

DESCRIPTION

TITLE OF INVENTION: HOT-DIP PLATED STEEL MATERIAL

TECHNICAL FIELD

5 [0001]

The present invention relates to a hot-dip plated steel material.

Priority is claimed on Japanese Patent Application No. 2023-067060, filed April 17, 2023, the content of which is incorporated herein by reference.

BACKGROUND ART

10 [0002]

In a case where a steel material is used for a long period of time, it is preferable to apply some kind of antirust treatment to resist corrosion of the steel material. A hot-dip Zn plating method is used in various fields where antirust for steel materials is required, such as the fields of civil engineering, construction, and automobiles, as a means for inexpensive antirust of steel materials.

[0003]

The corrosion protection provided by the plated layer is generally determined by the inherent corrosion resistance of the plated layer and the thickness of the plated layer. For example, Patent Document 1 states that a plated steel sheet is manufactured by a so-called continuous hot-dip plating method in which a steel sheet is continuously immersed in a hot-dip plating bath. Thereafter, the plated steel sheet is processed into a component shape to manufacture a component.

[0004]

In recent years, various elements other than Al and Mg have been added to a Zn alloy plating bath in order to impart performance other than corrosion resistance to a

25

plated layer.

[0005]

For example, Patent Documents 1 and 2 describe Zn-Al-Mg-based plated layers used as highly corrosion-resistant plating. A technique is disclosed in which these Zn-
5 Al-Mg-based plated layers improve designability and corrosion resistance by microstructural control, and further improve corrosion resistance by adding an element to the plated layer or actively forming a corrosion product.

Citation List

Patent Documents

10 [0006]

Patent Document 1: PCT International Publication No. WO 2018/139619

Patent Document 2: PCT International Publication No. WO 2019/230894

SUMMARY OF INVENTION

Technical Problem

15 [0007]

In the Zn-Al-Mg-based plated layer disclosed in Patent Document 1, elements such as Si and Sn added to the plated layer are easily bonded to Mg, Al, or Zn in a Zn alloy to form an intermetallic compound having a high melting point. Si, Sn, and the like are also bonded to steel components of a steel sheet passing through the plating bath
20 to form an intermetallic compound with Fe and the like, which become fine particles (fine dross) that float or settle in the plating bath. Such micro-sized intermetallic compounds adhere to the steel sheet to cause bare spots (portions where a plated layer is not formed on the steel sheet) or to make a surface of the plated layer uneven when hot-dip plating is performed, resulting in a problem of poor external appearance.

25 [0008]

In addition, in the conventional Zn-Al-Mg-based plated layers as described in Patent Documents 1 and 2, a method for adding an element to a plated layer finally manufactured and the form of an intermetallic compound of the plated layer have not been sufficiently studied, and there have been problems such as peeling of a plated layer
5 derived from an intermetallic compound (powdering phenomenon) and deterioration in workability.

[0009]

An object of an embodiment of the present invention is to provide a hot-dip plated steel material capable of achieving both excellent workability and corrosion
10 resistance.

Solution to Problem

[0010]

In order to solve the above-described problem, aspects of the present invention adopt the following configurations.

15 [1] A hot-dip plated steel material according to one aspect of the present invention is a hot-dip plated steel material including: a steel material; and a plated layer disposed on a surface of the steel material, in which

the plated layer has a chemical composition including, in terms of mass%,
more than 10.0% and less than 45.0% of Al,
20 4.0% or more and 15.0% or less of Mg,
0% or more and 2.0% or less of Si, and
0.03% or more and 1.50% or less of Sr, and
further including
0% or more and 0.7% or less of Sn,
25 0% or more and 0.3% or less of Bi,

- 0% or more and 0.3% or less of In,
 0% or more and 0.6% or less of Ca,
 0% or more and 0.3% or less of Y,
 0% or more and 0.3% or less of La,
 5 0% or more and 0.3% or less of Ce,
 0% or more and 0.3% or less of Li,
 0% or more and 1.0% or less of Ni,
 0% or more and 1.0% or less of Cu,
 0% or more and 0.25% or less of Ag,
 10 0% or more and 0.25% or less of Sb,
 0% or more and 0.25% or less of Pb,
 0% or more and 0.5% or less of B,
 0% or more and 0.5% or less of P,
 0% or more and 0.25% or less of Ti,
 15 0% or more and 0.25% or less of Co,
 0% or more and 0.25% or less of V,
 0% or more and 0.25% or less of Nb,
 0% or more and 0.25% or less of Mn,
 0% or more and 0.25% or less of Zr,
 20 0% or more and 0.25% or less of W,
 0% or more and 5.0% or less of Fe, and
 a remainder of Zn and impurities,
 the plated layer contains a Zn-Sr-based compound and a Zn-Sr-Si-based
 compound, and
 25 in a case where, in an elemental distribution profile obtained by a qualitative

analysis using a glow discharge optical emission spectrometry in a direction from a surface of the plated layer toward the steel material, the thickness of the plated layer is denoted by t , the average value of a qualitative analysis value of Sr from the surface of the plated layer to $0.05 t$ is denoted by Sr (surf), a qualitative analysis value in a range of $0.05 t$ to $0.66 t$ starting from the surface of the plated layer is denoted by Sr (center), and a qualitative analysis value in a range of $0.66 t$ to t starting from the surface of the plated layer is denoted by Sr (deep), Expression (1) is satisfied,

$$Sr \text{ (surf)} < Sr \text{ (deep)} < Sr \text{ (center)} \dots (1).$$

[2] In the hot-dip plated steel material according to [1], in the chemical composition of the plated layer, Sr is 0.10% or more and 1.50% or less, and in a case where the diffraction intensity of the Zn-Sr-based compound in a X-ray diffraction pattern of the surface of the plated layer is denoted by $I(SrZn_{13})$, the diffraction intensity being measured by using Cu-K α radiation under conditions of 50 kV and 300 mA X-ray output, Expression (2) may be satisfied,

$$\{I(14.48^\circ) + I(32.74^\circ)\}/2 \times I(12.50^\circ) \} > 2.0 \dots (2)$$

in Expression (2), $I(n^\circ)$ is the X-ray diffraction intensity at a diffraction angle n° , and n is a diffraction angle (2θ) indicated in Expression (2).

[3] In the hot-dip plated steel material according to [1] or [2], in the chemical composition of the plated layer, Si is 0.05% or more and 0.5% or less, and the Zn-Sr-Si-based compound and a Zn-Al-Sr-Si-based compound are contained in an area fraction of 5% to 30% in a cross section along the thickness direction of the plated layer.

Advantageous Effects of Invention

[0011]

According to the embodiment of the present invention, it is possible to provide a hot-dip plated steel material capable of achieving both excellent workability and

corrosion resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0012]

[FIG. 1] A diagram representing a result of GDS analysis performed on a plated
5 layer of a hot-dip plated steel material according to an embodiment of the present
invention, and a graph illustrating an example of an elemental distribution profile.

[FIG. 2] an example representing an X-ray diffraction pattern in the plated layer
according to the embodiment of the present invention.

DESCRIPTION OF EMBODIMENTS

10 [0013]

Hereinafter, a hot-dip plated steel material according to one embodiment of the
present invention will be described.

Note that, in the present specification, the “%” indication of the amount of each
element in a chemical composition of a plated layer means “mass%” unless otherwise
15 specified.

In addition, a numerical range represented by “to” means a range including the
numerical values described before and after “to” as the lower limit and the upper limit.
Note that a numerical range in which “more than” or “less than” is attached to the
numerical values described before and after “to” means a range not including these
20 numerical values as the lower limit or the upper limit.

[0014]

The “corrosion resistance” described in the present specification indicates a
property that the plated layer itself is hardly corroded. A Zn-based plated layer has a
sacrificial corrosion protection action on a steel material. Therefore, during the
25 corrosion process of a plated steel sheet, the plated layer corrodes and turns into white

rust before the steel material corrodes, and after the plated layer turns into white rust and disappears, the steel material corrodes, resulting in the formation of red rust.

The “sacrificial corrosion resistance” described in the present specification indicates a property of inhibiting corrosion of the steel material at a portion where the steel material is exposed (for example, a cut end surface portion of the plated steel material and a portion where the steel material is exposed due to cracking of the hot-dip plating layer during processing).

[0015]

First, the relationship between an intermetallic compound formed in the Zn-Al-Mg-based plated layer and the workability of the plated steel material was examined. Hereinafter, examination results will be described below.

[0016]

In general, in a case where an intermetallic compound having a covalent bond is contained in the plated layer, hard particles are formed, so that the hardness of the entire plated layer increases. In addition, since the intermetallic compound is also excellent in insulation properties, containment of the intermetallic compound in the plated layer results in high corrosion resistance.

