DESCRIPTION

TITLE

HOT-DIP AL-ZN ALLOY COATED STEEL SHEET AND METHOD OF PRODUCING SAME

TECHNICAL FIELD

[0001] This disclosure relates to a hot-dip Al-Zn alloy coated steel sheet having stable and excellent workability and corrosion resistance at processed parts, and a method of producing the same.

BACKGROUND

[0002] Hot-dip Al-Zn alloy coated steel sheets, typically represented by 55 % Al-Zn alloy coated steel sheets, are known to exhibit high corrosion resistance among hot-dip galvanized steel sheets, because they combine the sacrificial protection effect of Zn with the high corrosion resistance of Al, as described, for example, in JP S46-7161 B (PTL 1).

Hot-dip Al-Zn coated steel sheets, owing to their excellent corrosion resistance, are mainly used in the field of building materials such as roofs and walls that are exposed to outdoor environments for a long period of time, and the field of civil engineering and construction such as guardrails, wiring and piping, and soundproof walls. In recent years, the demand for hot-dip Al-Zn alloy coated steel sheets has been increasing due to the growing need for materials with excellent corrosion resistance and materials with maintenance-free properties to be used in harsher operating environments, such as in acid rain caused by air pollution, in snowy areas where snow-melting agents are applied to prevent roads from freezing, and in coastal area development.

[0003] The coating of the hot-dip Al-Zn alloy coated steel sheet is characterized by a structure composed of dendritically solidified Al containing supersaturated Zn (α-Al phase) and a Zn-Al eutectic structure present in the interdendritic regions, with multiple layers of the α-Al phase stacked in the thickness direction of the coating. Due to this characteristic coating structure, the corrosion path from the surface becomes more complex, making it more difficult for corrosion to proceed. As a result, it is also known that hot-dip Al-Zn alloy coated steel sheets can achieve excellent corrosion resistance compared to hot-dip galvanized steel sheets with the same coating thickness.

[0004] In general, hot-dip Al-Zn alloy coated steel sheets are produced by

using a thin steel sheet, obtained by hot rolling or cold rolling a slab, as a base steel sheet, and subjecting the base steel sheet to recrystallization annealing and hot-dip coating in an annealing furnace of a continuous galvanizing line (CGL).

It is common practice to add Si to the molten bath, in addition to Al and Zn at predetermined concentrations, in order to suppress excessive growth of the interfacial alloy layer formed at the interface between the base steel sheet and the coating. Owing to the effect of Si, the thickness of the interfacial alloy layer in hot-dip Al-Zn alloy coated steel sheets can be controlled to approximately 1 μm to 5 μm. It is known that, when the coating thickness is the same, suppressing the growth of the interfacial alloy layer leads to improved corrosion resistance, since a thinner interfacial alloy layer allows the main layer, which exhibits high corrosion resistance, to be thicker.

[0005] It is known that when hot-dip Al-Zn alloy coated steel sheets are subjected to processing such as bending, cracks may occur in the coating at the processed parts depending on the degree of deformation. In hot-dip Al-Zn alloy coated steel sheets, the aforementioned thick interfacial alloy layer tends to serve as an initiation point for cracks, and the interdendritic regions in the coating usually act as crack propagation paths. As a result, even when the same degree of bending deformation is applied, cracks tend to open wider in hot-dip Al-Zn alloy coated steel sheets than in hot-dip galvanized steel sheets with the same coating thickness. Therefore, in applications involving a high degree of deformation, there have been problems such as deterioration in appearance due to the formation of large cracks visible to the naked eye, and a significant reduction in corrosion resistance at the cracked areas where the base steel sheet is exposed, compared to areas without cracks (i.e., reduced corrosion resistance at processed parts).

[0006] To solve such problems related to workability and corrosion resistance at processed parts, for example, JP S61-28748 B (PTL 2) and JP 2002-275646 A (PTL 3) describe methods of producing hot-dip Al-Zn alloy coated steel sheets in which workability is improved by subjecting the hot-dip Al-Zn alloy coated steel sheets to predetermined heat treatment.

CITATION LIST

Patent Literature

[0007] PTL 1: JP S46-7161 B

PTL 2: JP S61-28748 B
PTL 3: JP 2002-275646 A
PTL 4: JP 2004-285387 A
PTL 5: JP 2016-540885 A

SUMMARY

(Technical Problem)

[0008] However, even when heat treatment as described in PTLs 2 and 3 is applied, hot-dip Al-Zn alloy coated steel sheets do not always exhibit excellent workability if, for example, impurities are mixed into the coating. Therefore, further improvements have been desired to stably achieve excellent workability and corrosion resistance at processed parts.

[0009] In hot-dip coating processes, it is generally known that impurities are inevitably introduced into the molten bath, and hot-dip Al-Zn alloy coatings are no exception. Impurities introduced into the coating may originate from impurities contained in the coating materials or from elution from the base steel sheet or in-bath equipment, and include elements such as Fe, Cr, Ni, Cu, Co, W, Mg, and Ca, which are therefore inevitably contained in the coating.

In recent years, the production volume of hot-dip Zn-Al-Mg alloy coated steel sheets and hot-dip Al-Zn-Si-Mg alloy coated steel sheets with high corrosion resistance has been increasing. With the expansion in circulation of Zn materials containing high concentrations of Mg that are produced through the recycling of dross generated during the production of such coated sheets, there has been a growing tendency for Mg to be inevitably introduced into the molten bath and, consequently, into the coating as an impurity.

[0010] As described above, inevitable impurities in the coating may cause deterioration in the properties of hot-dip coated steel sheets, such as appearance, corrosion resistance, and workability. Whether or not impurities affect these properties is often determined by the composition of the coating and the concentration of the impurities. In other words, even the same impurity component may be harmful or harmless to the properties of the coated steel sheet. Therefore, for each type of hot-dip coated steel sheet, the influence of impurities on the properties has been investigated, and technologies have been developed to control the impurity concentration to stably achieve the required properties.

