

[Document Type] Specification

[Title of the Invention] HOT-DIP PLATED STEEL SHEET AND METHOD OF
MANUFACTURING THE SAME

[Technical Field of the Invention]

[0001]

The present invention relates to a hot-dip plated steel sheet and a method of manufacturing the hot-dip plated steel sheet.

Priority is claimed on Japanese Patent Application No. 2020-075495, filed April 21, 2020, the content of which is incorporated herein by reference.

[Related Art]

[0002]

A Zn-Al-Mg-based hot-dip plated steel sheet has high corrosion resistance. Further, a Zn-Al-Mg-Si-based hot-dip plated steel sheet, which is obtained in a case where a small amount of Si is further contained in the Zn-Al-Mg-based hot-dip plated steel sheet, is excellent on both corrosion resistance and workability. For this reason, the Zn-Al-Mg-based hot-dip plated steel sheet and the Zn-Al-Mg-Si-based hot-dip plated steel sheet are used in various technical fields, such as the field of building materials, the field of home appliances, and the field of vehicles.

[0003]

Patent Document 1 discloses a highly corrosion-resistant hot-dip galvanized steel sheet that is excellent in external appearance evenness and includes a hot-dip galvanized layer provided on the surface thereof and containing Al: 4 to 22 mass%, Mg: 1 to 6 mass%, and a remainder consisting of Zn and unavoidable impurities. The degree of non-recrystallization of a surface layer of a plating base sheet is 30% or more, and an average grain size of a ternary eutectic phase of Al/MgZn₂/Zn among component

phases of a plating layer is in a range of 10 to 100 μm .

[0004]

Patent Document 2 discloses a highly corrosion-resistant hot-dip galvanized steel sheet that is excellent in external appearance evenness and includes a plating layer formed on the surface thereof and containing Al: 4 to 22 mass%, Mg: 1 to 6 mass%, Si: 0.001 to 1 mass%, and a remainder consisting of Zn and unavoidable impurities. Mg_2Si phases and Ca phases, which contain Ca or Ca compounds as main components, are present at an interface between the plating layer and a base steel sheet, and at least part of the Mg_2Si phases are precipitated using the Ca phases as nuclei.

[0005]

Patent Document 3 discloses an aluminum-plated steel sheet that is excellent in corrosion resistance and external appearance and includes a plating layer formed on at least one surface of a steel sheet and containing, by mass%, Si: 2% or more and 11% or less, Mg: 3% or more and 9% or less, Ca: 0.1% or more and 5% or less, Ti: 0.005% or more and 0.05% or less, and a remainder consisting of Al and unavoidable impurities. Mg_2Si particles, of which a diameter on a major axis is 10 μm or less and an aspect ratio as a ratio of a diameter on the major axis to a diameter on a minor axis is 1 or more and 3 or less, are present in the plating layer.

[Prior Art Document]

[Patent Document]

[0006]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2013-14794

[Patent Document 2] Republished Japanese Translation WO2013/002358 of the PCT International Publication for Patent Applications

[Patent Document 3] Republished Japanese Translation WO2013/008341 of
the PCT International Publication for Patent Applications

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0007]

The present inventors found that a coating film is likely to be peeled off from a coated steel sheet obtained in a case where coating is performed on the Zn-Al-Mg-Si-based hot-dip plated steel sheet. As the result of the detailed investigation of the coated steel sheet from which a coating film is peeled off, it was clarified that the peeling of a coating film tends to occur at an interface between plating and a base steel sheet. This result shows that there is a concern about the plating adhesion of a worked portion of the Zn-Al-Mg-Si-based hot-dip plated steel sheet. The plating adhesion of a worked portion means the adhesion of plating at a portion to which machining, such as bending and drawing, has been applied.

[0008]

There are few examples where focus has been on the plating adhesion of a worked portion in the related art of a Zn-Al-Mg-based hot-dip plated steel sheet or a Zn-Al-Mg-Si-based hot-dip plated steel sheet. Among the above-mentioned prior art documents, Patent Document 3 discloses that spherical Mg_2Si particles reduce pressure concentration in forming with high stress and suppress the occurrence and propagation of potential cracks. However, the peeling of plating has not been examined in Patent Document 3 at all.

[0009]

The present invention has been made in consideration of the above-mentioned circumstances and an object of the present invention is to provide a highly corrosion-

resistant hot-dip plated steel sheet that has excellent plating adhesion of a worked portion and a method of manufacturing the highly corrosion-resistant hot-dip plated steel sheet.

[Means for Solving the Problem]

[0010]

The gist of the present invention is as follows.

(1) A hot-dip plated steel sheet according to an aspect of the present invention includes a base steel sheet and a hot-dip plating layer; a chemical composition of the hot-dip plating layer contains Al: 4.0 to 22 mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities; a coating weight of the hot-dip plating layer is in a range of 40 to 600 g/m² on both surface in total; a total value of an interface contact length of interface Mg₂Si phases present at an interface between the base steel sheet and the hot-dip plating layer is 20% or less of the visual field, in which the total value is measured in a visual field having a length of 10 mm in a vertical cross section; and a number density of the interface Mg₂Si phases having an equivalent circle diameter of 30 μm or more present at the interface between the base steel sheet and the hot-dip plating layer is 10 pieces/mm² or less, in which the number density is measured in a plan view.

(2) In the hot-dip plated steel sheet according to (1), a maximum value of the interface contact length of the interface Mg₂Si phase may be 50 μm or less, in which the maximum value is measured in the visual field having a length of 10 mm in the vertical cross section.

(3) In the hot-dip plated steel sheet according to (1) or (2), a ratio b/a of a length b of the interface Mg₂Si phase in an interface-horizontal direction to a length a of the interface Mg₂Si phase in a plating-depth direction may be 0.1 or more and 10 or less

in the visual field having a length of 10 mm in the vertical cross section.

(4) In the hot-dip plated steel sheet according to any one of (1) to (3), the chemical composition of the hot-dip plating layer may contain 0.001 to 2 mass% of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf in total, instead of part of the Zn.