[0017]

In contrast, in a case where the intermetallic compound is excessively contained in the plated layer, the hardness of the entire plated layer increases. In a case where the hardness of the entire plated layer increases, the plated layer is easily broken during forming working of a plated steel material used as a raw material, and peeling of the plated layer such as powdering may occur.

Therefore, it is practically not preferable to contain a large amount of the intermetallic compound in the plated layer. Therefore, conventionally, there has been a

demand for a plated layer having a desired level of hardness and high corrosion resistance and having good workability without occurrence of peeling or the like.

[0018]

Here, there is a technique in which Ca is contained in the plated layer in order to
5 improve the hardness and corrosion resistance of the plated layer. In a case where a large amount of Ca is contained in the plated layer, an intermetallic compound is formed with Zn, Al or the like in the plated layer. The melting point of this Ca-containing intermetallic compound is very high in the solidification process of Zn-Al-Mg-based hot-dip plating. Therefore, Ca in the plated layer becomes a large Ca-containing
10 intermetallic compound at the initial stage after the steel material is pulled up from the plating bath, and grows in the plated layer.

[0019]

In a general hot-dip plating process, the surface of the plated layer is significantly cooled by the outside air, so that solidification of the plated layer proceeds
15 from the surface. Also, in the bath containing Ca, precipitation of the Ca-containing intermetallic compound is initiated from a low and stable free energy portion such as a surface or an interface of the plated layer by a similar mechanism. As a result, the Ca-containing intermetallic compound is likely to accumulate particularly on the surface of the plated layer, and the Ca-containing intermetallic compound may coarsely grow to be
20 continuous in layers.

[0020]

In a case of a plated layer in which Ca-containing intermetallic compounds are connected in layers, there is a possibility that a so-called “powdering phenomenon” occurs, in which the Ca-containing intermetallic compounds are brittly fractured during
25 forming working, and the plated layer is peeled off from the plated layer surface.

Therefore, in the plated layer containing Ca at a high concentration, it is difficult to improve all of hardness, workability, and corrosion resistance.

[0021]

Therefore, the present inventors examined an element that produces the same effect as Ca, and found that Sr is effective. Specifically, it has been found that Sr forms a covalent bond with Zn, Al, Si, or the like, and forms a Sr-based intermetallic compound excellent in corrosion resistance and hardness.

[0022]

[Hot-Dip Plated Steel Material]

Hereinafter, a hot-dip plated steel material according to the present embodiment will be described.

The hot-dip plated steel material according to the present embodiment includes a steel material and a plated layer disposed on a surface of the steel material.

The average chemical composition of the plated layer includes, in terms of mass%,

more than 10.0% and less than 45.0% of Al,

4.0% or more and 15.0% or less of Mg,

0% or more and 2.0% or less of Si, and

0.03% or more and 1.50% or less of Sr, and

further includes

0% or more and 0.7% or less of Sn,

0% or more and 0.3% or less of Bi,

0% or more and 0.3% or less of In,

0% or more and 0.6% or less of Ca,

0% or more and 0.3% or less of Y,

0% or more and 0.3% or less of La,

0% or more and 0.3% or less of Ce,

0% or more and 0.3% or less of Li,

0% or more and 1.0% or less of Ni,

5 0% or more and 1.0% or less of Cu,

0% or more and 0.25% or less of Ag,

0% or more and 0.25% or less of Sb,

0% or more and 0.25% or less of Pb,

0% or more and 0.5% or less of B,

10 0% or more and 0.5% or less of P,

0% or more and 0.25% or less of Ti,

0% or more and 0.25% or less of Co,

0% or more and 0.25% or less of V,

0% or more and 0.25% or less of Nb,

15 0% or more and 0.25% or less of Mn,

0% or more and 0.25% or less of Zr,

0% or more and 0.25% or less of W,

0% or more and 5.0% or less of Fe, and

a remainder of Zn and impurities.

20 [0023]

The plated layer in the hot-dip plated steel material of the present embodiment contains a Zn-Sr-based compound and a Zn-Sr-Si-based compound. In addition, in a case where, in an elemental distribution profile obtained by a qualitative analysis using a glow discharge optical emission spectrometry in a direction from a surface of the plated

25 layer toward the steel material, the thickness of the plated layer is denoted by t , the

average value of a qualitative analysis value of Sr from the surface of the plated layer to 0.05 t is denoted by Sr (surf), a qualitative analysis value in a range of 0.05 t to 0.66 t starting from the surface of the plated layer is denoted by Sr (center), and a qualitative analysis value in a range of 0.66 t to t starting from the surface of the plated layer is denoted by Sr (deep), Expression (1) is satisfied.

[0024]

$$Sr \text{ (surf)} < Sr \text{ (deep)} < Sr \text{ (center)} \dots (1).$$

[0025]

(Steel Material)

First, a steel material (original sheet) to be plated will be described.

The steel material is, for example, mainly a steel sheet, but its size is not particularly limited. The steel sheet may be a steel sheet applicable to a general hot-dip galvanizing step. In particular, steel sheets applicable in a step of solidification by immersion in molten metal, such as a continuous hot-dip galvanizing line (CGL), apply to this. As the size of the steel sheet, for example, a steel sheet having a sheet thickness of 10 mm or less and a sheet width of 2000 mm or less can be applied, but the size of the steel sheet is not limited thereto.

[0026]

The material of the steel material is not particularly limited. As the steel material, for example, various steel sheets such as a general steel, a pre-plated steel in which various metals are thinly plated, an Al killed steel, an ultra-low carbon steel, a high carbon steel, various high tensile strength steels, some high alloy steels (a steel containing a corrosion resistance reinforcing element such as Ni or Cr), steels for bolts, steel wire rods for bridge cables are applicable. More specifically, as the steel material, for example, a hot-rolled steel sheet defined in JIS G 3131 (2018) and a cold-rolled steel

sheet defined in JIS G 3141 (2017), a steel material included in a general structural rolled steel material corresponding to a so-called SS material, a so-called general steel included in a hot-rolled steel sheet defined in JIS G 3193 (2019), pre-plated steels in which various metals are thinly plated described in JIS H 8641 (2021), JIS G 3302 (2019), JIS G 3303 (2017), JIS G 3313 (2017), JIS G 3314 (2019), JIS G 3315 (2017), JIS G 3317 (2019), JIS G 3321 (2019), and the like, a rolled steel material for structural use in buildings described in JIS G 3136 (2012), Al killed steel described in JIS G 3126 (2015), ultra low carbon steel, high carbon steel, various high tensile strength steels described in JIS G 3113 (2018), JIS G 3134 (2018), and JIS G 3135 (2018), and some of high alloy steels (for example, steels containing corrosion resistance-enhancing elements such as Ni and Cr) are applicable.

[0027]

Examples of a step of manufacturing the steel material include general steps such as an iron making and steelmaking step by a blast furnace or an electric furnace, a hot rolling step, a pickling step, a cold rolling step, and a heat treatment step.

[0028]

(Plated Layer)

Next, the plated layer provided on the steel material will be described.

The plated layer according to the present embodiment includes a Zn-Al-Mg-based alloy layer. In a case where an alloying element such as Al or Mg is contained in the Zn phase, corrosion resistance is improved. Therefore, such a plated layer containing the Zn phase can exhibit corrosion resistance equivalent to that of a conventional Zn-plated layer even though the plated layer is formed as a thin film (for example, the thickness of about a half of the conventional Zn-plated layer). Similarly, even in a case where the plated layer of the present embodiment is formed as a thin film,

corrosion resistance equal to or higher than that of the conventional Zn-plated layer is ensured.

[0029]

The Zn-Al-Mg-based alloy layer is made of a Zn-Al-Mg-based alloy. The Zn-
5 Al-Mg-based alloy means a ternary alloy containing Zn, Al, and Mg.

[0030]

The plated layer may include an Al-Fe-based interfacial alloy layer (with the thickness of less than 5 μm). The Al-Fe-based interfacial alloy layer is an interfacial alloy layer between the steel material and the Zn-Al-Mg-based alloy layer, and is in
10 contact with a surface of the steel material. That is, the plated layer according to the present embodiment may have a single-layer structure including the Zn-Al-Mg-based alloy layer or a stacked layer structure including the Zn-Al-Mg-based alloy layer and the Al-Fe-based interfacial alloy layer disposed between the Zn-Al-Mg-based alloy layer and the steel material. In the case of the single-layer structure, the plated layer on the steel
15 material includes one layer composed of a Zn-Al-Mg-based alloy. That is, the plated layer of the present embodiment does not include, for example, a multi-layer structure in which an Al-plated layer and a Zn-plated layer are stacked. In a case where the plated layer of the present embodiment is a stacked layer structure, the Zn-Al-Mg-based alloy layer may be a layer constituting a surface of the plated layer.