For example, JP 2004-285387 A (PTL 4) describes a hot-dip galvanized

steel sheet having excellent appearance, comprising, in mass%, Al: 0.10 % to 0.6 % and Bi: 0.03 % to 0.3 %, with the balance being Zn and inevitable impurities, where the content of each of Pb, Sn, and Cd as the inevitable impurities is controlled to 0.002 %.

Further, JP 2016-540885 A (PTL 5) describes a hot-dip Zn-Al-Mg alloy coated steel sheet having excellent corrosion resistance, comprising Al: 4.4 % to 5.6 % and Mg: 0.3 % to 0.56 %, with the balance being Zn and inevitable impurities, where it is controlled so that Ni is not included as an inevitable impurity.

[0011] However, the technologies described in PTLs 4 and 5 focus on improving corrosion resistance, and do not sufficiently take into account the effects of inevitable impurities on workability and corrosion resistance at processed parts in hot-dip Zn-Al alloy coated steel sheets that do not contain Mg, or in hot-dip Al-Zn alloy coated steel sheets with high Al content. Accordingly, there has been a demand for the development of technologies that can more reliably and stably achieve excellent workability and corrosion resistance at processed parts.

[0012] It could thus be helpful to provide a hot-dip Al-Zn alloy coated steel sheet having reliably and stably excellent workability and corrosion resistance at processed parts, and a method of producing the same.

(Solution to Problem)

[0013] We conducted investigations to solve the above problems and found that, in hot-dip Al-Zn alloy coated steel sheets, it is important to control the concentration and presence state of Mg contained as an optional component or as an inevitable impurity in the hot-dip Al-Zn alloy coating. In particular, we found that by keeping the Mg content low and eliminating $MgZn_2$ and Mg_2Zn_{11} from the coating, it is possible to achieve reliably and stably excellent workability and corrosion resistance at processed parts.

[0014] The present disclosure is based on the above findings, and primary features thereof are as follows.

1. A hot-dip Al-Zn alloy coated steel sheet comprising a coating, wherein

the coating has a chemical composition containing (consisting of) Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 3.0 mass%, with the balance being Zn and inevitable impurities,

a Mg content is 0.3 mass% or less with respect to the total mass of the

coating, and

diffraction intensities of $MgZn_2$ and Mg_2Zn_{11} in the coating measured by X-ray diffraction satisfy the following relational expressions (1) and (2):

$MgZn_2\ (100) = 0$ ...(1)

$Mg_2Zn_{11}\ (321) = 0$ ...(2)

where $MgZn_2$ (100) is a diffraction intensity from a (100) plane of $MgZn_2$ having an interplanar spacing d = 0.4510 nm, and

Mg_2Zn_{11} (321) is a diffraction intensity from a (321) plane of Mg_2Zn_{11} having an interplanar spacing d = 0.2290 nm.

2. The hot-dip Al-Zn alloy coated steel sheet according to 1., wherein the coating further contains, in total, 0.01 mass% to 3.0 mass% of at least one selected from the group consisting of B, Ca, Ti, V, Cr, Mn, Sr, Mo, In, Sn, Sb, Ce, and Bi.

3. The hot-dip Al-Zn alloy coated steel sheet according to 1. or 2., wherein a total content of inevitable impurities in the coating is 5.0 mass% or less.

4. The hot-dip Al-Zn alloy coated steel sheet according to any one of 1. to 3., wherein a Mg content in the inevitable impurities in the coating is 0.3 mass% or less with respect to the total mass of the coating.

[0015] 5. A method of producing a hot-dip Al-Zn alloy coated steel sheet comprising a coating, wherein the method comprises:

forming the coating on a base steel sheet using a molten bath having a chemical composition containing (consisting of) Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 3.0 mass%, with the balance being Zn and inevitable impurities, and having a Mg content controlled to 0.3 mass% or less with respect to the total mass of the molten bath; and

reheating the steel sheet with the coating formed thereon to a reheating temperature T in a range of 130 °C to 300 °C, where the reheating temperature T is a maximum arrival temperature, and after the reheating, cooling the steel sheet such that an average cooling rate C (°C/hr) from the reheating temperature T (°C) to 100 °C satisfies the following relational expression (3):

$C \leq (T - 100)/2$ ...(3)

6. The method of producing a hot-dip Al-Zn alloy coated steel sheet according to 5., wherein the molten bath further contains, in total, 0.01 mass% to 3.0 mass% of at least one selected from the group consisting of B, Ca, Ti, V, Cr, Mn, Sr, Mo, In, Sn, Sb, Ce, and Bi.

7. The method of producing a hot-dip Al-Zn alloy coated steel sheet according to 5. or 6., wherein a total content of inevitable impurities in the molten bath is 5.0 mass% or less.

8. The method of producing a hot-dip Al-Zn alloy coated steel sheet according to any one of 5. to 7., wherein a Mg content in the inevitable impurities in the molten bath is 0.3 mass% or less with respect to the total mass of the molten bath.

(Advantageous Effect)

[0016] According to the present disclosure, it is possible to provide a hot-dip Al-Zn alloy coated steel sheet having reliably and stably excellent workability and corrosion resistance at processed parts, and a method of producing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] In the accompanying drawings:

FIG. 1 is an enlarged schematic view of a cross section of a hot-dip Al-Zn alloy coated steel sheet according to an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0018] (Hot-dip Al-Zn alloy coated steel sheet)

As illustrated in FIG. 1, a hot-dip Al-Zn alloy coated steel sheet of the present disclosure comprises a coating 20 on the surface of a base steel sheet 10. The coating 20 includes a main layer 21 and an interfacial alloy layer 22 formed at the interface between the main layer and the base steel sheet 10.

The coating 20 has a chemical composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 3.0 mass%, with the balance being Zn and inevitable impurities.