(5) In the hot-dip plated steel sheet according to any one of (1) to (4), the chemical composition of the hot-dip plating layer may contain 0.001 to 2 mass% of one or more selected from Ni, Ti, Zr, and Sr in total, instead of part of the Zn.

(6) A method of manufacturing a hot-dip plated steel sheet according to another aspect of the present invention is a method of manufacturing the hot-dip plated steel sheet according to any one of (1) to (5). The method includes: alkaline degreasing a base steel sheet using alkaline degreasing liquid containing 0.5 to 5.0 mass% of a surfactant; water rinsing the base steel sheet after the alkaline degreasing; annealing the base steel sheet after the water rinsing; and immersing the base steel sheet in a hot-dip plating bath containing Al: 4.0 to 22 mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities after the annealing, to form a hot-dip plating layer. A pH of rinsing water is always set to 8.7 or more and 12 or less in the water rinsing.

(7) In the method of manufacturing the hot-dip plated steel sheet according to (6), the hot-dip plating bath may contain 0.001 to 2 mass% of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf in total, instead of part of the Zn.

(8) In the method of manufacturing the hot-dip plated steel sheet according to (6) or (7), the hot-dip plating bath may contain 0.001 to 2 mass% of one or more selected from Ni, Ti, Zr, and Sr in total, instead of part of the Zn.

[Effects of the Invention]

[0011]

According to the present invention, it is possible to provide a highly corrosion-resistant hot-dip plated steel sheet that has excellent plating adhesion of a worked portion and a method of manufacturing the highly corrosion-resistant hot-dip plated steel sheet.

[Brief Description of the Drawings]

[0012]

FIG. 1 is a schematic cross-sectional view of a highly corrosion-resistant hot-dip plated steel sheet, which has excellent plating adhesion of a worked portion, according to an aspect of the present invention.

FIG. 2 is a schematic cross-sectional view of the highly corrosion-resistant hot-dip plated steel sheet, which has excellent plating adhesion of a worked portion, according to the aspect of the present invention.

[Embodiments of the Invention]

[0013]

The present inventors have performed the detailed structural analysis of plating peeling that occurs in a worked portion in a case where a plated steel sheet is applied to a test simulating forming with stress, such as a 180°-bending test. As a result, it has been clarified that the crystallization form of Mg_2Si phases at an interface between a base steel sheet and plating has a great influence on the plating adhesion of a worked portion.

[0014]

In a case where the cross-sectional observation of Mg_2Si phases (hereinafter, referred to as "interface Mg_2Si phases") present at an interface between a base steel

sheet and a hot-dip plating layer in a normal plated steel sheet is performed, the interface Mg_2Si phases are present along the interface. The present inventors have found that the plating adhesion of a worked portion is improved in a case where the lengths of the interface Mg_2Si phases along the interface (interface contact lengths) are reduced. Further, it can be confirmed that the interface Mg_2Si phases adhere to the base steel sheet in a case where the surface of the base steel sheet is observed using SEM after the removal of the plating of the plated steel sheet. The present inventors have found that the plating adhesion of a worked portion is further improved in a case where the number density of interface Mg_2Si phases, which have an equivalent circle diameter of 30 μm or more, (coarse interface Mg_2Si phases) of the interface Mg_2Si phases is reduced.

[0015]

In addition, the present inventors have found that there is a close relationship between the interface contact length of the interface Mg_2Si phases measured in a cross section and rinsing conditions before the plating of the base steel sheet, and between the number density of the coarse interface Mg_2Si phases measured in a plan view and rinsing conditions before the plating of the base steel sheet. Then, the present inventors have clarified rinsing conditions that allow the state of the interface Mg_2Si phases to be in a desirable range.

[0016]

As shown in, for example, FIG. 1, a highly corrosion-resistant hot-dip plated steel sheet 1, which is excellent in plating adhesion, according to an aspect of the present invention (a hot-dip plated steel sheet 1 according to the present embodiment), obtained from the above-mentioned knowledge includes a base steel sheet 11 and a hot-dip plating layer 12, in which the chemical composition of the hot-dip plating layer 12

contains Al: 4.0 to 22 mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities; the coating weight of the hot-dip plating layer 12 is in a range of 40 to 600 g/m² on both surface in total; the total interface contact length of interface Mg₂Si phases 13 is 20% or less of the visual field, in which the total value is measured in a visual field having a length of 10 mm in a vertical cross section; and the number density of the interface Mg₂Si phases 13 having an equivalent circle diameter of 30 μm or more present at an interface between the base steel sheet 11 and the hot-dip plating layer 12 is 10 pieces/mm² or less, in which the total value is measured in a plan view.

[0017]

The hot-dip plated steel sheet 1 according to the present embodiment includes the base steel sheet 11. The type of the base steel sheet 11 is not particularly limited. Various components, thicknesses, metallographic structures, mechanical properties, and the like can be applied to the base steel sheet 11 depending on the use of the hot-dip plated steel sheet 1.

[0018]

The hot-dip plated steel sheet 1 according to the present embodiment includes a hot-dip plating layer 12 provided on the surface of the base steel sheet 11. The hot-dip plating layer 12 may be provided on one surface of the base steel sheet 11 and may be provided on both surfaces of the base steel sheet 11. First, the chemical composition of the hot-dip plating layer 12 will be described below. Hereinafter, the unit "%" of the content of each element means mass% unless otherwise specified.

[0019]

(Al: 4.0 to 22 mass%)

In the hot-dip plating layer 12, the Al content is set to 4.0 mass% or more and

22 mass% or less. It is considered that an effect of improving corrosion resistance is not sufficiently obtained in a case where the Al content is less than 4.0 mass%. It is considered that an effect of improving corrosion resistance is saturated in a case where the Al content is 22 mass% or more. In order to further improve corrosion resistance, the Al content may be 5 mass% or more or 10 mass% or more. Further, in order to lower the melting point of a plating bath or improve plating adhesion, the Al content may be set to 20 mass% or less or 15 mass% or less.