20 [0031]

The Al-Fe-based interfacial alloy layer does not have a large influence on corrosion resistance, but has an influence on adhesion and workability (presence or absence of cracks) of the plated layer during processing of the hot-dip plated steel material. In particular, the Al-Fe-based interfacial alloy layer may affect powdering
25 resistance indicating the degree of peeling of the plated layer during processing.

Usually, an Al-Fe-based interfacial alloy layer having a thin thickness can reduce the number of crack initiation sites in the plated layer during processing, thereby further improving powdering resistance. Therefore, it is preferable that the thickness of the Al-Fe-based interfacial alloy layer is as thin as possible in a hot-dip plated steel material that may be subjected to high processing when used as a member or the like. Specifically, the thickness of an intermetallic compound constituting the Al-Fe-based interfacial alloy layer is less than 5 μm . The thickness is preferably 2 μm or less, more preferably 1 μm or less, and still more preferably 0.5 μm or less. The thickness may be 0.3 μm or less. As a result, the occurrence of cracks during processing can be minimized, and the powdering resistance can be further improved. Furthermore, a ratio of the thickness of the Al-Fe-based interfacial alloy layer to the thickness of the plated layer is less than 10% on average, more preferably less than 5%.

[0032]

The Al-Fe-based interfacial alloy layer is formed on a surface of the steel material, specifically, between the steel material and the Zn-Al-Mg-based alloy layer. The Al-Fe-based interfacial alloy layer is a layer in which an Al_5Fe_2 phase is the main phase as the microstructure. The Al-Fe-based interfacial alloy layer is formed by mutual atomic diffusion between the base metal (steel sheet) and the plating bath. In a case where a continuous hot-dip plating method is used as a procedure, the Al-Fe-based interfacial alloy layer is easily formed in the plated layer containing an Al element. In the present embodiment, since a certain concentration or more of Al is contained in the plating bath, the Al_5Fe_2 phase is the predominant phase formed in the Al-Fe-based interfacial alloy layer. However, since it takes time to diffuse atoms, the Fe concentration in the Al-Fe-based interfacial alloy layer is not uniform, and the Fe concentration may be high in a portion close to the base metal. Therefore, a small

amount of an AlFe phase, an Al₃Fe phase, an Al₅Fe₂ phase, or the like may be partially contained in the Al-Fe-based interfacial alloy layer. Since a certain concentration of Zn is also contained in the plating bath, a small amount of Zn may also be contained in the Al-Fe-based interfacial alloy layer. A small amount of Si that is likely to accumulate at the interface may also be contained in the Al-Fe-based interfacial alloy layer.

[0033]

In the present embodiment, the plated layer contains Si. Si is partially incorporated into the Al-Fe-based interfacial alloy layer to form an Al-Fe-Si intermetallic compound phase. One of the identified intermetallic compound phases is an AlFeSi phase. Examples of the isomer of the AlFeSi phase include an α phase, a β phase, a q1 phase, and a q2 phase. Therefore, these AlFeSi phases and the like may be detected in the Al-Fe-based interfacial alloy layer. The Al-Fe-based interfacial alloy layer containing these AlFeSi phases and the like is also referred to as an Al-Fe-Si alloy layer.

[0034]

Next, the average chemical composition of the plated layer will be described. In a case where the plated layer has a single-layer structure of the Zn-Al-Mg-based alloy layer, the average chemical composition of the entire plated layer is the average chemical composition of the Zn-Al-Mg-based alloy layer. In a case where the plated layer has a stacked layer structure including the Al-Fe-based interfacial alloy layer and the Zn-Al-Mg-based alloy layer, the average chemical composition of the entire plated layer is the total average chemical composition of the Al-Fe-based interfacial alloy layer and the Zn-Al-Mg-based alloy layer.

[0035]

In the plated layer of the present embodiment, the thickness of the Al-Fe-based interfacial alloy layer is preferably 10% or less with respect to the thickness of the entire

plated layer. In a case where the thickness of the Al-Fe-based interfacial alloy layer is sufficiently small with respect to the entire plated layer as described above, the Fe concentration of the plated layer is often 5% or less. Therefore, the average chemical composition of the plated layer is approximately the same as the components of the Zn-Al-Mg-based alloy layer. Furthermore, traces of a plating raw material are less likely to remain as chemical components of the plated layer. Therefore, the average chemical composition of the plated layer is substantially equal to the components of the plating bath used for manufacture.

[0036]

10 Al: More Than 10.0% and Less Than 45.0%

Al is an element mainly constituting the plated layer. In a case where the Al content is 10.0% or less, a sufficient amount of a Zn-Al phase may not be ensured.

Therefore, the Al content is more than 10.0%. On the other hand, in a case where the Al content is 45.0% or more, the Al-Zn (α) phase is mainly formed in the plated layer, and the Al-Zn (β) phase is not formed. Therefore, the upper limit of the Al content is less than 45.0%. The lower limit of the Al content is preferably 15.0% or more. The upper limit of the Al content is preferably 30.0% or less, and more preferably 25.0% or less.

[0037]

Mg: 4.0% Or More and 15.0% Or Less

20 Similarly to Zn, Mg is an element mainly constituting the plated layer. Mg is an important element for improving sacrificial corrosion resistance in the plated steel sheet according to the present embodiment. In a case where the Mg content in the plated layer is less than 4.0%, the improvement effect of sacrificial corrosion resistance is not clearly observed as compared with the case where Mg is not contained. Therefore, the Mg content is 4.0% or more. In contrast, in a case where Mg is excessively added in

the Zn-Al-Mg-based plating bath, a rapid oxidation reaction occurs on a bath surface of the plating bath, and plating cannot be stably performed. Therefore, in order to stably perform plating and ensure good manufacturability, the Mg content in the plated layer is 15% or less.

5 [0038]

Si: 0% Or More and 2.0% Or Less

Si suppresses an Al-Fe reaction, thereby inhibiting the formation of an Al-Fe-based interfacial alloy layer. In addition, Si is incorporated into part of the Al-Fe-based interfacial alloy layer to form an Al-Fe-Si compound. In the present embodiment, Si
10 may not be contained. However, in a case where Si is not contained, the Al-Fe reaction becomes active, the thickness of the Al-Fe alloy layer increases, powdering occurs during processing, and corrosion resistance may be impaired. On the other hand, in a case where the Si content is 0.01% or more, the growth rate of the thickness of the interfacial alloy layer is reduced. However, in a case where the Si content is more than 2.0%, an
15 intermetallic compound having a composition in which Mg reacts with Si to form Mg_2Si is formed in a large amount, resulting in the extremely high viscosity of the plating bath. Therefore, the adhesion amount of molten metal to the steel material is reduced when the steel material is pulled up from the plating bath, and the thickness of the plated layer is extremely thin. In addition, the plating appearance is significantly deteriorated.
20 Therefore, the upper limit of the Si content is 2.0% or less. The preferable range is 0.05% to 0.50%, more preferably 0.10% to 0.40%, and still more preferably 0.20% to 0.30%. In a case where the Si content is 1.50% or less, Mg_2Si is less likely to be formed.

[0039]

25 Sr: 0.03% Or More and 1.50% Or Less

Sr is an element that produces the same effect as Ca. Sr forms a covalent bond with Zn, Al, Si, or the like, and forms an intermetallic compound excellent in corrosion resistance and hardness. In a case where the Sr content is less than 0.03%, the amount of the intermetallic compound formed is insufficient. Therefore, the effect of improving corrosion resistance and hardness cannot be sufficiently obtained. In contrast, in a case where the Sr content exceeds 1.50%, a Sr-based intermetallic compound is excessively generated in the plated layer, and the hardness of the entire plated layer increases. As a result, the plated layer is easily broken during forming working of a plated steel material used as a raw material, and peeling of the plated layer such as powdering may occur.

Thus, the Sr content is 0.03% or more and 1.50% or less.

[0040]

Sn: 0% or more and 0.7% or less

Bi: 0% or more and 0.3% or less

In: 0% or more and 0.3% or less

Total amount ΣX of Sn, Bi, and In: 0% Or More and 0.7% Or Less

Each of Sn, Bi, and In is an element that promotes softening of the plated layer when contained in the plated layer. Since Sn, Bi, and In are elements that can be optionally contained, each content is 0% or more. When Sn is contained, Mg_9Sn_5 tends to be formed in the plated layer. Bi forms Mg_3Bi_2 , and In forms Mg_3In , for example.

These elements are softer than the $MgZn_2$ phase and have good workability, so that containment of these elements in the plated layer clearly improves workability. These elements also exhibit very low electrochemical nobility, and thus provide a high sacrificial anticorrosion effect. By containing at least one of Sn, Bi, and In within the above-described range, the effect of improving worked portion corrosion resistance can be obtained.