[0019] The Al content in the coating is 45 mass% to 65 mass%, preferably 50 mass% to 60 mass%, in view of the balance between corrosion resistance and operability. This is because, when the Al content in the coating is 45 mass% or more, dendritic solidification of Al occurs, and a coating structure mainly composed of a dendritic solidification structure of the α-Al phase can be obtained. The dendritic solidification structure is stacked in the thickness direction of the coating, which complicates the corrosion path and improves the corrosion resistance of the coating itself. In addition, the more the dendritic

portions of the α-Al phase are stacked, the more complex the corrosion path becomes, making it more difficult for corrosion to reach the base steel sheet, thereby improving corrosion resistance. Therefore, the Al content in the coating is preferably 50 mass% or more. On the other hand, when the Al content in the coating exceeds 65 mass%, the structure changes such that most of the Zn is dissolved into the α-Al phase, making it difficult to suppress the dissolution reaction of the α-Al phase, which leads to a deterioration in the corrosion resistance of the hot-dip Al-Zn alloy coating. Therefore, the Al content in the coating is required to be 65 mass% or less, and preferably 60 mass% or less.

[0020] Further, Si in the coating is added mainly for the purpose of suppressing the growth of Fe-Al and/or Fe-Al-Si interfacial alloy layers formed at the interface with the base steel sheet, so as not to impair the adhesion between the coating and the steel sheet. In fact, when a steel sheet is immersed in an Al-Zn molten bath containing Si, the Fe on the steel sheet surface reacts with the Al and Si in the bath to form Fe-Al and/or Fe-Al-Si intermetallic compound layers at the interface between the base steel sheet and the coating. Since the Fe-Al-Si alloy grows more slowly than the Fe-Al alloy, the higher the proportion of the Fe-Al-Si alloy, the more the overall growth of the interfacial alloy layer is suppressed. Therefore, the Si content in the coating is required to be 1.0 mass% or more. On the other hand, when the Si content in the coating exceeds 3.0 mass%, not only does the effect of suppressing the growth of the interfacial alloy layer become saturated, but the presence of excessive Si phases in the coating also deteriorates workability. Therefore, the Si content is set to 3.0 % or less.

[0021] The coating contains Zn and inevitable impurities, where the inevitable impurities include Fe. This Fe is inevitably contained in the coating as a result of being eluted from the steel sheet or in-bath equipment into the molten bath and being supplied through diffusion from the base steel sheet during the formation of the interfacial alloy layer. The Fe content in the coating is typically about 0.3 mass% to 2.0 mass%.

Other inevitable impurities include Cr, Ni, Cu, Co, W, Mg, Ca, and the like. These elements may be inevitably contained in the coating due to various factors, such as elution into the molten bath from the base steel sheet, stainless-steel in-bath equipment, or thermal sprayed coatings of W-C or Co-Cr-W alloy applied to the equipment; the presence of these elements as impurities in the

metal ingots used as raw materials for the molten bath; or the use of pots or in-bath equipment previously employed in the production of coated steel sheets to which such elements were intentionally added.

[0022] The total content of inevitable impurities in the coating is not particularly limited. However, if they are present in excessive amounts, various properties of the coated steel sheet may be affected. Therefore, it is preferable that the total content be 5.0 mass% or less, and more preferably 1.0 mass% or less.

[0023] In the hot-dip Al-Zn alloy coated steel sheet of the present disclosure, the Mg content in the coating should be 0.3 mass% or less with respect to the total mass of the coating. Because Mg contained in the coating may deteriorate the workability and corrosion resistance at processed parts of the hot-dip Al-Zn alloy coated steel sheet, it is possible to suppress such deterioration by appropriately controlling the Al, Zn, and Si contents in the coating as described above and by limiting the Mg content. From the same viewpoint, it is preferable that the Mg content in the coating be 0.1 mass% or less with respect to the total mass of the coating.

In the hot-dip Al-Zn alloy coated steel sheet of the present disclosure, when the Mg content is 0.3 mass% or less with respect to the total mass of the coating, Mg may be optionally contained. However, from the viewpoint of more reliably suppressing the deterioration of workability and corrosion resistance at processed parts in the hot-dip Al-Zn alloy coated steel sheet, it is preferable that Mg not be intentionally added to the coating. That is, it is preferable that the Mg content in the inevitable impurities in the coating be 0.3 mass% or less with respect to the total mass of the coating, and more preferably 0.1 mass% or less. Because the corrosion resistance of the hot-dip Al-Zn alloy coated steel sheet of the present disclosure improves as the Mg content in the coating decreases, there is no particular limitation on the lower limit. However, it is technically difficult to reduce the Mg content in the coating to a completely zero level (0.000 mass%), and thus the practical lower limit of the Mg content in the coating is approximately 0.001 mass%.

[0024] In the hot-dip Al-Zn alloy coated steel sheet of the present disclosure, the diffraction intensities of $MgZn_2$ and Mg_2Zn_{11} in the coating, as measured by X-ray diffraction, satisfy the following relational expressions (1) and (2):

$$MgZn_2\ (100) = 0 \quad \ldots(1)$$

$$Mg_2Zn_{11}\ (321) = 0 \quad \ldots(2)$$

Where $MgZn_2$ (100) refers to the diffraction intensity from the (100) plane of $MgZn_2$ (interplanar spacing d = 0.4510 nm), and Mg_2Zn_{11} (321) refers to the diffraction intensity from the (321) plane of Mg_2Zn_{11} (interplanar spacing d = 0.2290 nm).

[0025] When a small amount of Mg is contained in the coating, $MgZn_2$ and Mg_2Zn_{11} may be formed in the coating. These intermetallic compounds, $MgZn_2$ and Mg_2Zn_{11}, are generally hard and brittle. Therefore, the presence of such intermetallic compounds in the coating may serve as crack initiation points during severe bending or tensile deformation, potentially leading to deterioration in workability and corrosion resistance at processed parts of the hot-dip Al-Zn alloy coated steel sheet. Accordingly, as described above, by suppressing the Mg content in the coating to a low level and ensuring, as shown in the relational expressions (1) and (2), that $MgZn_2$ and Mg_2Zn_{11} are not present in the coating, it becomes possible to more reliably and stably improve the workability and corrosion resistance at processed parts.