[0020]

(Mg: 1 to 10 mass%)

In the hot-dip plating layer 12, the Mg content is set to 1 mass% or more and 10 mass% or less. It is considered that an effect of improving corrosion resistance is not sufficiently obtained in a case where the Mg content is less than 1 mass%. Further, it is considered that the plating layer is embrittled and plating adhesion deteriorates in a case where the Mg content exceeds 10 mass%. In order to further improve corrosion resistance, the Mg content may be set to 2 mass% or more or 3 mass% or more. In order to further improve the adhesion of the plating layer, the Mg content may be 9 mass% or less, 7 mass% or less, 5 mass% or less, 4.5 mass% or less, or 4 mass% or less.

[0021]

(Si: 0.0001 to 2 mass%)

In the hot-dip plating layer 12, the Si content is set to 0.0001 mass% or more and 2 mass% or less. Si has an effect of improving the corrosion resistance of the hot-dip plating layer 12, but it is considered that it is industrially difficult to control the Si content to less than 0.0001 mass%. Further, it is considered that an effect of improving corrosion resistance is saturated in a case where the Si content is 2 mass% or more. The Si content may be set to 0.001 mass% or more or 0.01 mass% or more.

The Si content may be set to 1.5 mass% or less or 1.0 mass% or less.

[0022]

(Remainder: Zn and impurities)

The remainder of the chemical composition of the hot-dip plating layer 12 is Zn and impurities. The impurities are components which is mixed in the hot-dip plating layer 12 due to various factors of, for example, raw materials for hot-dip galvanizing or a manufacturing step, and which are allowed within a range where the hot-dip plated steel sheet 1 according to the present embodiment is not adversely affected.

[0023]

The chemical composition of the hot-dip plating layer 12 may contain 0.001 to 2 mass% of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements (for example, Sc and the like), REM, and Hf in total, instead of part of Zn of the remainder. In a case where the content of these elements is 2 mass% or less, various properties, such as corrosion resistance, of the hot-dip plating layer 12 do not deteriorate. Further, there is also a possibility that the corrosion resistance of the hot-dip plating layer 12 will be improved by these elements. The total content of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf may be 0.002 mass% or more, 0.01 mass% or more, or 0.1 mass% or more. The total content of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf may be 1.5 mass% or less, 1.0 mass% or less, or 0.5 mass% or less.

[0024]

Further, the chemical composition of the hot-dip plating layer 12 may contain 0.001 to 2 mass% of one or more selected from Ni, Ti, Zr, and Sr in total, instead of part

of Zn of the remainder. In a case where the content of these elements is 0.001 mass% or more in total, the intermetallic compound of these elements and Al is crystallized and surface smoothness is improved. However, in a case where the total content of these elements exceeds 2 mass%, there is a concern that the external appearance of plating is rough and poor external appearance occurs. The total content of one or more selected from Ni, Ti, Zr, and Sr may be 0.002 mass% or more, 0.01 mass% or more, or 0.1 mass% or more. The total content of one or more selected from Ni, Ti, Zr, and Sr may be 1.5 mass% or less, 1.0 mass% or less, or 0.5 mass% or less.

[0025]

Next, the coating weight of the hot-dip plating layer 12 will be described. The coating weight of the hot-dip plating layer 12 is set in a range of 40 to 600 g/m² on both surface in total. In a case where the coating weight of the hot-dip plating layer 12 is set to 40 g/m² or more, high corrosion resistance can be given to the hot-dip plated steel sheet 1. On the other hand, in a case where the coating weight of the hot-dip plating layer 12 is set to 600 g/m² or less, plating adhesion (for example, the plating adhesion of a worked portion) can be ensured. The coating weight of the hot-dip plating layer 12 may be set to 50 g/m² or more, 100 g/m² or more, or 200 g/m² or more on both surface in total. The coating weight of the hot-dip plating layer 12 may be set to 550 g/m² or less, 500 g/m² or less, or 300 g/m² or less on both surface in total.

[0026]

In the hot-dip plated steel sheet 1 according to the present embodiment, Mg₂Si phases may be present at the interface between the base steel sheet 11 and the hot-dip plating layer 12. Hereinafter, the Mg₂Si phases present at the interface between the base steel sheet 11 and the hot-dip plating layer 12 are referred to as the interface Mg₂Si phases 13. An alloy layer having a thickness of about several hundred nm may be

formed at the interface between the base steel sheet 11 and the hot-dip plating layer 12. In this case, all of Mg_2Si phases in contact with an interface between the base steel sheet 11 and the alloy layer, Mg_2Si phases in contact with an interface between the alloy layer and the hot-dip plating layer 12, and Mg_2Si phases in contact with both these interfaces are regarded as the interface Mg_2Si phases 13.

[0027]

In the hot-dip plated steel sheet 1 according to the present embodiment, the total value of an interface contact length of the interface Mg_2Si phases 13 is 20% or less of the visual field, in which the total value is measured in a visual field having a length of 10 mm in a vertical cross section.

[0028]

Here, the interface contact lengths of the interface Mg_2Si phases 13 are the lengths of portions, which are included in the interface Mg_2Si phases, of the interface between the base steel sheet 11 and the hot-dip plating layer 12. A description will be given with reference to FIG. 1 by way of example. The interface between the base steel sheet 11 and the hot-dip plating layer 12 is in contact with each interface Mg_2Si phase 13 at two points. A distance between the two points is the interface contact length of the interface Mg_2Si phase 13.

[0029]

The total interface contact length of the interface Mg_2Si phases 13, which is measured in a visual field having a length of 10 mm in a vertical cross section, is a total value of the interface contact lengths of the interface Mg_2Si phases 13 that are included in an any visual field in a cross section perpendicular to the surface of the hot-dip plated steel sheet 1. Here, the number of visual fields is set to 5 and the average value of the total values of the interface contact lengths in these visual fields is calculated. Further,

the shape of a visual field is a 10 mm-by-10 mm square, and the interface between the base steel sheet 11 and the hot-dip plating layer 12 is substantially parallel to the horizontal side of the visual field. A description will be given with reference to FIG. 1 by way of example. Three interface Mg_2Si phases 13 are included in the visual field shown in FIG. 1 and the interface contact lengths thereof are L_1 to L_3 . The total interface contact length of the interface Mg_2Si phases 13, which is measured in a visual field having a length of 10 mm in a vertical cross section, is $L_1 + L_2 + L_3$.