[0041]

Ca: 0% or more and 0.6% or less

Y: 0% or more and 0.3% or less

La: 0% or more and 0.3% or less

5 Ce: 0% or more and 0.3% or less

Li: 0% or more and 0.3% or less

Ni: 0% or more and 1.0% or less

Cu: 0% or more and 1.0% or less

Ag: 0% or more and 0.25% or less

10 Sb: 0% or more and 0.25% or less

Pb: 0% or more and 0.25% or less

B: 0% or more and 0.5% or less

P: 0% or more and 0.5% or less

Ti: 0% or more and 0.25% or less

15 Co: 0% or more and 0.25% or less

V: 0% or more and 0.25% or less

Nb: 0% or more and 0.25% or less

Mn: 0% or more and 0.25% or less

Zr: 0% or more and 0.25% or less

20 W: 0% or more and 0.25% or less

Ca, Y, La, Ce, Sr, Li, Ni, Cr, Mo, Sb, Pb, B, P, Ti, Co, V, Nb, Mn, Zr, and W all

form an intermetallic compound with Si, Zn, Al, or the like. However, in a case where

the amounts of these elements are within the above-described range, the elements do not

affect the initial corrosion of the plated layer. In contrast, in a case where these

25 elements are excessively contained, a potential difference may be generated in the plated

layer, and a large amount of initial white rust may be formed. Therefore, in the case where these elements are contained, the amounts thereof may be within the above-described range.

[0042]

5 Fe: 0% Or More and 5.0% Or Less

Since the hot-dip plated steel material of the present embodiment is manufactured by a continuous hot-dip plating method, Fe may be diffused into the plated layer from the plating raw material during manufacturing. As described above, in the present embodiment, the Al concentration of the plated layer is high, and the Al-Fe-based
10 interfacial alloy layer may be formed, but the thickness thereof is thin. As a result, Fe may be contained in the plated layer up to 5.0%, but Fe does not affect the frequency of occurrence of cracks and the like in the plated layer as long as the Fe concentration is limited to 5.0% or less. Therefore, the Fe content is 0 to 5.0%. The Fe content may be more than 0%.

15 [0043]

Remainder: Zn and Impurities

The remainder preferably contains Zn. Since the hot-dip plated steel material of the present embodiment is a highly versatile Zn-based plated steel material, the element constituting the main phase of the plated layer is Zn.

20 [0044]

The impurity refers to a component that is contained in the raw material or mixed in the manufacturing step and not intentionally contained. For example, in the plated layer, a small amount of component other than Fe may be mixed as the impurity due to mutual atomic diffusion between the steel material (base metal) and the plating
25 bath. In addition, since a metal having a purity of 3 N is usually used for manufacturing

a plating alloy, the concentration of impurities may be approximately 0.03% or less in total.

[0045]

In order to identify the average chemical composition of the plated layer, an acid solution is obtained in which the plated layer is peeled off and dissolved with an acid containing an inhibitor that inhibits corrosion of the base metal (steel material). Next, the obtained acid solution is measured by ICP emission spectrometry or an ICP-MS method to obtain the chemical composition. The type of the acid is not particularly limited as long as the acid can dissolve the plated layer. In a case where the area and weight before and after peeling are measured, a plating adhesion amount (g/m^2) can also be obtained at the same time.

[0046]

Next, the intermetallic compound contained in the plated layer will be described.

Since the plated layer according to the present embodiment is made of Zn-Al-Mg-based alloy plating, the plated layer contains a Zn phase, an Al phase, and a MgZn_2 phase. In addition, the plated layer of the present embodiment contains a Sr-containing intermetallic compound. Furthermore, the plated layer of the present embodiment may contain other intermetallic compounds.

[0047]

20 MgZn_2 Phase

The MgZn_2 phase is a phase intentionally contained in the plated layer in order to achieve high corrosion resistance of the plated layer. When a certain amount of the MgZn_2 phase is contained in the plated layer, corrosion resistance in an environment with water exposure can be further improved.

25 [0048]

Zn phase (Al-Zn phase and Zn-Al phase)

A Zn phase is mainly present in the plated layer as a ternary eutectic structure (Zn/Al/MgZn₂ ternary eutectic structure). In a case where the plated layer contains a large amount of Al, Zn in the Zn phase and Al may be mixed with each other in the solid state, whereby an Al-Zn phase is formed, and Zn may also dissolve as a solid solution within the Al phase. On the other hand, Al may form a solid solution in the Zn phase to form a Zn-Al phase (the Al concentration in the phase is up to about 20%). The phase containing Zn and Al has extremely high workability.

[0049]

10 Al Phase

An Al phase is present in a massive form as an Al primary phase in the plated layer. The Al phase forms a solid solution with various elements, particularly Zn, within its phase during the solidification process of the plated layer. Since the plated layer of the present embodiment has a high Al content, the Al phase contains an element such as Zn in a supersaturated manner in the solidification process. In the solidification process, the Al phase forms a dendrite microstructure spreading in a dendritic shape in the plated layer and forms a frame of the plated layer. Since the Al phase is soft and rich in workability, the Al phase inhibits the propagation of cracks that have occurred and reduces critical defects in the plated layer

20 [0050]

Sr-Containing Intermetallic Compound

The plated layer according to the present embodiment includes Sr-containing intermetallic compounds exemplified by a Zn-Sr-based compound, a Zn-Sr-Si-based compound, and a Zn-Al-Sr-Si-based compound. These are formed in the plated layer by containing Sr in the plated layer.

[0051]

The intermetallic compounds formed in the plated layer generally serve to enhance corrosion resistance and hardness due to the intricate bonding of individual atoms. On the other hand, in a case where the content is too large, plastic deformability
5 may be lost. In particular, in a case where metal compounds are continuously formed in a layered manner on the plated surface and the interface, cohesive peeling may occur during bending, and surface peeling and/or interface peeling may occur due to a difference in corrosion rate during corrosion. Therefore, it is necessary to reduce the accumulation of the intermetallic compound on the surface and in the vicinity of the
10 interface.

[0052]

Here, Ca is known as an element effective for improving the corrosion resistance and hardness of the plated layer, but as described above, the Ca-containing intermetallic compound is a compound that is easily formed into a layer, and particularly easily
15 accumulates at the interface. This is because an intermetallic compound based on CaZn_4 tends to be formed easily in a case where Ca is excessively contained in the Zn-Al-Mg-based plated layer. On the other hand, Sr has almost the same action as Ca, but the Zn-Sr-based compound is an intermetallic compound based on SrZn_{13} , and tends to be less likely to accumulate at the interface as compared with the Ca-containing
20 intermetallic compound.

In addition, the more the intermetallic compound is accumulated in the central part of the plated layer, the more workability is improved, so that powdering does not occur even under severe working conditions. In particular, by containing the Sr-containing intermetallic compound so as to satisfy each expression described later, the
25 hardness of the plated layer is further increased to improve the defect resistance, the flat

portion corrosion resistance is improved, the steel material is hard as a plated steel material, and good workability and corrosion resistance can be secured.

[0053]

Thus, by containing the Sr-containing intermetallic compound in the central part
5 of the plated layer, the powdering phenomenon can be more efficiently avoided, and both workability and corrosion resistance can be improved.

[0054]

In order to further obtain the above-described effects, it is preferable that the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound are contained at an area
10 fraction of 5% to 30%.

In a case where Si is excessively contained in the plated layer, Mg_2Si is formed. However, Mg_2Si has a strong sacrificial corrosion resistance, and is an undesirable compound for improving the corrosion resistance of a flat portion. On the other hand, the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound exhibit a potential
15 slightly less noble than that of Zn, do not exhibit excessive sacrificial corrosion resistance, and gradually corrode Zn. That is, the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound, each having a complex metal element bond, exhibit an appropriate value as a potential while having a property of a low corrosion rate, and the bond is further strengthened by dissolving Si in a solid solution, and therefore corrosion
20 resistance can be extremely increased by containing the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound. That is, the corrosion resistance is significantly improved by appropriately controlling the area fractions of the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound. The area fractions of the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound are preferably as large as possible.
25 However, from the upper limit value of the amount of Sr that can be contained in the

plated layer, the area fractions of the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound are substantially 30% or less in total.

[0055]

These intermetallic compounds can be measured using an electron beam microanalyzer (EPMA). Specifically, first, EPMA analysis of a cross section along the thickness direction of the plated layer is performed at an analysis magnification of 1000 times, and all microstructures in which Zn, Sr, and Si are detected at the same position are specified. Then, using commercially available image editing software “Photoshop (registered trademark)”, each of the microstructures specified above is surrounded, the number of pixels (px) in the surrounded range is calculated, and the number of px in each microstructure is summed to obtain the total px number of intermetallic compounds in the field of view. Thereafter, the obtained total px number is converted into an area to calculate the area fractions of the intermetallic compound. In the present embodiment, the same operation as described above is performed in 20 fields of view. That is, 20 different fields of view are randomly selected in the cross section of the plated layer, the area fraction of the intermetallic compound is determined in each field of view by the above method, and the average value thereof is used as the area fraction of the metal compound in the plated layer.

