous solution containing 50 g/L of magnesium phosphate, 10 g/L of potassium fluorotitanate, and 3 g/L of an organic acid was used as chemical conversion treatment liquid. The chemical conversion

treatment liquid was applied to have an adhering amount of metal components of 50 mg/m² by a roll coat method.

[0072] In chemical conversion treatment conditions C, an aqueous solution containing 20 g/L of a urethane resin, 3 g/L of ammonium dihydrogen phosphate, and 1 g/L of vanadium pentoxide was used as chemical conversion treatment liquid. The chemical conversion treatment liquid was applied to have a dried film thickness of 2 μm by a roll coat method.

[0073] In the evaluation of the appearance for each of the plated steel sheets after the chemical conversion treatment, the evaluation was ranked as "B" for the chemical conversion treatment coating having no white turbidity, and "D" for the chemical conversion treatment coating having white turbidity.

[0074] For each of the plated steel sheets, the relation between the type of the original sheet for the chemical conversion treatment and the type of chemical conversion treatment, and the evaluation results of the degree of blackening and the appearance is described in Table 7 to Table 10.

[0075]

[Table 7]

Category	Test piece No.	Chemical conversion treatment	Original sheet for chemical conversion treatment (test piece No.)	Blackening test result	Appearance
Ex.	103	A	1	B	B
Ex.	104	B	2	B	B
Ex.	105	C	3	B	B
Ex.	106	A	4	B	B
Ex.	107	B	5	B	B
Ex.	108	C	6	B	B
Ex.	109	A	7	A	B
Ex.	110	B	8	A	B
Ex.	111	C	9	A	B
Ex.	112	A	10	A	B
Ex.	113	B	11	A	B
Ex.	114	C	12	A	B
Ex.	115	A	13	A	B
Ex.	116	B	14	A	B
Ex.	117	C	15	A	B
Ex.	118	A	16	A	B
Ex.	119	B	17	A	B
Ex.	120	C	18	A	B
Ex.	121	A	19	A	B
Ex.	122	B	20	A	B
Ex.	123	C	21	A	B
Ex.	124	A	22	A	B
Ex.	125	B	23	A	B
Ex.	126	C	24	A	B
Ex.	127	A	25	A	B
Ex.	128	B	26	A	B
Ex.	129	C	27	A	B
Ex.	130	A	28	A	B
Ex.	131	B	29	A	B
Ex.	132	C	30	A	B

[0076]

[Table 8]

Category	Test piece No.	Chemical conversion treatment	Original sheet for chemical conversion treatment (test piece No.)	Blackening test result	Appearance
Ex.	133	A	31	A	D
Ex.	134	B	32	A	D
Ex.	135	C	33	A	D
Ex.	136	A	34	A	D
Ex.	137	B	35	A	D
Ex.	138	C	36	A	D
Comp. Ex.	139	A	37	D	B
Comp. Ex.	140	B	38	D	B
Comp. Ex.	141	C	39	D	B
Comp. Ex.	142	A	40	D	B
Comp. Ex.	143	B	41	D	B
Comp. Ex.	144	C	42	D	B
Comp. Ex.	145	A	43	D	B
Comp. Ex.	146	B	44	D	B
Comp. Ex.	147	C	45	D	B
Comp. Ex.	148	A	46	D	B
Comp. Ex.	149	B	47	D	B
Comp. Ex.	150	C	48	D	B
Comp. Ex.	151	A	49	D	B
Comp. Ex.	152	B	50	D	B
Comp. Ex.	153	C	51	D	B

[0077]

[Table 9]

Category	Test piece No.	Chemical conversion treatment	Original sheet for chemical conversion treatment (test piece No.)	Blackening test result	Appearance
Ex.	154	A	52	B	B
Ex.	155	B	53	B	B
Ex.	156	C	54	B	B
Ex.	157	A	55	B	B
Ex.	158	B	56	B	B
Ex.	159	C	57	B	B
Ex.	160	A	58	A	B
Ex.	161	B	59	A	B
Ex.	162	C	60	A	B
Ex.	163	A	61	A	B
Ex.	164	B	62	A	B
Ex.	165	C	63	A	B
Ex.	166	A	64	A	B
Ex.	167	B	65	A	B
Ex.	168	C	66	A	B
Ex.	169	A	67	A	B
Ex.	170	B	68	A	B
Ex.	171	C	69	A	B
Ex.	172	A	70	A	B
Ex.	173	B	71	A	B
Ex.	174	C	72	A	B
Ex.	175	A	73	A	B
Ex.	176	B	74	A	B
Ex.	177	C	75	A	B
Ex.	178	A	76	A	B
Ex.	179	B	77	A	B
Ex.	180	C	78	A	B
Ex.	181	A	79	A	B
Ex.	182	B	80	A	B
Ex.	183	C	81	A	B

[0078]

[Table 10]

