

SPECIFICATION

TITLE OF THE INVENTION: MOLTEN ZN-AL ALLOY-PLATED STEEL SHEET AND MANUFACTURING METHOD THEREOF

5

TECHNICAL FIELD

[0001] The present invention relates to a molten Zn-Al alloy-plated steel sheet, called also as a hot-dip Zn-Al alloy coated steel sheet, hereinafter, that possesses excellent corrosion resistance and is preferably used for various members, such as those used in construction, civil engineering and household appliances and a method for manufacturing the same, and in particular, to a hot-dip Zn-Al alloy coated steel sheet with a coating layer having improved workability and corrosion resistance.

BACKGROUND ART

15 [0002] Conventionally, hot-dip zinc or zinc alloy coated steel sheets that are used in various fields, such as construction, civil engineering or household appliances, are required to have excellent corrosion resistance. For example, in the field of construction, hot-dip zinc or zinc alloy coated steel sheets are formed into predetermined shapes and used as structural members, such as roofs, walls or other structures. Such applications require excellent corrosion resistance and superior workability, and furthermore, excellent corrosion resistance in a formed portion. Thus, the corrosion resistance of the material including a formed portion is an important factor for determining the durability of the relevant structural members. Consequently, from the viewpoint of improving the durability of structural members, there is a strong demand for improvement in corrosion resistance of hot-dip zinc or zinc alloy coated steel sheets used as materials. In this case, excellent uniformity of appearance and blackening resistance are required. As used herein, blackening is a phenomenon where a part or the whole of a coated surface is discolored to a blackish gray color.

30

In addition, since hot-dip zinc or zinc alloy coated steel sheets have superior corrosion resistance even under a severe environment, such as in a coastal area exposed to high airborne sea-salt concentrations, such hot-dip zinc or zinc alloy

coated steel sheets are often used without coating in the field of construction.

[0003] To satisfy these requirements, JP-B-3179401 (Patent Document 1) describes a continuous hot-dip Zn-Al-Mg coated steel sheet. According to the technique disclosed in Patent Document 1, it is supposed that a continuous hot-dip Zn-Al-Mg coated steel sheet is provided that has a coating layer formed on a surface of the steel sheet, the coating layer containing: Al: 4.0-10%; Mg: 1.0-4.0%; and the balance consisting of Zn and incidental impurities, and that is given good corrosion resistance and surface appearance by controlling the cooling rate after galvanizing at 0.5°C/sec or higher and providing the coating layer with a metallic structure in which the primary Al phase is mixed in the base material having a ternary eutectic alloy structure of Al/Zn/Zn₂Mg.

[0004] In addition, JP-A-2008-138285 (Patent Document 2) describes a hot-dip Zn-Al alloy coated steel sheet that has aesthetic surface appearance with metallic luster and excellent blackening resistance. According to the technique disclosed in Patent Document 2, it is supposed that a hot-dip Zn-Al alloy coated steel sheet that has aesthetic surface appearance with metallic luster and excellent blackening resistance is provided by dipping a steel sheet into a hot-dip Zn-Al alloy molten bath and pulling up and cooling the steel sheet so as to form a hot-dip Zn-Al alloy coating layer on a steel sheet surface, characterized in that the steel sheet pulled up from the molten bath is cooled at a cooling rate until 250°C of 1°C to 15°C/sec, and the hot-dip Zn-Al alloy coating layer contains: Al: 1.0-10%; Mg: 0.2-1.0% percent; Ni: 0.005-0.1%; and the balance being Zn and incidental impurities. Additionally, it is supposed that the technique disclosed in Patent Document 2 facilitates concentration of Ni into an outermost surface portion of a coating layer due to a synergetic effect of Mg and Ni by controlling the cooling rate after galvanizing within a specific range. According to the technique disclosed in Patent Document 2, it also appears that the Zn-Al alloy coating layer preferably contains ternary eutectic alloys of an Al-Zn-Mg intermetallic compound in an amount of 10 to 30 area % in the cross-section of the coating layer. Further, in the technique described in Patent Document 2, it is supposed that a chemical conversion treatment layer, a primer layer and a resin layer may be formed as upper layers on top of the coating layer, and as a chemical conversion treatment layer, chromium-free treatment may be applied

using a treatment liquid that does not contain chromium, such as a titanium- or zirconium-based treatment liquid.