[0056]

Next, a method for identifying the Sr-containing intermetallic compound in the plated layer according to the present embodiment will be described.

[0057]

As the analysis method for components in the plated layer in the depth direction, a glow discharge optical emission spectrometry (GDS) with a glow discharge optical emission spectrometer may be used. In the present embodiment, LECO Japan 850A is

used as the glow discharge optical emission spectrometer, but the measurement apparatus is not limited thereto. In addition, in a case of performing analysis in the depth direction, it is preferable to perform the analysis while performing Ar sputtering, the analysis conditions include an argon pressure of 0.27 MPa, an output power of 30 W, an output voltage of 1000 V, and a discharge region in a circular region having a diameter of 4 mm.

The component analysis by GDS is performed from the surface of the plated layer toward the depth direction until the Fe concentration reaches 100% (reaches the base metal). Therefore, the analysis range of the depth direction analysis carried out by GDS is a range reaching from the plated surface to the Zn-Al-Mg plated layer, the Al-Fe alloy layer, and part of the steel material. After the GDS analysis, the sputtering depth of the cross section is measured using surfcom130A manufactured by Tokyo Seimitsu Co. Ltd. The elemental distribution profile of the plated layer in the depth direction is obtained by the component analysis using GDS. In the elemental distribution profile, in a case where the total amount of the detected elements is 100%, the distribution of the amount of each element in the depth direction is illustrated.

[0058]

In the present embodiment, in a case where, in an elemental distribution profile obtained by a qualitative analysis using GDS in a direction from a surface of the plated layer toward the steel material, the thickness of the plated layer is denoted by t , the average value of a qualitative analysis value of Sr from the surface of the plated layer to $0.05 t$ is denoted by Sr (surf), a qualitative analysis value in a range of $0.05 t$ to $0.66 t$ starting from the surface of the plated layer is denoted by Sr (center), and a qualitative analysis value in a range of more than $0.66 t$ and t starting from the surface of the plated layer is denoted by Sr (deep), the following Expression (1) is satisfied.

[0059]

$Sr(\text{surf}) < Sr(\text{deep}) < Sr(\text{center}) \dots (1).$

[0060]

By accumulating the Sr-based intermetallic compound in the central part of the plated layer to satisfy the above Expression (1), workability can be improved, and powdering can be avoided even under severe working conditions. That is, by satisfying Expression (1), the hardness of the plated layer is further increased to improve the defect resistance, the flat portion corrosion resistance is improved, the steel material is hard as a plated steel material, and good workability and corrosion resistance can be secured.

10 [0061]

In the present embodiment, in the elemental distribution profile obtained by the qualitative analysis using the GDS method in the direction from a surface of the plated layer toward the steel material, the depth position where the Fe intensity corresponding to 5% with respect to the maximum intensity of Fe is detected is defined as an “interface”, and the region up to this interface is referred to as a “plated layer”.

[0062]

FIG. 1 illustrates an example of a depth direction analysis result by GDS in the plated layer according to the present embodiment. The graph illustrated in FIG. 1 is an elemental distribution profile. An interface between the plated layer and the steel material is determined to be a position where the Fe intensity is more than 5% of the maximum intensity, and a region deeper than the position is determined to be a base metal (steel material). For example, the analysis result as illustrated in FIG. 1 demonstrates that since Fe has a maximum intensity of 1.5 cps, a position at which the intensity is 5%, that is, a position at which the Fe intensity is 0.075 cps is set as an interface between the plated layer and the steel material.

[0063]

In order to achieve an appropriate distribution of the Sr-containing intermetallic compound in the plated layer, it is effective to appropriately control the manufacturing conditions. A suitable manufacturing method will be described later.

5 [0064]

Next, an index of the Sr-containing intermetallic compound by X-ray diffraction will be described.

[0065]

In the plated layer according to the present embodiment, in a case where a
10 diffraction intensity of the Zn-Sr-based compound in a X-ray diffraction pattern of the surface of the plated layer is denoted by $I(\text{SrZn}_{13})$, the diffraction intensity being measured by using Cu-K α radiation under conditions of 50 kV and 300 mA X-ray output, Expression (2) is satisfied,

[0066]

15
$$\{I(14.48^\circ) + I(32.74^\circ)\} / 2 \times I(12.50^\circ) > 2.0 \dots (2)$$

Here, in Expression (2), $I(n^\circ)$ is the X-ray diffraction intensity at a diffraction angle n° , and n is a diffraction angle (2θ) indicated in Expression (2).

[0067]

FIG. 2 illustrates an example representing an X-ray diffraction pattern in the
20 plated layer according to the present embodiment. As illustrated in FIG. 2, the peaks of the Zn-Sr-based compound composed of the Sr-containing intermetallic compound appear in the vicinity of 14.48° and in the vicinity of 32.74° . In a case where the intensity of the background is $I(12.50^\circ)$, an intermetallic compound excellent in corrosion resistance and hardness is formed in the plated layer by satisfying the above
25 Expression (2). As a result, high hardness and corrosion resistance can be exhibited

while maintaining the plastic deformability of the plated surface and the interface.

[0068]

[Method for Manufacturing Hot-Dip Plated Steel Material]

Next, a method for manufacturing the hot-dip plated steel material of the present
5 embodiment will be described.

As a method for forming the plated layer as described above, it is conceivable to perform plating by directly adding Sr to a Zn-Al-Mg-based plating bath. However, in this method, there is a concern that the Sr-based intermetallic compound is formed not at the central part of the plated layer but at the surface and the vicinity thereof. Therefore,
10 as an example of a suitable procedure for manufacturing the hot-dip plated steel material of the present embodiment, a method for supplying Sr from a pre-plated layer provided on a plating original sheet to a plated layer will be described below as an example. Note that, in the present specification, as described above, a method for forming a predetermined pre-plated layer in advance on the plating original sheet and then
15 sequentially performing Zn-Al-Mg-based hot-dip plating is referred to as a “two-stage plating method”.

[0069]

First, an Al-Sr pre-plated layer is formed in advance on a plating original sheet such as a cold-rolled or hot-rolled steel sheet. The plating means may be hot-dip
20 plating, electro plating, substitution plating, vapor deposition, or the like. Furthermore, these pre-plated layers may be heated and alloyed.

[0070]

In a case where the pre-plating on the original sheet is performed by hot-dip plating, the pre-plating may be performed by a method for adding Sr to conditions for
25 forming normal aluminum plating, such as an Al-0.3% Sr bath and an Al-5% Sr bath, and

there is no particular limitation.

[0071]

Next, the plating original sheet is heated to 450°C to 600°C, and is preferably heated to the same temperature as the temperature of the plating bath described later.

- 5 The heating may also serve as annealing of the original sheet (hereinafter, the heating may be referred to as pre-annealing). By heating the steel sheet before immersion in a plating bath to be described later, temperature fluctuation of the plating bath can be reduced.

[0072]

- 10 The heated original sheet on which the pre-plated layer is formed is immersed in the plating bath, and then pulled up. The temperature of the plating bath is preferably in a range of 450°C to 600°C. In a case where the temperature of the plating bath is too low, the reaction between the pre-plated layer and the hot-dip plating bath does not proceed, and Sr cannot be sufficiently supplied to the plating bath. In addition, in a case
- 15 where the temperature of the plating bath is too low, the plating adhesion of the resulting plated steel material is poor. Therefore, the bath temperature is preferably 450°C or higher. The temperature is more preferably 470°C or higher, still more preferably 500°C or higher, and even still more preferably 550°C or higher. On the other hand, in a case where the temperature of the plating bath is too high, evaporation of Zn in the
- 20 plating bath is significant, and it is practically difficult to perform a stable operation. Therefore, the bath temperature is preferably 600°C or lower. The bath temperature is more preferably 580°C or lower.

- Furthermore, in the present embodiment, temperature control is preferably performed when the plating original sheet is pulled up. That is, by performing
- 25 appropriate temperature control and cooling control after immersion, Sr is contained in

the plated layer. Therefore, a desired Sr-based intermetallic compound can be formed.

[0073]

The Sr-based intermetallic compound is an element that is likely to form a solid solution. This is because Mg is contained in the plated layer.

5 [0074]

In addition, in order to sufficiently form the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound, the average cooling rate in a temperature range of 450°C to 350°C is preferably 10°C/sec or less. In a case where the average cooling rate in a temperature range of 450°C to 350°C is more than 10°C/sec, Sr and Si are uniformly
10 dispersed in the thickness direction of the plated layer, and a desired plated layer may not be obtained.

[0075]

The cooling condition in the temperature range of lower than 350°C is not particularly limited because it does not affect the formation of the intermetallic
15 compound, and the like.