[0030]

In the hot-dip plated steel sheet 1 according to the present embodiment, the state of the interface Mg_2Si phases 13 is defined on the basis of a ratio of the total interface contact length to the width (10 mm) of the visual field. In a case where the total interface contact length (an average value in five visual fields) of the interface Mg_2Si phases 13 is set to 20% or less of the visual field, the area of a region in which plating peeling is likely to occur is reduced. As a result, high plating adhesion of a worked portion is obtained. The total interface contact length of the interface Mg_2Si phases 13 may be set to 18% or less, 15% or less, or 10% or less of the visual field.

The lower limit of the total interface contact length of the interface Mg_2Si phases 13 is not particularly limited in terms of ensuring the plating adhesion of a worked portion. Accordingly, the total interface contact length of the interface Mg_2Si phases 13 may be 0% of the visual field. However, the total interface contact length of the interface Mg_2Si phases 13 may be set to 0.5% or more of the visual field. The total interface contact length of the interface Mg_2Si phases 13 may be set to 1.0% or more, 2.0% or more, or 5.0% or more of the visual field.

[0031]

Further, in the hot-dip plated steel sheet 1 according to the present

embodiment, the number density of the interface Mg_2Si phases having an equivalent circle diameter of $30\text{ }\mu\text{m}$ or more present at the interface between the base steel sheet and the hot-dip plating layer (hereinafter, referred to as "coarse interface Mg_2Si phases") is 10 pieces/ mm^2 or less, in which the number density is measured in a plan view.

"Plan view" is a visual field in a case where an object is viewed in a direction perpendicular to the interface or the base steel sheet. It should be noted here that the number density of the coarse interface Mg_2Si phases is measured on the surface of the base steel sheet in a plan view in contrast to the fact that the above-mentioned interface contact lengths of the interface Mg_2Si phases 13 are measured in the cross section of the hot-dip plated steel sheet 1. Specifically, the number density of the coarse interface Mg_2Si phases is measured according to the following procedure.

1. The hot-dip plated steel sheet is immersed in 0.5% hydrochloric acid containing an inhibitor. Accordingly, the hot-dip plating layer can be dissolved and removed from the hot-dip plated steel sheet. On the other hand, the interface Mg_2Si phases present at the interface between the base steel sheet and the hot-dip plating layer remain on the surface of the base steel sheet.

2. The number of interface Mg_2Si phases (coarse interface Mg_2Si phases), which are included in an any 1 mm-by-1 mm square region on the surface of the base steel sheet and have an equivalent circle diameter of $30\text{ }\mu\text{m}$ or more, is counted through SEM observation. Here, the number of any 1 mm-by-1 mm square regions to be observed is set to 5, and the average value of the numbers of coarse interface Mg_2Si phases of these regions is calculated. This average value is defined as the number density of the interface Mg_2Si phases (coarse interface Mg_2Si phases). Here, the equivalent circle diameter of the interface Mg_2Si phases is an equivalent circle diameter in a case where the base steel sheet is viewed in a plan view.

There is a concern that the coarse interface Mg_2Si phases are not captured in the above-mentioned cross-sectional observation. There is a possibility that coarse interface Mg_2Si phases not appearing in the cross section are present even though an interface contact length measured through the cross-sectional observation is in the above-mentioned range. There is a concern that the plating adhesion of a worked portion of the hot-dip plated steel sheet deteriorates in a case where such coarse interface Mg_2Si phases are present. As the result of evaluation of various hot-dip plated steel sheets performed by the present inventors, it has been confirmed that the number density of coarse interface Mg_2Si phases to be measured in a plan view may be increased even in a hot-dip plated steel sheet having a small interface contact length of interface Mg_2Si phases in the cross section.

For this above-mentioned reason, in the hot-dip plated steel sheet according to the present embodiment, the total interface contact length of the interface Mg_2Si phases is in the above-mentioned range and the number density of the coarse interface Mg_2Si phases measured in a plan view is 10 pieces/ mm^2 or less. In a case where the number density of the coarse interface Mg_2Si phases measured in a plan view exceeds 10 pieces/ mm^2 , sufficient plating adhesion of a worked portion cannot be ensured. The number density of the coarse interface Mg_2Si phases measured in a plan view may be 9 pieces/ mm^2 or less, 8 pieces/ mm^2 or less, or 7 pieces/ mm^2 or less. Since a smaller number density of the coarse interface Mg_2Si phases measured in a plan view is more preferable, the lower limit thereof is not particularly limited. The number density of the coarse interface Mg_2Si phases measured in a plan view may be, for example, 0 piece/ mm^2 or more, 1 piece/ mm^2 or more, or 2 pieces/ mm^2 or more.

[0032]

In addition, in the hot-dip plated steel sheet 1 according to the present

embodiment, it is preferable that the maximum value of the interface contact length of the interface Mg₂Si phase 13 is 50 μm or less, in which the maximum value is measured in a visual field having a length of 10 mm in a vertical cross section. The maximum value of the interface contact length of the interface Mg₂Si phase 13, which is measured in a visual field having a length of 10 mm in a vertical cross section, is the maximum value among the interface contact lengths of these interface Mg₂Si phases 13 that are included in an any visual field in a cross-section perpendicular to the surface of the hot-dip plated steel sheet 1. The number of visual fields is set to 5 and the average value of the maximum values of the interface contact lengths of the interface Mg₂Si phases 13 in these visual fields is calculated. A description will be given with reference to FIG. 1 by way of example. The maximum value among the interface contact lengths L1 to L3 of three interface Mg₂Si phases 13 included in the visual field shown in FIG. 1 is L3. Accordingly, the maximum value of the interface contact length of the interface Mg₂Si phase 13, which is measured in the visual field shown in FIG. 1, is L3.