[0005] Next, described in JP-A-2008-291350 (Patent Document 3) is a hot-dip Zn-Al alloy coated steel sheet that includes: a hot-dip Zn-Al alloy coating layer formed on at least one surface of a steel sheet; and a surface treatment coating film further formed on a surface of the coating layer. According to the technique described in Patent Document 3, it is supposed that by providing a hot-dip Zn-Al alloy coating layer that contains in mass %: Al: 1.0-10%; Mg: 0.2-1.0%; Ni: 0.005-0.1%; and the balance being Zn and incidental impurities, as well as a surface treatment coating film that is formed on a surface of the coating layer and has a surface treatment composition containing a particular titanium-containing aqueous liquid, nickel compound and/or cobalt compound and fluorine-containing compound at a predetermined proportion, superior blackening resistance is obtained in combination with optimization of the coating composition, while enhanced reactivity is achieved due to the effect of the fluorine-containing compound so that a dense reaction layer is formed on the coating surface, and furthermore, high barrier properties are offered by the surface treatment coating film itself so that superior corrosion resistance is provided.

20 PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006] Patent Document 1: JP-B-3179401

Patent Document 2: JP-A-2008-138285

Patent Document 3: JP-A-2008-291350

25 SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0007] However, the coated steel sheet manufactured using the technique disclosed in Patent Document 1 contains large amounts of Al and Mg, each having a higher oxidizability than Zn, in the coating layer. If the coated steel sheet thus manufactured is stored in a warehouse for a long period of time in the form of coil or sheet, a problem arises that a part or the whole of the coated surface will be discolored to a blackish gray color (a blackening phenomenon), reducing the commercial value of the product. In addition, since the technique

disclosed in Patent Document 1 contains a large amount of Mg in the coating layer, it also has a problem that the coating layer is hardened and causes a crack in a formed portion, which accelerates corrosion (red rust) in the base material underlying the coating layer.

5 [0008] The technique disclosed in Patent Document 2 mainly aims at improving blackening resistance with a Zn-Al-Mg-based composition containing Ni in the coating layer. However, in the case of a quaternary system of Al-Mg-Ni-Zn, a problem arises that chemical conversion treatment reaction may result
10 the coating layer depending on the composition of the coating layer, which renders the effect of suppressing blackening unstable.

[0009] Moreover, in the technique disclosed in Patent Document 3, the coating layer is formed with a Zn-Al-Mg-based composition containing Ni, and, additionally, a special surface treatment coating film is formed as an upper layer
15 on the coating layer to improve blackening resistance. However, as the amount of a nickel compound and/or a cobalt compound increases, corrosion resistance deteriorates. Therefore, there remains an issue regarding the difficulty in achieving both corrosion resistance and blackening resistance.

An object of the present invention is to solve these problems in the prior art and
20 to provide a hot-dip Zn-Al alloy coated steel sheet that is excellent in blackening resistance and corrosion resistance, and a method for manufacturing the same.

MEANS FOR SOLVING THE PROBLEM

[0010] To obtain the above-described object, the inventors of the present invention have made various studies on different factors that affect blackening
25 resistance and corrosion resistance of the hot-dip Zn-Al alloy coated steel sheet. As a result, the inventors have found that a coating layer formed on the surface of the steel sheet is provided with a Zn-Al-Mg-based composition containing Ni in an appropriate amount, and then provided with a surface structure where Zn-Al-Mg ternary eutectic alloys exist in an amount of 1-50% by area ratio, whereby a
30 good chemical conversion treatment coating film may be formed on a surface of the coating layer having superior reactivity during the subsequent chemical conversion treatment and blackening resistance may be improved in a steady manner, while effectively suppressing the occurrence of cracks in the coating

layer and significantly enhancing corrosion resistance in a formed portion.

[0011] The inventors of the present invention have also obtained a finding that after forming the Zn-Al-Mg alloy coating layer with the composition as described above, further forming as an upper layer on the coating layer a chemical conversion treatment coating film containing molybdate significantly suppresses blackening in combination with the composition of the coating layer, and thus remarkably improves blackening resistance.

Based on these findings and further considerations, the present invention has been accomplished. That is, the subject matter of the present invention is as follows:

[1] A hot-dip Zn-Al alloy coated steel sheet excellent in blackening resistance and corrosion resistance comprising: a hot-dip Zn-Al alloy coating layer formed on at least one surface of the steel sheet; and a chemical conversion treatment coating film further formed as an upper layer on the hot-dip Zn-Al alloy coating layer,

wherein the hot-dip Zn-Al alloy coating layer has a composition containing in mass %:

Al: 3.0 to 6.0%;

Mg: 0.2 to 1.0%;

Ni: 0.01 to 0.10%; and

the balance being Zn and incidental impurities,

wherein the coating layer has a surface structure containing Zn-Al-Mg ternary eutectic alloys in an amount of 1 to 50% by area ratio, and

wherein the chemical conversion treatment coating film contains molybdate.