[0076]

As described above, by appropriately controlling the cooling rate after the plating original sheet is pulled up from the bath, the formation of the Sr-based intermetallic compound on the surface and interface of the plated layer can be
20 suppressed, and the Sr-based intermetallic compound can be appropriately dispersed in the vicinity of the central part of the plated layer. As a result, high plating hardness, workability, and corrosion resistance can be exhibited while maintaining the plastic deformability of the plated surface and the interface.

[0077]

25 In addition, in a case where a steel sheet on which the Al-Sr pre-plated layer is

formed is used as a plated substrate, the plating bath and the Al-Sr-based intermetallic compound have moderate reactivity. Therefore, the traces of the Al-Sr pre-plated layer disappear immediately at the same time as immersion in the Zn-Al-Mg-based plating bath at around 550°C, and the immersion plating bath and the Al-Sr-based intermetallic compound can be easily blended. As a result, a desired plated layer of the present embodiment can be formed.

[0078]

Next, a method for evaluating performance of the hot-dip plated steel material will be described.

10 [0079]

(Bending Workability)

A bending workability of the plated steel material of the present embodiment can be evaluated by measuring the powdering amount (peeling amount) after 0 R to 5 R-60 degrees-V-bending, and then straightening.

15 [0080]

Specifically, after forming with a 2 R-60 degree-V-shaped die press, the plated steel material is further subjected to reverse bending using a flat sheet die. After the V-shaped processing, a cellophane tape having a width of 24 mm is pressed against the former bend bottom and pulled off, and a portion having a length of 90 mm of the cellophane tape is visually determined.

20

Here, the evaluation criteria are as follows.

[0081]

<Evaluation Criteria>

A: There are no peeled portions.

25

B: There are some peeled portions in the form of spots. (accounting for less

than 5% with respect to the processed area).

C: There are line-shaped peeled portions (accounting for 5% to less than 10% of the processed area).

5 D: There are line-shaped peeled portions (accounting for 10% to less than 20% of the processed area).

E: Peeled portions are almost entirely peeled off (accounting for 20% or more of the processed area).

[0082]

(Corrosion Resistance)

10 A flat portion test piece having the thickness of 2.3 mm is prepared, and the corrosion weight loss of JASO is measured at 120 cycles.

The evaluation criteria were as follows.

[0083]

<Evaluation Criteria>

15 E: A case where the corrosion weight loss is 25 g/m² or more.

D: A case where the corrosion weight loss is 20 g/m² or more.

C: A case where the corrosion weight loss is 15 g/m² or more.

B: A case where the corrosion weight loss is 10 g/m² or more.

A: A case where the corrosion weight loss is 5 g/m² or more.

20 S: A case where the corrosion weight loss is less than 5 g/m².

[0084]

(Hardness)

As an evaluation index of the defect resistance of the plated layer, hardness by the Vickers test is adopted. Specifically, the Vickers hardness of the surface of the
25 plated layer is measured under a load of 10 gf. The Vickers hardness is the average

hardness of the plated layer at 10 points.

[0085]

After the plated layer is formed, various chemical conversion treatments and coating treatments may be performed.

5 [0086]

In the hot-dip plated steel material of the present embodiment, a film may be formed on the plated layer. A film having a single layer or two or more layers may be formed. Examples of the type of the film immediately above the plated layer include a chromate film, a phosphate film, and a chromate-free film. A chromate treatment, a phosphating treatment, and a chromate-free treatment for forming these films can be performed by known methods.

[0087]

The chromate treatment includes an electrolytic chromate treatment in which a chromate film is formed by electrolysis, a reaction type chromate treatment in which a film is formed by utilizing a reaction with the material and then the excess treatment liquid is washed away, and an application type chromate treatment in which a film is formed by applying a treatment liquid to an object to be coated and drying the treatment liquid without washing with water. Any treatment may be adopted.

[0088]

20 Examples of the electrolytic chromate treatment include an electrolytic chromate treatment using chromic acid, a silica sol, a resin (phosphoric acid, an acrylic resin, a vinyl ester resin, a vinyl acetate acrylic emulsion, a carboxylated styrene-butadiene latex, a diisopropanolamine-modified epoxy resin, and the like), and hard silica.

[0089]

25 Examples of the phosphating treatment include a zinc phosphate treatment, a

zinc calcium phosphate treatment, and a manganese phosphate treatment.

[0090]

The chromate-free treatment which does not impose a burden on the environment is particularly suitable. The chromate-free treatment includes an electrolytic chromate-free treatment in which a chromate-free film is formed by electrolysis, a reaction type chromate-free treatment in which a film is formed by utilizing a reaction with the material and then the excess treatment liquid is washed away, and an application type chromate-free treatment in which a film is formed by applying a treatment liquid to an object to be coated and drying the treatment liquid without washing with water. Any treatment may be adopted.

[0091]

Further, an organic resin film made of a single layer or two or more layers may be formed on the film immediately above the plated layer. The organic resin is not limited to a specific type, and examples thereof include polyester resins, polyurethane resins, epoxy resins, acrylic resins, polyolefin resins, and modified products of these resins. Here, the modified product refers to a resin obtained by causing a reactive functional group included in the structures of these resins to react with another compound (a monomer, a crosslinking agent, or the like) having a functional group capable of reacting with the functional group in the structure thereof.

[0092]

As such an organic resin, one or more types of organic resins (unmodified organic resins) may be mixed and used, or one or more types of organic resins obtained by modifying, in the presence of at least one type of organic resin, at least one type of other organic resin may be mixed and used. The organic resin film may contain any coloring pigment or antirust pigment. Also, water-based organic resins which are

dissolved or dispersed in water may be used.

Examples

[0093]

Next, Examples of the present invention will be described, but conditions in

5 Examples are examples of conditions adopted to confirm feasibility and an effect of the present invention, and the present invention is not limited to these examples of conditions. The present invention may adopt various conditions as long as an object of the present invention is achieved without departing from the gist of the present invention.

[0094]

10 First, a cold-rolled steel sheet (SPCC) having a size of 100 mm × 200 mm and a sheet thickness of 0.8 mm was prepared as a plating original sheet. For this cold-rolled steel sheet, first, an Al-Sr pre-plated layer as described in Tables 1A and 1B was formed on the sheet surface using the following Al-Sr-based plating bath. The term “Two-stage” in the “Procedure” column in Tables 1A and 1B indicates that the above-described
15 two-stage plating method was applied. “Sendimer” in Tables 1A and 1B indicates that a method without performing pre-plating was applied. “SPCC” in the item of “Composition” in the “Pre-plated layer” column in Tables 1A and 1B indicates that there is no pre-plated layer (therefore, the cold-rolled steel sheet (SPCC) of the original sheet appears.).

20 [0095]

Al-Sr-based Plating Bath: Sr: 0.3 to 10mass% and Bath Temperature: 650°C.

[0096]

After an Al-Sr pre-plated layer was formed on the plating original sheet, the plating original sheet was heated at 550°C for 0.5 to 3.0 minutes to perform pre-
25 annealing.

[0097]

The resulting plated substrate was hot-dip plated in a hot-dip plating simulator.

First, alloys having plating bath components illustrated in Tables 1A to 1B were prepared by a vacuum dissolution method, and a plating bath was formed in a completely
5 oxygen-free and nitrogen-substituted atmosphere (O_2 concentration: less than 5 ppm).

Next, one point (the center rear surface of the evaluation surface) of the plating original sheet was bonded to a K thermocouple by spot welding, and the temperature history until the completion of plating solidification was grasped. The plated steel sheet is heated to a predetermined temperature in a H_2 (25%) - N_2 atmosphere. The plating
10 bath temperature was set to 550°C, the plated substrate was immersed at an immersion rate of 600 mm/sec, stopped in the bath for 3 seconds, and the plated substrate was then pulled up at 600 mm/sec.

Immediately after the pulling up, the plating thickness was adjusted to 40 μm with N_2 wiping gas, and N_2 gas whose flow rate was controlled in an oxygen-free and
15 nitrogen-replaced atmosphere was then blown and cooled at the average cooling rate illustrated in Table 1.

A plated steel sheet was obtained by the above-described steps.

[0098]

Next, samples for evaluation were cut out from the various plated steel sheets.
20 Each sample for GDS analysis and SEM observation was cut out at a 30 mm square position on the opposite side to the thermocouple position. As the sample for corrosion, 100 × 50 mm was taken from the center portion of the plated steel sheet.

[0099]

As the evaluation of the various samples that have been cut, a bending test,
25 Vickers hardness measurement, and a corrosion test SST were performed. Among the

compositions of the plated layer, the composition of Fe was not described in the tables, but was in a range of 0% to 5%.

The evaluation results, the composition of the plated layer, the GDS analysis results, the X-ray diffraction (XRD) results, the area fraction of the Zn-Sr-Si-based compound and the Zn-Al-Sr-Si-based compound, and the like are illustrated in Tables 2A and 2B. Note that the underline in each table indicates that the numerical value is out of the range of the present invention or out of the preferable manufacturing conditions, or the characteristic value is not preferable.