[0033]

It is supposed that plating peeling is more likely to occur in the case of an interface Mg₂Si phase 13 having a longer interface contact length. Accordingly, it is considered that plating peeling can be more effectively suppressed in a case where not only a ratio of the total value of the interface contact lengths of the interface Mg₂Si phases 13, which are included in the visual field, to the visual field but also the interface contact length of each interface Mg₂Si phase 13 is reduced. For this above-mentioned reason, it is preferable that the maximum value of the interface contact length of the interface Mg₂Si phase 13 is 50 μm or less. The maximum value of the interface contact length of the interface Mg₂Si phase 13 may be 45 μm or less, 40 μm or less, or 30 μm or less.

[0034]

The lower limit of the maximum value of the interface contact length of the interface Mg₂Si phase 13 is not particularly limited in terms of ensuring the plating adhesion of a worked portion. Accordingly, the maximum value of the interface contact length of the interface Mg₂Si phase 13 may be 0 μm. In a case where the interface Mg₂Si phase 13 is not included in a measurement visual field at all, the maximum value of the interface contact length of interface Mg₂Si phase 13 is 0 μm. However, in consideration of the capacity of manufacturing equipment, the maximum value of the interface contact length of the interface Mg₂Si phase 13 may be 1 μm or more, 2 μm or more, or 5 μm or more.

[0035]

In addition, in the hot-dip plated steel sheet 1 according to the present embodiment, a ratio b/a of a length b of the interface Mg₂Si phase 13 in an interface-horizontal direction to a length a of the interface Mg₂Si phase 13 in a plating-depth direction may be 0.1 or more and 10 or less in a visual field having a length of 10 mm in a vertical cross section. The length a of the interface Mg₂Si phase 13 in the plating-depth direction is the size of the interface Mg₂Si phase 13 measured in the plating-depth direction as shown in FIG. 2. The length b of the interface Mg₂Si phase 13 in the interface-horizontal direction is the size of the interface Mg₂Si phase 13 measured in a horizontal direction along the interface (that is, a direction perpendicular to the plating-depth direction) as shown in FIG. 2. Hereinafter, the ratio of the length b of the interface Mg₂Si phase 13 in the interface-horizontal direction to the length a of the interface Mg₂Si phase 13 in the plating-depth direction may be referred to as the aspect ratio of the interface Mg₂Si phase 13. The aspect ratio of the interface Mg₂Si phase 13 is evaluated in five visual fields. In a case where two or more interface Mg₂Si phases

13 are included in five visual fields, "the ratio b/a of the length b of the interface Mg_2Si phase 13 in the interface-horizontal direction to the length a of the interface Mg_2Si phase 13 in the plating-depth direction is 0.1 or more and 10 or less in a visual field having a length of 10 mm in a vertical cross section" means that the aspect ratios of all interface Mg_2Si phases 13 included in the five visual fields are in a range of 0.1 or more and 10 or less.

[0036]

An interface Mg_2Si phase 13 having a high aspect ratio has a shape extending along the interface between the base steel sheet 11 and the hot-dip plating layer 12. In a case where the aspect ratio of the interface Mg_2Si phase 13 is set to 10 or less, plating peeling can be more effectively suppressed. The aspect ratio of the interface Mg_2Si phase 13 may be set to 9 or less, 8 or less, or 5 or less.

[0037]

Further, there is a concern that an interface Mg_2Si phase 13 having a low aspect ratio serves as a crack propagation path of the plating layer during the working of the hot-dip plated steel sheet 1 and causes plating cracks and the deterioration of corrosion resistance. In a case where the aspect ratio of the interface Mg_2Si phase 13 is set to 0.1 or more, the corrosion resistance and the like of the hot-dip plating layer 12 can be further improved. The aspect ratio of the interface Mg_2Si phase 13 may be set to 0.2 or more, 0.5 or more, or 1.0 or more.

[0038]

The hot-dip plated steel sheet 1 according to the present embodiment may include a chemical conversion film layer, a coating film layer, and the like on the surface of the hot-dip plating layer 12 in order to improve, for example, design, corrosion resistance, and the like. Here, the types of the chemical conversion film

layer and the coating film layer are not particularly limited and chemical conversion film layers and coating film layers having been publicly known can be applied. Even in this case, the number density of the coarse interface Mg_2Si phases can be easily measured in a case where the chemical conversion film layer, the coating film layer, and the like are appropriately removed using a publicly known method before the dissolution of the hot-dip plating layer.

[0039]

Next, a method of manufacturing a highly corrosion-resistant hot-dip plated steel sheet, which is excellent in plating adhesion, according to another aspect of the present invention will be described. The method of manufacturing a highly corrosion-resistant hot-dip plated steel sheet, which is excellent in plating adhesion, according to the present embodiment (hereinafter, this may be abbreviated to a method of manufacturing a hot-dip plated steel sheet according to the present embodiment) includes: alkaline degreasing a base steel sheet 11; water rinsing the base steel sheet 11 after the alkaline degreasing; annealing the base steel sheet 11 after the water rinsing; and immersing the base steel sheet 11 in a hot-dip plating bath containing Al: 4.0 to 22 mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities after the annealing, to form a hot-dip plating layer 12, in which the pH of rinsing water is always set to 8.7 or more and 12 or less.

[0040]

In the method of manufacturing a hot-dip plated steel sheet according to the present embodiment, at first, the base steel sheet 11 is alkaline degreased. The alkaline degreasing is performed using alkaline degreasing liquid containing 0.5 to 5.0 mass% of a surfactant. In a case where the concentration of the surfactant is set to 0.5 mass% or more, materials that may serve as the nuclei of crystallization for the interface Mg_2Si

phases 13 can be well removed from the surface of the base steel sheet 11. However, in a case where the concentration of the surfactant exceeds 5.0 mass%, there is a concern that carbon, by which the surfactant adhering to the surface of the base steel sheet 11 is configured, remains on the surface of the base steel sheet 11 even after the annealing of the base steel sheet 11 to be described later. There is a concern that this carbon serves as the nuclei of crystallization for the interface Mg_2Si phases 13 and increases the interface contact length of the interface Mg_2Si phase. For this above-mentioned reason, the concentration of the surfactant in the alkaline degreasing liquid, which is used for alkaline degreasing, is set in a range of 0.5 to 5.0 mass%.