[0026] Here, in the above relational expressions (1) and (2), $MgZn_2$ (100) refers to the diffraction intensity from the (100) plane of $MgZn_2$, where the interplanar spacing d = 0.4510 nm, and Mg_2Zn_{11} (321) refers to the diffraction intensity from the (321) plane of Mg_2Zn_{11}, where the interplanar spacing d = 0.2290 nm.

As a method of measuring the $MgZn_2$ (100) and Mg_2Zn_{11} (321) by X-ray diffraction, the measurement can be performed by mechanically extracting a portion of the coating, converting it into powder form, and conducting X-ray diffraction on the powdered sample (powder X-ray diffraction method). To determine the diffraction intensity, it is sufficient to measure the diffraction peak intensity corresponding to the interplanar spacing d = 0.4510 nm for $MgZn_2$ and the diffraction peak intensity corresponding to the interplanar spacing d = 0.2290 nm for Mg_2Zn_{11}.

[0027] In conducting powder X-ray diffraction measurements, the required amount of the coating to be scraped off should be at least 0.1 g to ensure accurate measurement of $MgZn_2$ (100) and Mg_2Zn_{11} (321), and preferably 0.3 g or more. When scraping the coating, components from the base steel sheet may be included in the resulting powder. However, the intermetallic compound phases of interest exist only in the coating, and these inclusions do not affect the above-described peak intensity. Further, performing X-ray diffraction on the powdered coating is necessary because conducting X-ray diffraction

directly on the coating formed on the coated steel sheet can be influenced by the crystallographic orientation of the solidified coating structure, making it difficult to obtain peak intensities corresponding to the actual amount of each substance present.

[0028] The method for satisfying the above relational expressions (1) and (2) is not particularly limited. For example, by controlling the Mg content in the coating to a low level and reducing the ratio of Mg content to Zn content (e.g., setting the Mg/Zn ratio to 0.008 or less, preferably 0.006 or less), the presence of $MgZn_2$ and Mg_2Zn_{11} (specifically, the diffraction intensities of $MgZn_2$ (100) and Mg_2Zn_{11} (321)) can be controlled to a low level.

[0029] Further, in addition to controlling the Mg content in the coating, the relational expressions (1) and (2) can also be satisfied by adjusting the coating formation conditions, such as the cooling conditions after coating treatment, while maintaining the Mg content of the coating at a specific level.

[0030] The coating may further contain, in total, 0.01 mass% to 3.0 mass% of at least one selected from the group consisting of B, Ca, Ti, V, Cr, Mn, Sr, Mo, In, Sn, Sb, Ce, and Bi. These elements can provide effects such as improving the stability of corrosion products during corrosion of the coating to delay the progress of corrosion, and stabilizing the spangle size on the coating surface to improve surface appearance.

[0031] It is preferable that the coating weight of the coating be in the range of 45 g/m² to 120 g/m² per side from the viewpoint of satisfying various required properties. When the coating weight is 45 g/m² or more, sufficient corrosion resistance can be obtained even for applications such as building materials that require long-term durability. When the coating weight is 120 g/m² or less, excellent corrosion resistance can be achieved while suppressing the occurrence of coating cracks during processing. From the same viewpoint, the coating weight is more preferably in the range of 45 g/m² to 100 g/m².

[0032] The coating weight of the coating can be determined, for example, by dissolving and removing the coating over a specified area using a mixed solution of hydrochloric acid and hexamethylenetetramine as described in JIS H 0401:2013, and calculating the difference in weight of the steel sheet before and after the removal. To measure the coating weight per side using this method, the surface on the opposite side should be sealed with tape to prevent exposure, and then the dissolution is carried out as described above.

In addition, the chemical composition of the coating can also be

determined by dissolving the coating in a hydrochloric acid solution or the like, in the same manner as the above-described method of measuring coating weight, and analyzing the resulting solution using ICP emission spectrometry, atomic absorption spectrometry, or other methods. This method is merely an example, and any method capable of accurately and quantitatively determining the chemical composition of the coating may be used. The method is not particularly limited.

[0033] The coating of the hot-dip Al-Zn alloy coated steel sheet obtained by the present disclosure generally has a composition substantially equivalent to that of the molten bath. Therefore, the composition of the coating can be accurately controlled by controlling the composition of the molten bath.

[0034] The base steel sheet of the hot-dip Al-Zn alloy coated steel sheet of the present disclosure is not particularly limited, and cold-rolled steel sheets, hot-rolled steel sheets, or the like may be appropriately used depending on the required properties and specifications.

Further, the method of obtaining the base steel sheet is also not particularly limited. For example, in the case of a hot-rolled steel sheet, one that has undergone hot rolling and pickling processes may be used, and in the case of a cold-rolled steel sheet, it may be further subjected to a cold rolling process. Additionally, in order to impart specific properties to the steel sheet, a recrystallization annealing process or the like may be applied before the hot-dip coating process.

[0035] As illustrated in FIG. 1, the hot-dip Al-Zn alloy coated steel sheet of the present disclosure has a coating 20 formed on a base steel sheet 10, and, if necessary, an intermediate layer and/or a coating film may be further formed on the coating.

The type of the coating film and the method of forming it are not particularly limited and may be appropriately selected according to the required performance. Examples of the forming method include roll coating, curtain flow coating, and spray coating. After applying a paint containing an organic resin, the coating film can be formed by heating and drying the paint using hot air drying, infrared heating, induction heating, or the like.