In Comparative Example No. 49, since the temperature of the plating bath was low, the reaction between the Al-Sr pre-plated layer and the plating bath did not sufficiently proceed. As a result, the Al-Sr pre-plated layer remained between the original sheet and the plated layer, and a suitable hot-dip plated steel material could not be obtained. The plated steel material of No. 49 had deteriorated plating adhesion, and therefore could not be soundly evaluated for the GDS analysis result, X-ray diffraction (XRD), and each performance (indicated by “-” in the table).

[0100]

[Table 1A]

No.	Type	Manufacturing method							Type				
		Procedure	Bath temperature (°C)	Average cooling rate(°C/sec) 450°C to 350°C	Pre-plated layer		Plating bath component(mass%) : remainder Zn						
					Composition	Adhesion amount (g/m ²)	Al	Mg		Ca	Sr	Si	Others
1	Comparative Example	Sendimer	550	15	SPCC	-	11.0	5.0	0	0.02	0		Comparative Example
2	Comparative Example	Two-stage	550	5	Al-0.3%Sr	14	4.7	5.4	0	0	0		Comparative Example
3	Comparative Example	Sendimer	550	15	SPCC	-	11.0	5.0	0	0.03	0		Comparative Example
4	Example	Two-stage	550	5	Al-0.48%Sr	13	5.4	5.3	0	0	0.0		Example
5	Example	Two-stage	550	5	Al-0.48%Sr	13	5.4	5.3	0	0	0.0		Example
6	Example	Two-stage	550	6	Al-0.48%Sr	13	5.4	5.3	0	0	0.0		Example
7	Example	Two-stage	550	5	Al-1.5%Sr	14	4.7	5.4	0	0	0	La, Ce = 0.05	Example
8	Example	Two-stage	550	10	Al-1.5%Sr	14	4.7	5.4	0	0	0	La, Ce = 0.05	Example
9	Example	Two-stage	550	10	Al-1.5%Sr	14	4.7	5.4	0	0	0	La, Ce = 0.05	Example
10	Example	Two-stage	550	10	Al-1.5%Sr	14	4.7	5.4	0	0	0	La, Ce = 0.05	Example
11	Example	Two-stage	550	5	Al-1.5%Sr	14	4.7	5.4	0	0	0	Y = 0.05	Example
12	Example	Two-stage	550	10	Al-1.5%Sr	14	4.7	5.4	0	0	0	Y = 0.05	Example
13	Example	Two-stage	550	10	Al-1.5%Sr	14	4.7	5.4	0	0	0	Y = 0.05	Example
14	Example	Two-stage	550	10	Al-1.5%Sr	14	4.7	5.4	0	0	0	Y = 0.05	Example
15	Comparative Example	Sendimer	550	15	SPCC	-	11.0	5.0	0	0.3	0		Comparative Example
16	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0		Example
17	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0		Example
18	Example	Two-stage	550	10	Al-5%Sr	13	5.6	5.3	0	0	0		Example
19	Example	Two-stage	550	10	Al-5%Sr	13	5.6	5.3	0	0	0		Example
20	Example	Two-stage	550	4	Al-5%Sr	18	10.2	6.8	0.2	0	0.1	Sn = 0.1	Example
21	Example	Two-stage	550	4	Al-3%Sr	30	3.7	7.3	0.2	0.23	0.1	Sn = 0.1	Example
22	Example	Two-stage	550	4	Al-5%Sr	34	0.5	10.3	0.2	0.40	0.1	Sn = 0.1	Example
23	Example	Two-stage	550	4	Al-5%Sr	9	21.0	8.6	0.2	0	0.1	Sn = 0.1	Example
24	Example	Two-stage	550	4	Al-5%Sr	9	21.0	8.6	0.2	0	0.1	Sn = 0.1	Example
25	Example	Two-stage	550	4	Al-5%Sr	16	18.2	8.9	0.4	0	0.1	Sn = 0.1	Example

[0101]

[Table 1B]

No.	Type	Manufacturing method							Type				
		Procedure	Bath temperature (°C)	Average cooling rate(°C/sec) 450°C to 350°C	Pre-plated layer		Plating bath component(mass%) : remainder Zn						
					Composition	Adhesion amount (g/m ²)	Al	Mg		Ca	Sr	Si	Others
26	Example	Two-stage	550	4	Al-5%Sr	31	10.7	9.7	0.5	0	0.1	Ni = 0.1	Example
27	Example	Two-stage	550	4	Al-10%Sr	23	15.3	9.3	0.5	0	0.1	Cr = 0.1	Example
28	Example	Two-stage	550	4	Al-10%Sr	23	14.3	9.3	0.5	0.77	0.1	Mo = 0.1	Example
29	Example	Two-stage	550	4	Al-5%Sr	20	18.9	11.2	0.4	0.33	0.1	Cu = 0.1	Example
30	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.1	Ti = 0.05	Example
31	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.1	W = 0.05	Example
32	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.3	Co = 0.05	Example
33	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.5	V = 0.05	Example
34	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.5	V = 0.05	Example
35	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.5	V = 0.05	Example
36	Example	Two-stage	550	10	Al-5%Sr	13	5.6	5.3	0	0	0.5	V = 0.05	Example
37	Example	Two-stage	550	4	Al-5%Sr	13	5.6	5.3	0	0	0.8		Example
38	Example	Two-stage	550	4	Al-5%Sr	11	13.9	4.9	0	0	0.1		Example
39	Example	Two-stage	550	4	Al-5%Sr	11	13.9	4.9	0	0	0.3	Sb = 0.05	Example
40	Example	Two-stage	550	4	Al-5%Sr	11	13.9	4.9	0	0	0.5		Example
41	Example	Two-stage	550	4	Al-5%Sr	11	13.9	4.8	0	0	0.8		Example
42	Example	Two-stage	550	4	Al-3%Sr	17	19.3	4.7	0	0	0.1		Example
43	Example	Two-stage	550	4	Al-3%Sr	17	19.2	4.7	0	0	0.3		Example
44	Example	Two-stage	550	4	Al-3%Sr	17	19.2	4.7	0	0	0.5		Example
45	Example	Two-stage	550	4	Al-3%Sr	17	19.1	4.7	0	0	1.1		Example
46	Example	Two-stage	550	4	Al-3%Sr	17	19.1	4.7	0	0	1.1		Example
47	Example	Two-stage	550	4	Al-3%Sr	17	19.1	4.7	0	0	1.1		Example
48	Example	Two-stage	550	10	Al-3%Sr	17	19.1	4.7	0	0	0.1		Example
49	Comparative Example	Two-stage	400	4	Al-5%Sr	13	5.6	5.3	0	0	0		Comparative Example

[0102]

[Table 2A]

No.	Plated layer							GDS (Intensity cps)				XRD	Area fraction (%)	Performance			Type
	Chemical composition (mass%) : remainder Zn							Sr (surf)	Sr (center)	Sr (deep)	I (SrZn ₁₃)			Hardness (Hv)	Bending workability	Flat portion corrosion resistance	
	Al	Mg	Ca	Sr	Si	Others											
1	11.0	5.0	0	0.02	0			0.04	0.03	0.02	1.1	1	270	E	E	Comparative Example	
2	11.0	5.4	0	0.02	0			0.01	0.01	0.04	1.2	1	270	E	E	Comparative Example	
3	11.0	5.0	0	0.03	0			0.05	0.04	0.03	1.2	1	275	E	E	Comparative Example	
4	11.0	5.3	0	0.03	0			0.028	0.032	0.029	1.5	4	300	D	D	Example	
5	11.0	5.3	0	0.03	0			0.028	0.032	0.029	1.5	4	300	D	D	Example	
6	11.0	5.3	0	0.03	0			0.028	0.031	0.029	1.5	2	300	D	D	Example	
7	11.0	5.4	0	0.1	0	La, Ce = 0.05		0.11	0.14	0.12	2.0	5	300	B	B	Example	
8	11.0	5.4	0	0.1	0	La, Ce = 0.05		0.11	0.14	0.12	1.8	5	300	C	B	Example	
9	11.0	5.4	0	0.1	0	La, Ce = 0.05		0.11	0.14	0.12	2.0	3	300	B	C	Example	
10	11.0	5.4	0	0.1	0	La, Ce = 0.05		0.11	0.14	0.12	1.8	3	310	C	C	Example	
11	11.0	5.4	0	0.2	0	Y = 0.05		0.1	0.14	0.12	2.0	5	300	A	A	Example	
12	11.0	5.4	0	0.2	0	Y = 0.05		0.1	0.14	0.12	1.8	5	305	B	A	Example	
13	11.0	5.4	0	0.2	0	Y = 0.05		0.1	0.14	0.12	2.0	3	300	A	B	Example	
14	11.0	5.4	0	0.2	0	Y = 0.05		0.1	0.14	0.12	1.8	3	305	B	B	Example	
15	11.0	5.0	0	0.3	0			0.4	0.2	0.1	2.3	4	290	C	D	Comparative Example	
16	11.0	5.3	0	0.3	0			0.1	0.4	0.3	2.5	10	305	A	B	Example	
17	11.0	5.3	0	0.3	0			0.1	0.4	0.3	1.9	10	310	B	B	Example	
18	11.0	5.3	0	0.3	0			0.25	0.39	0.35	2.5	4	305	A	B	Example	
19	11.0	5.3	0	0.3	0			0.25	0.39	0.35	1.9	4	310	B	B	Example	
20	20.0	6.8	0.2	0.5	0.1	Sn = 0.1		0.25	0.39	0.35	2.6	20	310	A	S	Example	
21	20.0	7.3	0.2	0.5	0.1	Sn = 0.1		0.25	0.39	0.35	3.0	15	305	A	S	Example	
22	20.0	10.3	0.2	1	0.1	Sn = 0.1		0.25	0.39	0.35	2.9	30	305	A	S	Example	
23	30.0	8.6	0.2	0.3	0	Sn = 0.1		0.2	0.3	0.25	3.0	13	310	A	A	Example	
24	30.0	8.6	0.2	0.3	0	Sn = 0.1		0.2	0.3	0.25	3.1	3	305	A	B	Example	
25	30.0	8.9	0.4	0.5	0.1	Sn = 0.1		0.3	0.6	0.4	2.6	20	305	A	S	Example	