[0041]

Then, the base steel sheet 11 after the alkaline degreasing is rinsed with water. Water rinsing is performed to remove the alkaline degreasing liquid from the surface of the base steel sheet 11. The pH of liquid for this water rinsing is set to 8.7 or more and 12 or less. Accordingly, it is possible to prevent components, which are caused by the liquid for the water rinsing and may serve as the nuclei of crystallization for the interface Mg_2Si phases 13, from adhering to the base steel sheet 11.

It should be noted here that the pH of the rinsing water is always set to 8.7 or more and 12 or less during the water rinsing. In normal cascade type water rinsing, neutral water having a pH of about 7 is used to perform finish rinsing. However, neutral water is not used during the water rinsing in the method of manufacturing a hot-dip plated steel sheet according to the present embodiment. In a case where, for example, a water rinsing tank is used to rinse the base steel sheet 11 after alkaline degreasing with water, the pH of the rinsing water in contact with the base steel sheet 11 is set to 8.7 or more and 12 or less in the entire region from the entrance side to the exit side of the water rinsing tank. In a case where the pH of the rinsing water is

inappropriate, that is, the pH of the rinsing water is less than 8.7 in part or all of the water rinsing tank, it is not possible to sufficiently prevent components, which may serve as the nuclei of crystallization for the interface Mg_2Si phases 13, from adhering to the base steel sheet 11. On the other hand, in a case where the pH of the rinsing water exceeds 12, there is a concern that dissolution on the surface of the base steel sheet 11 is not uniform and unevenness occurs in the adhesion of hot-dip plating. For this reason, it is not preferable that the pH of the rinsing water exceeds 12.

In a case where the pH of the rinsing water in contact with the base steel sheet 11 is set to 8.7 or more and 12 or less in the entire region from the entrance side to the exit side of the water rinsing tank as described above, it is possible to prevent components, which may serve as the nuclei of crystallization for the interface Mg_2Si phases 13, from adhering to the base steel sheet 11. For this reason, the formation of nuclei of crystallization for the interface Mg_2Si phases 13 is suppressed in the subsequent step. Accordingly, the formation of the interface Mg_2Si phases 13 and the coarsening of the interface Mg_2Si phases 13 caused by pile-up or the like can be suppressed.

[0042]

Then, the base steel sheet 11 after water rinsing is annealed. In addition, the base steel sheet 11 after annealing is immersed in the hot-dip plating bath to form the hot-dip plating layer 12 on the surface of the base steel sheet 11. Annealing conditions are not particularly limited, and various conditions can be employed according to the components, use, thickness, metallographic structure, mechanical properties, and the like of the base steel sheet 11. The components of the hot-dip plating bath may be the same as those of the hot-dip plating layer 12 of the hot-dip plated steel sheet according to the present embodiment, that is, the hot-dip plating bath may contain Al: 4.0 to 22

mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities. The preferred upper and lower limits of the content of each element of the hot-dip plating bath are based on the preferred upper and lower limits of the content of each element of the hot-dip plating layer 12. The hot-dip plating bath may contain 0.001 to 2 mass% of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf in total, instead of part of Zn. The chemical composition of the hot-dip plating bath may contain 0.001 to 2 mass% of one or more selected from Ni, Ti, Zr, and Sr in total, instead of part of Zn.

[0043]

In a case where a chemical conversion layer is to be formed on the surface of the hot-dip plating layer 12, chemical conversion is performed on the hot-dip plated steel sheet on which the hot-dip plating layer is formed. The type of the chemical conversion is not particularly limited, and publicly known chemical conversion can be applied. Further, in a case where a coating film layer is to be formed on the surface of the hot-dip plating layer 12, the surface of the chemical conversion layer, and the like, coating treatment is performed on the hot-dip plated steel sheet on which the hot-dip plating layer or the chemical conversion layer is formed. The type of the coating is not particularly limited, and publicly known coating can be applied.

[Examples]

[0044]

An effect of an aspect of the present invention will be more specifically described using Examples. However, conditions in Examples are merely one condition example employed to confirm the feasibility and effects of the present invention. The present invention is not limited to this condition example. The present invention may employ various conditions to achieve the object of the present invention without

departing from the scope of the present invention.

[0045]

Various hot-dip plated steel sheets were manufactured through alkaline degreasing a base steel sheet, water rinsing the base steel sheet after the alkaline degreasing with water, annealing the base steel sheet after the water rinsing, and immersing the base steel sheet in a hot-dip plating bath after the annealing to form a hot-dip plating layer.

A cold-rolled steel sheet to which cold rolling oil adhered and which had a thickness of 0.8 mm was used as the base steel sheet.

When the base steel sheet was alkaline degreased, the concentration of a surfactant included in alkaline degreasing liquid was as shown in Table 1.

In a case where the base steel sheet was to be rinsed with water, the pH of the rinsing water was set to the following three types. Rinsing water used in the manufacture of each of Examples was shown in Table 1.

A: The pH of the rinsing water was always 8.7 or more and 12 or less during water rinsing.

B: The pH of the rinsing water was always less than 8.7 during water rinsing.

C: The pH of the rinsing water was mainly 8.7 or more and 12 or less during water rinsing and the pH of part of the rinsing water was less than 8.7.

The base steel sheet after water rinsing was annealed, and then, the base steel sheet was immersed in the hot-dip plating bath to form the hot-dip plating layer on the surface of the base steel sheet. The components of the hot-dip plating bath were as shown in Table 1. Since being substantially the same as that of the composition of the plating bath, the composition of the obtained plating obtained in this way was omitted in Table 1 or 2.

The coating weight of the hot-dip plating layer was adjusted by gas wiping after plating.

In Table 1, an underline was given to a value out of the range of the present invention. Further, the content of an element not intentionally added to the plating bath (and the plating) was left blank in Table 1.