Further, the intermediate layer is not particularly limited as long as it is a layer formed between the coating and the coating film of the hot-dip Al-Zn alloy coated steel sheet. Examples thereof include a chemical conversion coating or a primer layer such as an adhesive layer. The chemical conversion

coating can be formed, for example, by chromate treatment or chromium-free conversion treatment, where a chromate treatment solution or a chromium-free conversion treatment solution is applied, followed by a drying treatment at a steel sheet temperature of 80 °C to 300 °C without rinsing. These chemical conversion coatings may be a single layer or multilayer, and in the case of multilayer coatings, multiple chemical conversion treatments may be performed sequentially.

[0036] (Method of producing hot-dip Al-Zn alloy coated steel sheet)

The method of producing a hot-dip Al-Zn alloy coated steel sheet of the present disclosure is a method of producing a hot-dip Al-Zn alloy coated steel sheet having a coating.

[0037] The method of producing a hot-dip Al-Zn alloy coated steel sheet of the present disclosure comprises forming the coating on a base steel sheet using a molten bath having a chemical composition containing 45 mass% to 65 mass% of Al and 1.0 mass% to 3.0 mass% of Si, with the balance being Zn and inevitable impurities, where the Mg content in the molten bath is controlled to be 0.3 mass% or less with respect to the total mass of the molten bath.

[0038] The formation of the coating is not particularly limited, except for the molten bath conditions described later.

For example, the coated steel sheet can be produced using a continuous galvanizing line (CGL) by cleaning and heating the base steel sheet and immersing the base steel sheet into the molten bath. When heating the steel sheet, recrystallization annealing or the like may be performed to control the microstructure of the base steel sheet itself, and heating under a reducing atmosphere such as a nitrogen–hydrogen atmosphere is effective for preventing oxidation of the steel sheet and reducing minute oxide films present on the surface.

[0039] The molten bath used for forming the coating has a chemical composition containing Al: 45 mass% to 65 mass% and Si: 1.0 mass% to 3.0 mass%, with the balance being Zn and inevitable impurities. This is because, as described above, the composition of the coating generally corresponds to that of the molten bath.

[0040] In the method of producing a hot-dip Al-Zn alloy coated steel sheet of the present disclosure, the Mg content in the molten bath is controlled to be 0.3 mass% or less with respect to the total mass of the molten bath.

As described above, Mg contained in the coating may cause

deterioration in the workability and corrosion resistance at processed parts of the hot-dip Al-Zn alloy coated steel sheet. Therefore, it is possible to suppress the deterioration in the workability and corrosion resistance at processed parts not only by appropriately controlling the Al, Zn, and Si contents in the molten bath, but also by suppressing the Mg content.

[0041] The Mg content in the molten bath should be controlled to 0.3 mass% or less with respect to the total mass of the molten bath, and preferably to 0.1 mass% or less. When the Mg content in the molten bath is 0.3 mass% or less, the resulting hot-dip Al-Zn alloy coated steel sheet can exhibit sufficiently excellent workability and corrosion resistance at processed parts. When the Mg content is 0.1 mass% or less, even better workability and corrosion resistance at processed parts can be achieved. Because the corrosion resistance of the hot-dip Al-Zn alloy coated steel sheet improves with decreasing Mg content in the molten bath, no specific lower limit is set for the Mg content. However, it is technically difficult to reduce the Mg content in the molten bath completely to 0.000 mass%, and thus the practical lower limit of the Mg content in the coating is approximately 0.001 mass%.

[0042] The method of reducing the Mg content in the molten bath is not particularly limited. For example, it is effective not to intentionally add Mg to the molten bath, and to avoid using pots or in-bath equipment that were used in the production of Mg-containing coated steel sheets, such as Zn-Al-Mg alloy coated steel sheets or Al-Zn-Si-Mg alloy coated steel sheets, for the production of the hot-dip Al-Zn alloy coated steel sheets. This helps to prevent metal lumps containing Mg, which may have adhered to the pot or in-bath equipment, from dissolving and contaminating the molten bath.

It is preferable to use metal ingots with a low Mg impurity content as raw materials for the molten bath, which is another method of reducing the Mg content in the molten bath.

[0043] The bath temperature of the molten bath is not particularly limited, but is preferably in the range of (melting point + 20 °C) to 650 °C.

The lower limit of the bath temperature is set to (melting point + 20 °C) to ensure the bath temperature remains above the solidification point, which is necessary for hot-dip coating treatment, and to prevent local solidification in the molten bath due to temperature drops. The upper limit of the bath temperature is set to 650 °C because if the temperature exceeds 650 °C, it becomes difficult to rapidly cool the coating, which may lead to

excessive growth of the interfacial alloy layer formed between the coating and the steel sheet.

[0044] The temperature of the base steel sheet upon immersion into the molten bath (entering sheet temperature) is also not particularly limited. However, from the viewpoint of ensuring coating properties during the continuous hot-dip coating operation and preventing bath temperature fluctuation, it is preferable to control it within ±20 °C of the molten bath temperature.

[0045] Further, the immersion time of the base steel sheet in the molten bath is preferably 0.5 seconds or more. This is because when the immersion time is less than 0.5 seconds, there is a risk that a sufficient coating may not be formed on the surface of the base steel sheet. Although the upper limit of the immersion time is not particularly limited, it is more preferable to set it within 8 seconds, because an excessively long immersion time may lead to excessive growth of the interfacial alloy layer formed between the coating and the steel sheet.

[0046] In the production of the hot-dip Al-Zn alloy coated steel sheet of the present disclosure, the steel sheet with the coating formed thereon is reheated to a reheating temperature T (°C) in the range of 130 °C to 300 °C, where the reheating temperature T is the maximum arrival temperature. After the reheating, the steel sheet is cooled such that the average cooling rate C (°C/hr) from the reheating temperature T (°C) to 100 °C satisfies the following relational expression (3):

$$C \leq (T - 100)/2 \quad \ldots(3)$$

By performing heat treatment under the above conditions, the coating becomes softened and its ductility is improved, thereby imparting excellent workability to the hot-dip Al-Zn alloy coated steel sheet.