[0103]

[Table 2B]

No.	Plated layer							GDS (Intensity cps)				XRD		Area fraction (%)	Performance			Type
	Chemical composition (mass%) : remainder Zn							Sr (surf)	Sr (center)	Sr (deep)	I (SrZn ₁₃)	Hardness (Hv)	Bending workability		Flat portion corrosion resistance			
	Al	Mg	Ca	Sr	Si	Others												
26	30.0	9.7	0.5	1	0.1	Ni = 0.1		0.28	0.6	0.45	2.7		20	320	A	S	Example	
27	30.0	9.3	0.5	1.5	0.1	Cr = 0.1		0.3	0.61	0.52	2.7		20	305	A	S	Example	
28	30.0	9.3	0.5	1.5	0.1	Mo = 0.1		0.25	0.63	0.5	2.6		20	305	A	S	Example	
29	35.0	11.2	0.4	0.7	0.1	Cu = 0.1		0.23	0.6	0.5	2.7		20	310	A	S	Example	
30	11.0	5.3	0	0.3	0.08	Ti = 0.05		0.15	0.32	0.25	2.8		10	305	A	B	Example	
31	11.0	5.3	0	0.4	0.1	W = 0.05		0.1	0.4	0.35	2.9		15	305	A	S	Example	
32	11.0	5.3	0	0.4	0.3	Co = 0.05		0.22	0.35	0.3	2.6		15	320	A	S	Example	
33	11.0	5.3	0	0.4	0.5	V = 0.05		0.26	0.35	0.32	2.5		15	305	A	S	Example	
34	11.0	5.3	0	0.4	0.5	V = 0.05		0.26	0.35	0.32	1.9		15	310	B	S	Example	
35	11.0	5.3	0	0.4	0.5	V = 0.05		0.26	0.35	0.32	2.6		4	305	A	B	Example	
36	11.0	5.3	0	0.4	0.5	V = 0.05		0.26	0.35	0.32	2.8		4	305	A	B	Example	
37	11.0	5.3	0	0.4	0.7			0.21	0.35	0.32	2.9		16	320	A	S	Example	
38	20.0	4.9	0	0.4	0.1			0.18	0.37	0.33	3.0		17	305	A	S	Example	
39	20.0	4.9	0	0.4	0.3	Sb = 0.05		0.25	0.38	0.3	3.1		19	310	A	S	Example	
40	20.0	4.9	0	0.4	0.5			0.24	0.36	0.29	2.7		29	305	A	S	Example	
41	20.0	4.8	0	0.4	0.7			0.23	0.35	0.3	2.9		18	305	A	S	Example	
42	30.0	4.7	0	0.4	0.1			0.23	0.33	0.3	2.7		16	320	A	S	Example	
43	30.0	4.7	0	0.4	0.3			0.22	0.35	0.3	2.7		16	305	A	S	Example	
44	30.0	4.7	0	0.4	0.5			0.25	0.37	0.3	2.8		15	310	A	S	Example	
45	30.0	4.7	0	0.4	1			0.22	0.36	0.31	1.9		16	305	B	S	Example	
46	30.0	4.7	0	0.4	1			0.22	0.36	0.31	2.7		15	305	A	S	Example	
47	30.0	4.7	0	0.4	1			0.22	0.36	0.31	1.9		3	320	B	B	Example	
48	30.0	4.7	0	0.4	1			0.22	0.36	0.31	2.7		4	305	A	B	Example	
49	11.0	5.3	0	0.3	0			-	-	-	-		-	-	-	-	Comparative Example	

INDUSTRIAL APPLICABILITY

[0104]

According to the above aspect of the present invention, the hot-dip plated steel material excellent in plating hardness, corrosion resistance, and workability can be

5 obtained. Therefore, the obtained hot-dip plated steel material can be suitably applied to the fields of automobiles and building materials, and thus has high industrial applicability.

CLAIMS

[Claim 1] A hot-dip plated steel material comprising:

a steel material; and

a plated layer disposed on a surface of the steel material, wherein

5 the plated layer has a chemical composition including, in terms of mass%,

more than 10.0% and less than 45.0% of Al,

4.0% or more and 15.0% or less of Mg,

0% or more and 2.0% or less of Si, and

0.03% or more and 1.50% or less of Sr, and

10 further including

0% or more and 0.7% or less of Sn,

0% or more and 0.3% or less of Bi,

0% or more and 0.3% or less of In,

0% or more and 0.6% or less of Ca,

15 0% or more and 0.3% or less of Y,

0% or more and 0.3% or less of La,

0% or more and 0.3% or less of Ce,

0% or more and 0.3% or less of Li,

0% or more and 1.0% or less of Ni,

20 0% or more and 1.0% or less of Cu,

0% or more and 0.25% or less of Ag,

0% or more and 0.25% or less of Sb,

0% or more and 0.25% or less of Pb,

0% or more and 0.5% or less of B,

25 0% or more and 0.5% or less of P,

0% or more and 0.25% or less of Ti,

0% or more and 0.25% or less of Co,

0% or more and 0.25% or less of V,

0% or more and 0.25% or less of Nb,

5 0% or more and 0.25% or less of Mn,

0% or more and 0.25% or less of Zr,

0% or more and 0.25% or less of W,

0% or more and 5.0% or less of Fe, and

a remainder of Zn and impurities,

10 the plated layer contains a Zn-Sr-based compound and a Zn-Sr-Si-based compound, and

in a case where, in an elemental distribution profile obtained by a qualitative analysis using a glow discharge optical emission spectrometry in a direction from a surface of the plated layer toward the steel material, a thickness of the plated layer is
15 denoted by t , an average value of a qualitative analysis value of Sr from the surface of the plated layer to $0.05 t$ is denoted by $Sr(\text{surf})$, a qualitative analysis value in a range of $0.05 t$ to $0.66 t$ starting from the surface of the plated layer is denoted by $Sr(\text{center})$, and a qualitative analysis value in a range of $0.66 t$ to t starting from the surface of the plated layer is denoted by $Sr(\text{deep})$, Expression (1) is satisfied,

20 $Sr(\text{surf}) < Sr(\text{deep}) < Sr(\text{center}) \dots (1).$

[Claim 2] The hot-dip plated steel material according to claim 1, wherein

in the chemical composition of the plated layer,

Sr is 0.10% or more and 1.50% or less, and

in a case where a diffraction intensity of the Zn-Sr-based compound in a X-ray
25 diffraction pattern of the surface of the plated layer is denoted by $I(\text{SrZn}_{13})$, the

diffraction intensity being measured by using Cu-K α radiation under conditions of 50 kV and 300 mA X-ray output, Expression (2) is satisfied,

$$\{I(14.48^\circ) + I(32.74^\circ)\}/2 \times I(12.50^\circ) \} > 2.0 \dots (2)$$

in Expression (2), $I(n^\circ)$ is the X-ray diffraction intensity at a diffraction angle n° , and n is a diffraction angle (2θ) indicated in Expression (2).

[Claim 3] The hot-dip plated steel material according to claim 1 or 2, wherein

in the chemical composition of the plated layer,

Si is 0.05% or more and 0.5% or less, and

the Zn-Sr-Si-based compound and a Zn-Al-Sr-Si-based compound are contained

in an area fraction of 5% to 30% in a cross section along a thickness direction of the plated layer.