[0046]

[Table 1]

No.	Alkaline degreasing	Water rinsing	Plating composition (Remainder is Zn and impurities) [mass%]											Coating weight of plating [g/m ²]
	Concentration of surfactant [%]	Rinsing liquid	Al	Mg	Si	Ti	Zr	Sr	Hf	Sc	B	Ni	Others	
1	1.25	A	4.0	3.2	0.080									352
2	4.15	A	5.4	1.0	0.001								Co: 0.004	551
3	3.30	A	6.2	2.8	1.800	0.0045							Mn: 0.002	42
4	2.60	A	7.7	4.1	1.130		0.0009						B: 0.006	133
5	1.80	A	8.6	9.8	1.080			1.0000					Hf: 0.005	310
6	1.65	A	9.4	1.4	0.030				0.0013				P: 0.002	76
7	5.00	A	10.5	5.5	0.210					0.0012			Bi: 0.008	596
8	0.55	A	11.1	2.8	0.180						0.0008		Co: 0.009	421
9	2.20	A	12.0	3.2	1.470							0.0032	P: 0.008	447
10	1.90	A	13.3	1.6	1.980								Fe: 0.009	119
11	3.45	A	14.6	7.1	0.540								Sb: 0.003	222
12	1.80	A	16.1	4.4	0.060								Pb: 0.004, Sn: 0.003	348
13	3.30	A	18.0	2.0	0.980								Ca: 0.005	294
14	0.95	A	20.1	1.1	1.660								Cr: 0.001	167
15	0.50	A	21.9	5.5	1.030								La: 0.002, Ce: 0.008	399
16	<u>0.35</u>	A	6.2	2.8	0.750	0.0045								42
17	<u>5.30</u>	A	9.4	1.4	1.110				0.0013					76
18	<u>5.80</u>	<u>B</u>	12.0	3.2	0.040							0.0032		447
19	3.15	A	<u>3.5</u>	<u>0.2</u>	0.165								Pb: 0.004, Sn: 0.003	348
20	2.60	<u>B</u>	21.9	5.5	0.040								La: 0.002, Ce: 0.008	399
21	2.60	<u>C</u>	12.4	4.1	0.030									418

[0047]

A ratio of the total interface contact length of interface Mg₂Si phases to the visual field, the number density of coarse interface Mg₂Si phases, and the maximum value of the interface contact length of the interface Mg₂Si phase in various hot-dip

plated steel sheets obtained from the above-mentioned procedure were measured in accordance with the above-mentioned methods. Measurement results were shown in Table 2. Further, the corrosion resistance and workability of the various hot-dip plated steel sheets obtained from the above-mentioned procedure were also evaluated.

[0048]

In order to evaluate corrosion resistance, a hot-dip plated steel sheet was cut into a shape having a length of 150 mm and a width of 70 mm, a cyclic corrosion test (CCT) based on JASO-M609 was performed on the cut hot-dip plated steel sheet for 30 cycles, and corrosion weight loss was then measured. Determination criteria were as follows and determination results were shown in Table 2. Hot-dip plated steel sheets for which the determination corresponded to "B" or "A" were determined as highly corrosion-resistant hot-dip plated steel sheets.

A: Corrosion weight loss was less than 30 g/m².

B: Corrosion weight loss was 30 g/m² or more and less than 50 g/m².

C: Corrosion weight loss was 50 g/m² or more and less than 70 g/m².

D: Corrosion weight loss was 70 g/m² or more.

[0049]

In order to evaluate workability, a bending test for bending the hot-dip plated steel sheet at a bending angle of 180° was performed and a tape peeling test was performed at a bent portion. The tape peeling test was based on a tape test method defined in JIS H 8504:1999 "plating adhesion test method". In a case where a hot-dip plated steel sheet was bent, a spacing inside the bending was set to correspond to one sheet (that is, about 0.8 mm). Determination criteria were as follows and determination results were shown in Table 2. Hot-dip plated steel sheets for which the determination corresponded to "B" or "A" were determined as hot-dip plated steel sheet

excellent in plating adhesion.

A: No plating peeling.

B: A plating peeling area ratio was less than 1%.

C: A plating peeling area ratio was 1% or more and less than 10%.

D: A plating peeling area ratio was 10% or more.

In Table 2, an underline was given to a value out of the range of the present invention.

[0050]

[Table 2]

No.	Interface Mg ₂ Si phase				Evaluation result		Note
	Ratio of total interface contact length to visual field [%]	Number density of coarse interface Mg ₂ Si phases [pieces/mm ²]	Maximum value of interface contact length [μm]	Aspect ratio	Corrosion resistance	Workability	
1	10.5	3	27	1.5	B	A	Inventive Example
2	6.5	5	34	1.1	B	A	Inventive Example
3	4.5	1	18	2.4	A	B	Inventive Example
4	8.0	2	21	0.8	A	A	Inventive Example
5	5.0	0	16	3.1	A	A	Inventive Example
6	11.0	4	33	1.7	A	A	Inventive Example
7	19.5	6	42	9.7	A	B	Inventive Example
8	17.0	6	47	8.5	A	B	Inventive Example
9	0.6	0	7	2.7	A	A	Inventive Example
10	8.0	2	11	2.3	A	A	Inventive Example
11	1.5	1	6	1.2	A	A	Inventive Example
12	9.5	5	37	0.6	A	A	Inventive Example
13	4.5	4	27	1.4	A	A	Inventive Example
14	12.0	4	24	0.2	A	B	Inventive Example
15	14.5	3	15	1.7	A	A	Inventive Example
16	<u>24.0</u>	<u>23</u>	61	10.4	A	D	Comparative Example
17	<u>27.0</u>	8	36	4.1	A	C	Comparative Example
18	<u>25.5</u>	<u>19</u>	54	11.3	A	D	Comparative Example
19	12.5	9	52	8.4	C	C	Comparative Example
20	<u>20.5</u>	<u>24</u>	55	11.0	A	D	Comparative Example
21	17.4	<u>13</u>	54	9.1	A	C	Comparative Example

[0051]

In Comparative example 16, the concentration of a surfactant in alkaline

degreasing liquid was insufficient. In Comparative example 16, a ratio of the total interface contact length of interface Mg_2Si phases, which were present at the interface between a base steel sheet and a hot-dip plating layer, to a visual field was excessive and the number density of the interface Mg_2Si phases having an equivalent circle diameter of 30 μm or more present at the interface between the base steel sheet and the hot-dip plating layer, (the number density of coarse interface Mg_2Si phases), which was measured in a plan view, was excessive. As a result, workability deteriorated.