[0047] Generally, in the production of hot-dip Al-Zn alloy coated steel sheets, solidification of the coating proceeds under non-equilibrium conditions due to a high cooling rate. As a result, the α-Al phase in the coating contains supersaturated Zn, and the resulting hot-dip Al-Zn alloy coating tends to be hard and low in ductility.

When the above-described heat treatment (reheating) is applied to such a hot-dip Al-Zn alloy coating, the strain accumulated in the coating during solidification is released, and solid-state diffusion occurs within the coating, promoting phase separation between Al and Zn. In other words, in a hot-dip Al-Zn alloy coated steel sheet that has undergone the heat treatment, the solid solubility of Zn in the α-Al phase decreases, resulting in a softened coating

with improved ductility, thereby achieving excellent workability and corrosion resistance at processed parts.

[0048] In the reheating process, the reheating temperature T is in the range of 130 °C to 300 °C. When the reheating temperature T is less than 130 °C, solid-state diffusion is too slow for sufficient phase separation to occur, and the coating is not adequately softened. On the other hand, when the reheating temperature T exceeds 300 °C, it promotes growth of the alloy phase at the interface between the base steel sheet and the coating, which may adversely affect workability. Therefore, the range for the reheating temperature T is set to 130 °C to 300 °C. From the same viewpoint, it is preferable that the reheating temperature T be in the range of 130 °C to 200 °C.

[0049] Furthermore, the reason for cooling the steel sheet after the reheating such that the average cooling rate C (°C/hr) from the reheating temperature T (°C) to 100 °C satisfies the above relational expression (3) is to promote the phase separation between Al and Zn. Because solid-state diffusion between Al and Zn continues during the cooling process, securing sufficient cooling time as defined by the relational expression (3) enables effective promotion of the phase separation between Al and Zn. On the other hand, when the average cooling rate C (°C/hr) exceeds (T − 100)/2, phase separation between Al and Zn becomes insufficient, resulting in inadequate softening of the coating, and the desired workability and corrosion resistance at processed parts cannot be achieved.

[0050] The heating for providing the above-described reheating process, as well as subsequent heat retention, may be performed using a heating or heat-retaining device installed either within or outside a continuous galvanizing line (CGL). For example, a heating mechanism (such as an induction heater or hot air oven) may be installed within the CGL to perform continuous inline heating. Alternatively, heating may be performed offline in batch mode after winding the steel sheet into a coil. Heating may also be carried out continuously in a separate continuous processing facility outside the coating line using a heating mechanism such as an induction heater or hot air oven. Furthermore, after continuous heating in the coating line or in the continuous processing facility, the coated steel sheet may be wound into a coil and then subjected to appropriate heat retention or holding.

Additionally, during the cooling process after solidification of the molten metal of the coating, a heat-retaining device may be installed to retain

heat and allow slow cooling of the coating. However, the method, shape, and scale of the heating or heat-retaining device are not particularly limited, as long as it can apply the thermal history described above to the coating.

[0051] In the method of producing a hot-dip Al-Zn alloy coated steel sheet of the present disclosure, in addition to the coating forming process and the reheating and cooling processes after coating formation as described above, it is also possible to carry out other processes used in conventional coated steel sheet production, as appropriate.

EXAMPLES

[0052] [Samples 1 to 37]

Cold-rolled steel sheets with a thickness of 0.8 mm, obtained by conventional methods, were used as base steel sheets. Samples 1 to 37 of hot-dip coated steel sheets were produced by annealing and coating processes carried out with a hot-dip coating simulator manufactured by Reska Co., Ltd., under the conditions listed in Table 1.

The composition of the molten bath used to produce the hot-dip coated steel sheets was adjusted so that the resulting coating composition of each sample would correspond to those listed in Table 1. The molten bath compositions were varied as follows: Al: 0.2 mass% to 70 mass%, Si: 0.0 mass% to 3.2 mass%, B: 0.00 mass% to 0.02 mass%, Ca: 0.0 mass% to 1.0 mass%, Ti: 0.0 mass% to 0.1 mass%, V: 0.1 mass% to 0.1 mass%, Cr: 0.0 mass% to 0.2 mass%, Mn: 0.0 mass% to 0.1 mass%, Sr: 0.0 mass% to 0.1 mass%, Mo: 0.0 mass% to 0.1 mass%, In: 0.0 mass% to 0.5 mass%, Sn: 0.0 mass% to 0.1 mass%, Sb: 0.0 mass% to 0.1 mass%, Ce: 0.0 mass% to 1.0 mass%, Bi: 0.00 mass% to 0.05 mass%. The molten bath temperature was controlled as follows: 460 °C for Al: 0.2 mass% to 5 mass%, 600 °C for Al: 35 mass% to 55 mass%, and 660 °C for Al exceeding 60 mass%. The temperature of the base steel sheet as it entered the bath was adjusted to be equal to the molten bath temperature. Additionally, for Al contents between 35 mass% and 70 mass%, coating was carried out under a cooling condition in which the sheet temperature was lowered to the range of 520 °C to 500 °C within 3 seconds.

The coating weight per side was controlled as follows: 85 ± 5 g/m² for Samples 1 to 34, 50 ± 5 g/m² for Sample 35, 100 ± 5 g/m² for Sample 36, and 125 ± 5 g/m² for Sample 37.

Furthermore, all samples from 1 to 37 except Sample 16 were subjected

to a predetermined thermal history (heating and cooling) in a heating furnace after the above-described coating treatment. The thermal history conditions are listed in Table 1.

[0053] [Evaluation]

Each of the obtained hot-dip coated steel sheet samples was subjected to the following evaluations. The evaluation results are listed in Table 1.