[2] The hot-dip Zn-Al alloy coated steel sheet according to item [1] above, wherein the chemical conversion treatment coating film containing molybdate has a coating weight per side of 0.05 to 1.5 g/m².

[3] A method for manufacturing a hot-dip Zn-Al alloy coated steel sheet excellent in blackening resistance and corrosion resistance, the method

comprising: immersing a steel sheet in a hot-dip Zn-Al alloy molten bath with a composition containing in mass %: Al: 3 to 6%; Mg: 0.2 to 1.0%; Ni: 0.01 to 0.10%, and the balance being Zn and incidental impurities; then removing the steel sheet from the molten bath and cooling the steel sheet to form a hot-dip Zn-

Al alloy coating layer on a surface of the steel sheet; and further subjecting the steel sheet to chemical conversion treatment to form a chemical conversion treatment coating film as an upper layer on the hot-dip Zn-Al alloy coating layer, wherein the steel sheet is immersed in the hot-dip Zn-Al alloy molten bath, while
5 controlling the hot-dip Zn-Al alloy molten bath at a temperature within a range of 420 to 520°C, and controlling the steel sheet to be immersed in the hot-dip Zn-Al alloy molten bath at a temperature within a range of 420 to 600°C and equal to or higher than the temperature of the hot-dip Zn-Al alloy molten bath, wherein the steel sheet is then removed from the hot-dip Zn-Al alloy molten bath
10 and subsequently cooled at an average cooling rate until 350°C of 1 to 100°C/sec in terms of a surface temperature of the steel sheet, and wherein the chemical conversion treatment is performed using a chemical conversion treatment liquid containing molybdate.
[4] The method for manufacturing the hot-dip Zn-Al alloy coated steel sheet
15 according to item [3] above, wherein the chemical conversion treatment liquid has a pH of 2 to 6.

EFFECT OF THE INVENTION

[0012] According to the present invention, it is possible to manufacture a hot-dip Zn-Al alloy coated steel sheet in an easy and inexpensive way that
20 steadily exhibits excellent blackening resistance, providing industrially advantageous effects. According to the present invention, it is also possible to manufacture a hot-dip Zn-Al alloy coated steel sheet that exhibits superior corrosion resistance after forming because, by virtue of improved workability of the coating layer, cracks are prevented from occurring in the coating layer at the
25 time of forming and corrosion in the base steel sheet is inhibited in an effective manner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a scanning electron microscope image of the structure showing an exemplary surface structure of a coating layer of a hot-dip Zn-Al
30 alloy coated steel sheet according to the present invention; and

FIG. 2 is an analyzed image showing the surface distribution of Zn-Al-Mg ternary eutectic alloys in the surface structure of the coating layer as depicted in FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

[0014] A hot-dip Zn-Al alloy coated steel sheet of the present invention (hereinafter, also referred to as "the coated steel sheet of the present invention") has, on at least one surface of the steel sheet, a hot-dip Zn-Al alloy coating layer containing in mass %: Al: 3.0 to 6.0%; Mg: 0.2 to 1.0%; Ni: 0.01 to 0.1%; and the balance being Zn and incidental impurities, and further, as an upper layer thereon, a chemical conversion treatment coating film containing molybdate.

[0015] First, the reasons for limiting the composition of the steel sheet of the present invention will be explained. Mass % is simply noted as % hereinafter.

10 <Al: 3.0 to 6.0%>

If Al is contained in the coating layer in an amount less than 3.0%, a Fe-Al alloy layer is formed thick at an interface between the coating layer and the base steel sheet, which results in a deterioration in workability. On the other hand, if Al is contained in an amount more than 6.0%, the sacrificial anti-corrosive effect of Zn is reduced, and so are corrosion resistance and blackening resistance. This also increases the formation of Zn-Al-Mg ternary eutectic alloys, destabilizes the chemical conversion treatment properties and reduces the workability of the coating layer. Thus, Al in the coating layer is limited within a range of 3.0 to 6.0%, preferably 4.0 to 5.5%.

20 [0016] <Mg: 0.2 to 1.0%>

Mg is contained in the coating layer for improved corrosion resistance. If Mg is contained in the coating layer in an amount less than 0.2%, there is less effect on the improvement of corrosion resistance. Alternatively, if Mg is contained in large amounts exceeding 1.0%, the formation of Zn-Al-Mg ternary eutectic alloys increases and the workability of the coating layer deteriorates. As such, Mg in the coating layer is limited within a range of 0.2 to 1.0%, preferably 0.3 to 0.8%.