In Comparative example 17, the concentration of a surfactant in alkaline degreasing liquid was excessive. In Comparative example 17, a ratio of the total interface contact length of interface Mg_2Si phases, which were present at the interface between a base steel sheet and a hot-dip plating layer, to a visual field was excessive. As a result, workability deteriorated.

In Comparative example 18, the concentration of a surfactant in alkaline degreasing liquid was excessive and the pH of rinsing water used for the water rinsing of a base steel sheet subjected to alkaline degreasing was insufficient. In Comparative example 18, a ratio of the total interface contact length of interface Mg_2Si phases, which were present at the interface between a base steel sheet and a hot-dip plating layer, to a visual field was excessive and the number density of coarse interface Mg_2Si phases was excessive. As a result, workability deteriorated.

In Comparative example 19, the amounts of Al and Mn included in plating were insufficient. In Comparative example 19, both corrosion resistance and workability deteriorated.

In Comparative example 20, the pH of rinsing water used for the water rinsing of a base steel sheet subjected to alkaline degreasing was insufficient. In Comparative example 20, a ratio of the total interface contact length of interface Mg_2Si phases, which

were present at the interface between a base steel sheet and a hot-dip plating layer, to a visual field was excessive and the number density of coarse interface Mg_2Si phases was excessive. As a result, workability deteriorated.

In Comparative example 21, the pH of rinsing water used for the water rinsing of a base steel sheet subjected to alkaline degreasing was insufficient in part of a rinsing step. In Comparative example 21, the number density of coarse interface Mg_2Si phases was excessive. As a result, workability deteriorated.

[0052]

On the other hand, since Examples Nos. 1 to 15 of the present invention were subjected to degreasing and water rinsing under appropriate conditions, the total value of an interface contact length of interface Mg_2Si phases present at the interface between a base steel sheet and a hot-dip plating layer was 20% or less of the visual field, in which the total value was measured in a visual field having a length of 10 mm in a vertical cross section, and the number density of the interface Mg_2Si phases having an equivalent circle diameter of 30 μm or more present at the interface between the base steel sheet and the hot-dip plating layer was 10 pieces/ mm^2 or less, in which the number density was measured in a plan view. Further, Examples Nos. 1 to 15 of the present invention were excellent in both corrosion resistance and the plating adhesion of a worked portion.

[Industrial Applicability]

[0053]

According to the present invention, it is possible to provide a highly corrosion-resistant hot-dip plated steel sheet that has excellent plating adhesion of a worked portion and a method of manufacturing the highly corrosion-resistant hot-dip plated steel sheet. Accordingly, the present invention has high industrial applicability.

[Brief Description of the Reference Symbols]

[0054]

1: hot-dip plated steel sheet

11: base steel sheet

12: hot-dip plating layer

13: interface Mg_2Si phase

a: maximum length of interface Mg_2Si phase in plating-depth direction

b: maximum length of interface Mg_2Si phase in interface-horizontal direction

L1 to L3: interface contact length of interface Mg_2Si phase

1. A hot-dip plated steel sheet comprising:

a base steel sheet; and

a hot-dip plating layer,

wherein a chemical composition of the hot-dip plating layer contains Al: 4.0 to 22 mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities,

a coating weight of the hot-dip plating layer is in a range of 40 to 600 g/m² on both surface in total,

a total value of an interface contact length of interface Mg₂Si phases present at an interface between the base steel sheet and the hot-dip plating layer is 20% or less of the visual field, in which the total value is measured in a visual field having a length of 10 mm in a vertical cross section, and

a number density of the interface Mg₂Si phases having an equivalent circle diameter of 30 μm or more present at the interface between the base steel sheet and the hot-dip plating layer is 10 pieces/mm² or less, in which the number density is measured in a plan view.

2. The hot-dip plated steel sheet according to claim 1,

wherein a maximum value of the interface contact length of the interface Mg₂Si phase is 50 μm or less, in which the maximum value is measured in the visual field having a length of 10 mm in the vertical cross section.

3. The hot-dip plated steel sheet according to claim 1 or 2,

wherein a ratio b/a of a length b of the interface Mg₂Si phase in an interface-horizontal direction to a length a of the interface Mg₂Si phase in a plating-depth direction is 0.1 or more and 10 or less in the visual field having a length of 10 mm in the

vertical cross section.

4. The hot-dip plated steel sheet according to any one of claims 1 to 3,
wherein the chemical composition of the hot-dip plating layer contains 0.001 to 2 mass% of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf in total, instead of part of the Zn.

5. The hot-dip plated steel sheet according to any one of claims 1 to 4,
wherein the chemical composition of the hot-dip plating layer contains 0.001 to 2 mass% of one or more selected from Ni, Ti, Zr, and Sr in total, instead of part of the Zn.

6. A method of manufacturing the hot-dip plated steel sheet according to any one of claims 1 to 5, the method comprising:

alkaline degreasing a base steel sheet using alkaline degreasing liquid containing 0.5 to 5.0 mass% of a surfactant;

water rinsing the base steel sheet after the alkaline degreasing;

annealing the base steel sheet after the water rinsing; and

immersing the base steel sheet in a hot-dip plating bath containing Al: 4.0 to 22 mass%, Mg: 1 to 10 mass%, Si: 0.0001 to 2 mass%, and a remainder consisting of Zn and impurities after the annealing, to form a hot-dip plating layer,

wherein a pH of rinsing water is always set to 8.7 or more and 12 or less in the water rinsing.

7. The method of manufacturing the hot-dip plated steel sheet according to claim 6,

wherein the hot-dip plating bath contains 0.001 to 2 mass% of one or more selected from Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Group 3 elements, REM, and Hf in total, instead of part of the Zn.

8. The method of manufacturing the hot-dip plated steel sheet according to claim 6 or 7,

wherein the hot-dip plating bath contains 0.001 to 2 mass% of one or more of Ni, Ti, Zr, and Sr in total, instead of part of the Zn.