[0054] (1) Coating (composition, coating weight, and X-ray diffraction intensities of $MgZn_2$ and Mg_2Zn_{11})

For each of the prepared coated steel sheet samples, a 100 mm diameter disc was punched out, and the non-measured surface was sealed with tape. The coating was then dissolved and removed using a mixed solution of hydrochloric acid and hexamethylenetetramine, as specified in JIS H 0401:2013. The coating weight was calculated based on the difference in sample weight before and after removal. The calculated coating weights are listed in Table 1.

Subsequently, the removal solution was filtered, and the filtrate and the solid residues were analyzed separately. Specifically, the filtrate was analyzed by ICP emission spectrometry to quantify all elements except insoluble Si.

The solid residues were dried and ashed in a heating furnace at 650 °C, then fused by adding sodium carbonate and sodium tetraborate. The fused product was then dissolved in hydrochloric acid, and the resulting solution was analyzed by ICP emission spectrometry to quantify the insoluble Si. The Si concentration in the coating was determined by adding the soluble Si concentration from the filtrate analysis and the insoluble Si concentration from the solid residue analysis. The resulting compositions of the coatings are listed in Table 1.

For each sample, a 100 mm × 100 mm piece was cut, and the coating on the evaluation surface was mechanically removed until the base steel sheet was exposed. The resulting powder was thoroughly mixed, and 0.3 g was extracted for qualitative analysis using an X-ray diffractometer (SmartLab, Rigaku Co., Ltd.) under the following conditions: X-ray source: Cu-Kα (wavelength = 1.54178 Å); Kβ removal: Ni filter; tube voltage: 40 kV; tube current: 30 mA; scanning speed: 4°/min; sampling interval: 0.020°; divergence slit: 2/3°; solar slit: 5°; detector: high-speed 1D detector (D/teX Ultra). The diffraction intensity (kcps) was calculated by subtracting the base intensity from the corresponding peak intensity, and the diffraction intensity of the (100) plane of $MgZn_2$, where interplanar spacing d = 0.4510 nm, and the diffraction

intensity of the (321) plane of Mg_2Zn_{11}, where interplanar spacing d = 0.2290 nm, were measured. The measurement results are listed in Table 1.

[0055] (2) Evaluation of workability

Each of the obtained hot-dip coated steel sheet samples was sheared to a size of 70 mm × 150 mm, then n sheets (n = 4, 5, 6, 7, 8) of the same thickness were placed on the inner side, and a 180° bending process (nT bending) was applied to form a vertex of 150 mm. After bending, Sellotape® (Sellotape is a registered trademark in Japan, other countries, or both) was firmly applied to the outer surface of the bent portion and then peeled off. The outer surface of the bent portion (vertex area) was observed using a scanning electron microscope (ULTRA55, Carl Zeiss) under an accelerating voltage of 5 kV to examine the crack formation, and the workability was evaluated based on the following criteria. The evaluation results are listed in Table 1.

O: No occurrence of large cracks with an opening width of 20 μm or more is observed

×: Occurrence of large cracks with an opening width of 20 μm or more is observed

[0056] (3) Evaluation of corrosion resistance at processed part

Each of the obtained hot-dip coated steel sheet samples was sheared to a size of 70 mm × 150 mm, then the end faces were sealed with tape, 6 or 8 sheets of the same thickness were placed on the inner side, and 6T and 8T bending processes were applied respectively to form a vertex of 150 mm.

All the samples prepared as described above were subjected to a cyclic corrosion test according to the Japanese Automotive Standards Organization (JASO-CCT). The corrosion test started in wet condition and continued for 60 cycles. After the test, the outer surface (vertex area) of the bent portion of each sample was visually observed, and the corrosion resistance was evaluated based on the following criteria. The evaluation results are listed in Table 1.

O: No occurrence of red rust or white rust observed on the sample subjected to 8T bending

×: Occurrence of red rust or white rust observed on the sample subjected to 8T bending

[0057] [Table 1]

[0058] The results in Table 1 indicate that the samples of Examples exhibit a

[Table 1]