Category	Test piece No.	Chemical conversion treatment	Original sheet for chemical conversion treatment (test piece No.)	Blackening test result	Appearance
Ex.	184	A	82	A	D
Ex.	185	B	83	A	D
Ex.	186	C	84	A	D
Ex.	187	A	85	A	D
Ex.	188	B	86	A	D
Ex.	189	C	87	A	D
Ex.	190	A	88	D	B
Ex.	191	B	89	D	B
Comp. Ex.	192	C	90	D	B
Comp. Ex.	193	A	91	D	B
Comp. Ex.	194	B	92	D	B
Comp. Ex.	195	C	93	D	B
Comp. Ex.	196	A	94	D	B
Comp. Ex.	197	B	95	D	B
Comp. Ex.	198	C	96	D	B
Comp. Ex.	199	A	97	D	B
Comp. Ex.	200	B	98	D	B
Comp. Ex.	201	C	99	D	B
Comp. Ex.	202	A	100	D	B
Comp. Ex.	203	B	101	D	B
Comp. Ex.	204	C	102	D	B

[0079] As shown in Table 7 to Table 10, the plated steel sheets having a composite oxide film including vanadium, with the surface having a Zn hydroxide ratio of 40% or less, had excellent blackening resistance even when a chemical conversion coating is formed. In contrast, in the case of an adhering amount of vanadium in the composite oxide film of more than 10.0 mg/m² (test piece Nos. 31 to 36 and Nos. 82 to 87), the reactivity between the chemical conversion treatment liquid and the surface of the plating layer (composite oxide film) was decreased, and the chemical conversion treatment coating had white turbidity.

[0080] From the results, it is found that in the case of chemical conversion treatment, the adhering amount of vanadium in the composite oxide film is preferably adjusted to 10.0 mg/m² or less.

[0081] This application claims priority based on Japanese patent Application No. 2013-250139, filed on December 3, 2013, the entire contents of which including the specification and the drawings are incorporated herein by reference.

Industrial Applicability

[0082] The hot-dip Zn alloy-plated steel sheet obtained by the production method of the present invention is excellent in blackening resistance, and useful as plated steel sheet for use in, for example, roof materials and exterior materials for buildings, home appliances, and automobiles.

20

Reference Signs List

- [0083]
- 100, 200 Cooling apparatus
 - 110 Spray nozzle
 - 120, 230 Squeeze roll
 - 130 Housing

25

- 210 Dip tank
- 220 Dip roller
- 300 Production line
- 310 Furnace
- 5 320 Plating bath
- 330 Wiping nozzle
- 340 Air jet cooler
- 350 Mist cooling zone
- 360 Water quenching zone
- 10 370 Skin pass mill
- 380 Tension leveler
- 390 Tension reel
- 400 Roll coater
- 410 Drying zone
- 15 420 Air cooling zone
- S: Steel strip

CLAIMS:

1. A method of producing a hot-dip Zn alloy-plated steel sheet comprising:
dipping a base steel sheet in a hot-dip Zn alloy plating bath to form a hot-dip Zn alloy plating layer on a surface of the base steel sheet; and

contacting an aqueous solution containing a vanadium compound with a surface of the hot-dip Zn alloy plating layer to cool the base steel sheet and the hot-dip Zn alloy plating layer having a raised temperature through formation of the hot-dip Zn alloy plating layer and to form a composite oxide film on a surface of the hot-dip Zn alloy plating layer;

wherein a temperature of the surface of the hot-dip Zn alloy plating layer when the aqueous solution is to be contacted with the surface of the hot-dip Zn alloy plating layer is equal to or more than 100°C and equal to or less than a solidifying point of the hot-dip Zn alloy plating layer; and

the composite oxide film comprises constituent components of the hot-dip Zn alloy plating layer and vanadium, and the composite oxide film satisfies, at a whole of a surface of the composite oxide film, following Equation 1:

$$\frac{S[Hydroxide]}{S[Hydroxide] + S[Oxide]} \times 100 \leq 40 \quad (\text{Equation 1})$$

S[Oxide] is a peak area derived from Zn oxide and centered at approximately 1022 eV in an intensity profile of the XPS analysis of the surface of the composite oxide film; and S[Hydroxide] is a peak area derived from Zn hydroxide and centered at approximately 1023 eV in the intensity profile of the XPS analysis of the surface of the composite oxide film.

2. The method of producing a hot-dip Zn alloy-plated steel sheet according to claim 1, wherein:

the hot-dip Zn alloy plating layer comprises 1.0 to 22.0% by mass of Al, 0.1 to 10.0% by mass of Mg, and the balance of the hot-dip Zn alloy plating layer being Zn and unavoidable impurities.

3. The method of producing a hot-dip Zn alloy-plated steel sheet according to claim 2, wherein:

the hot-dip Zn alloy plating layer further comprises at least one selected from the group consisting of 0.001 to 2.0% by mass of Si, 0.001 to 0.1% by mass of Ti, and 0.001 to 0.045% by mass of B.

4. The method of producing a hot-dip Zn alloy-plated steel sheet according to any one of claims 1 to 3, wherein an adhering amount of the vanadium contained in the composite oxide film is in the range of 0.01 to 10.0 mg/m².