No.	Molten bath					Thermal history *1		Coating								Workability					Corrosion resistance at processed part			Remarks
	Composition (mass%)					Reheating temperature T (°C) *2	Cooling rate (°C/hr) *3	Composition (mass%)					Coating weight (g/m^2)	Mg-Zn-based compound		Degree of deformation					Degree of deformation		Evaluation	
	Al	Si	Fe	Mg	Others			Al	Si	Fe	Mg	Others		$MgZn_2$ (100) kcps	Mg_2Zn_{11} (321) kcps	4T	5T	6T	7T	8T	6T	8T		
1	0.2	-	0.01	0.002	-	200	20	0.2	-	0.41	0.002	-	85	0.00	0.00	O	O	O	O	O	×	×	×	Comparative Example
2	5	-	0.19	0.002	-	200	20	5	-	0.32	0.002	-	85	0.00	0.00	O	O	O	O	O	×	×	×	Comparative Example
3	35	1.6	0.21	0.002	-	200	20	35	1.5	0.49	0.002	-	84	0.00	0.00	×	O	O	O	O	×	×	×	Comparative Example
4	46	1.6	0.26	0.003	-	200	20	45	1.5	0.55	0.003	-	86	0.00	0.00	×	O	O	O	O	O	O	O	Example
5	55	0.4	0.34	0.003	-	200	20	55	0.3	1.89	0.003	-	84	0.00	0.00	×	×	×	×	×	×	×	×	Comparative Example
6	55	1.1	0.32	0.002	-	200	20	55	1.0	0.68	0.002	-	85	0.00	0.00	×	×	O	O	O	O	O	O	Example
7	56	1.7	0.33	0.002	-	130	20	55	1.6	0.58	0.002	-	85	0.00	0.00	×	×	×	×	O	×	O	O	Example
8	56	1.7	0.33	0.002	-	170	15	55	1.6	0.58	0.002	-	85	0.00	0.00	×	×	×	O	O	×	O	O	Example
9	56	1.7	0.33	0.002	-	200	20	55	1.6	0.58	0.002	-	85	0.00	0.00	×	O	O	O	O	O	O	O	Example
10	56	1.7	0.33	0.002	-	200	45	55	1.6	0.58	0.002	-	85	0.00	0.00	×	×	×	O	O	×	O	O	Example
11	56	1.7	0.33	0.002	-	265	80	55	1.6	0.58	0.002	-	85	0.00	0.00	×	×	×	×	O	×	O	O	Example
12	56	1.7	0.33	0.002	-	300	65	55	1.6	0.58	0.002	-	85	0.00	0.00	×	×	×	O	O	×	O	O	Example
13	55	1.7	0.29	0.059	-	200	20	55	1.6	0.58	0.057	-	83	0.00	0.00	×	×	O	O	O	O	O	O	Example
14	55	1.7	0.32	0.164	-	200	20	55	1.6	0.57	0.161	-	83	0.00	0.00	×	×	×	O	O	×	O	O	Example
15	55	1.7	0.30	0.246	-	200	20	55	1.6	0.55	0.244	-	85	0.00	0.00	×	×	×	×	O	×	O	O	Example
16	55	1.7	0.32	0.378	-	-	-	55	1.6	0.59	0.771	-	84	0.46	0.00	×	×	×	×	×	×	×	×	Comparative Example
17	55	1.7	0.33	0.378	-	200	20	55	1.6	0.59	0.771	-	84	0.18	0.98	×	×	×	×	×	×	×	×	Comparative Example
18	55	1.7	0.30	0.561	-	200	20	55	1.6	0.61	1.032	-	85	0.23	1.46	×	×	×	×	×	×	×	×	Comparative Example
19	55	3.0	0.34	0.003	-	200	20	55	2.9	0.58	0.002	-	84	0.00	0.00	×	×	×	×	O	×	O	O	Example
20	55	3.2	0.36	0.002	-	200	20	55	3.1	0.56	0.003	-	85	0.00	0.00	×	×	×	×	×	×	×	×	Comparative Example
21	65	1.8	0.43	0.002	-	200	20	64	1.6	0.77	0.002	-	84	0.00	0.00	×	×	O	O	O	O	O	O	Example
22	70	2.0	0.55	0.002	-	200	20	69	1.8	0.88	0.002	-	84	0.00	0.00	×	×	×	×	O	×	×	×	Comparative Example
23	56	1.6	0.35	0.002	Ti: 0.1 B: 0.02	200	20	55	1.6	0.55	0.002	Ti: 0.1 B: 0.02	85	0.00	0.00	×	O	O	O	O	O	O	O	Example
24	57	1.6	0.34	0.002	Ca: 1.0	200	20	55	1.6	0.59	0.002	Ca: 1.0	84	0.00	0.00	×	×	O	O	O	O	O	O	Example
25	56	1.7	0.33	0.001	V: 0.1	200	20	55	1.6	0.58	0.001	V: 0.1	84	0.00	0.00	×	O	O	O	O	O	O	O	Example
26	55	1.7	0.32	0.002	Cr: 0.2	200	20	55	1.6	0.63	0.002	Cr: 0.2	86	0.00	0.00	×	O	O	O	O	O	O	O	Example
27	56	1.6	0.36	0.003	Mn: 0.1	200	20	55	1.6	0.68	0.003	Mn: 0.1	85	0.00	0.00	×	×	×	O	O	×	O	O	Example
28	55	1.6	0.33	0.002	Sr: 0.1	200	20	55	1.6	0.45	0.002	Sr: 0.1	82	0.00	0.00	×	O	O	O	O	O	O	O	Example
29	57	1.6	0.34	0.002	Mo: 0.1	200	20	55	1.6	0.45	0.002	Mo: 0.1	82	0.00	0.00	×	O	O	O	O	O	O	O	Example
30	55	1.6	0.33	0.002	In: 0.5	200	20	55	1.6	0.45	0.002	In: 0.5	82	0.00	0.00	×	O	O	O	O	O	O	O	Example
31	56	1.7	0.31	0.002	Sn: 0.1	200	20	55	1.6	0.56	0.002	Sn: 0.1	84	0.00	0.00	×	O	O	O	O	O	O	O	Example
32	55	1.6	0.33	0.002	Sb: 0.1	200	20	55	1.6	0.56	0.002	Sb: 0.1	85	0.00	0.00	×	O	O	O	O	O	O	O	Example
33	56	1.7	0.32	0.002	Ce: 1.0	200	20	55	1.6	0.45	0.002	Ce: 1.0	82	0.00	0.00	×	O	O	O	O	O	O	O	Example
34	55	1.6	0.29	0.002	Bi: 0.05	200	20	55	1.6	0.45	0.002	Bi: 0.05	82	0.00	0.00	×	O	O	O	O	O	O	O	Example
35	56	1.7	0.33	0.002	-	200	20	55	1.6	0.58	0.002	-	45	0.00	0.00	×	O	O	O	O	O	O	O	Example
36	56	1.7	0.33	0.002	-	200	20	55	1.6	0.58	0.002	-	100	0.00	0.00	×	×	O	O	O	O	O	O	Example
37	56	1.7	0.33	0.002	-	200	20	55	1.6	0.58	0.002	-	125	0.00	0.00	×	×	×	O	O	×	O	O	Example

*1 Reheating and cooling applied by heat treatment after solidification of the coating

*2 Reheating temperature of the coating

*3 Average cooling rate of the coating from the reheating temperature T to 100 °C

well-balanced superiority in both workability and corrosion resistance at processed parts compared to the samples of Comparative Examples.

INDUSTRIAL APPLICABILITY

[0059] According to the present disclosure, it is possible to provide a hot-dip Al-Zn alloy coated steel sheet having reliably and stably excellent workability and corrosion resistance at processed parts, and a method of producing the same.

REFERENCE SIGNS LIST

[0060]

15	Base steel sheet
20	Coating
21	Main layer
22	Interfacial alloy layer
211	Dendrite
212	Interdendrite