[0017] <Ni: 0.01 to 0.10%>

Ni is contained in the coating layer for improved corrosion resistance and blackening resistance. If Ni is contained in the coating layer in an amount less than 0.01%, there is less effect on the improvement of corrosion resistance and blackening resistance. Alternatively, if Ni is contained in large amounts exceeding 0.10%, a surface of the coating layer is excessively activated and

becomes more susceptible to corrosion, and furthermore, white rust is more likely to occur in the early stage. Thus, Ni in the coating layer is limited within a range of 0.01 to 0.10%.

The balance other than the above-described components includes Zn and incidental impurities. It should be noted that the impurities include Si, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Sr, Zr, Nb, Mo, and so on, each of which may be contained in an amount up to 0.01%, respectively.

[0018] Additionally, the coating layer formed on the surface of the coated steel sheet of the present invention has the above-described composition as well as the structure containing Zn-Al-Mg ternary eutectic alloys in an amount of 1 to 50% by area ratio in the surface of the coating layer.

The coating layer of the coated steel sheet of the present invention has a surface structure where Zn-Al-Mg ternary eutectic alloys are exposed 1 to 50% by area ratio on its surface. The presence (exposure) of a predetermined amount of Zn-Al-Mg ternary eutectic alloys on the surface of the coating layer allows the coating layer to combine corrosion resistance with workability.

[0019] That is, if Zn-Al-Mg ternary eutectic alloys exist in an amount less than 1% by area ratio in the surface of the coating layer, there is less effect on the improvement of corrosion resistance. Alternatively, if Zn-Al-Mg ternary eutectic alloys exist in an amount exceeding 50% by area ratio in the surface, this results in reduced reactivity of chemical conversion treatment for the surface of the coating layer, more difficulties in obtaining a good chemical conversion treatment coating film, and unstable blackening resistance, and furthermore, the surface of the coating layer becomes excessively hard and therefore more susceptible to cracks during forming. Thus, Zn-Al-Mg ternary eutectic alloys in the surface structure of the coating layer are limited within a range of 1 to 50%, preferably 5 to 40%, by area ratio.

[0020] It should be noted that an area ratio of Zn-Al-Mg ternary eutectic alloys in the surface of the coating layer is preferably determined by, e.g., observing the surface of the coating layer with a scanning electron microscope (magnified about 1000x), imaging the surface structure of the coating layer from some fields of view randomly, and calculating the area ratio for each field of view (image) using image processing software. In the present invention, an

arithmetic mean of the area ratios obtained in these fields of view is considered as an area ratio of Zn-Al-Mg ternary eutectic alloys in the coating layer. FIG. 1 illustrates an exemplary surface structure of the coating layer of the coated steel sheet of the present invention. Striped crystals are Zn-Al-Mg ternary eutectic

5 alloys. Then, FIG. 2 is an analyzed image showing a result of analyzing the surface of the coating layer shown in FIG. 1 for Mg using EPMA as a surface distribution condition of the Zn-Al-Mg ternary eutectic alloys. Using this image analysis diagram, an area ratio of the Zn-Al-Mg ternary eutectic alloys in the surface may also be calculated by a method for converting the image to a black and white image and calculating the area ratio from the histogram. Black areas
10 are Zn-Al-Mg ternary eutectic alloys.

[0021] In the coated steel sheet of the present invention, a coating weight of the Zn-Al-Mg alloy coating layer may be determined depending on its use as usual, and is preferably, but not necessarily, about 30 to 300 g/m² per side. If
15 the coating weight of the coating layer is 30 g/m² or higher, there will not be a lack of thickness in the coating layer and the desired corrosion resistance may be retained. On the other hand, if the coating weight is 300 g/m² or less, there will not be an excess of thickness in the coating layer and the coating layer will not come off.

20 [0022] In the coated steel sheet of the present invention, provided as an upper layer on the hot-dip Zn-Al-Mg alloy coating layer is a chemical conversion treatment coating film containing molybdate. The chemical conversion treatment coating film, which is formed as an upper layer on the coating layer and contains molybdate, improves blackening resistance and corrosion resistance
25 with a combination of this molybdate with Zn-Al-Mg ternary eutectic alloys. It should be noted that the molybdate is not particularly limited and any molybdate may be used that can be dissolved state during chemical conversion treatment. Examples of the molybdate may include a salt of ammonium, sodium and so on. Without limitation, the molybdate is advantageously contained in the chemical
30 conversion treatment coating film in an amount within a range of 0.3 to 3 mass % in molybdenum equivalent, in the light of blackening resistance and corrosion resistance.

[0023] In addition to the molybdate, the chemical conversion treatment

coating film may further contain a chromic acid, a phosphate or a fluoride or salt of Ti, Zr, V, Mn, Ni, Co or the like, a silane compound, a metal chelator, an aqueous resin, an oxide sol such as a silica sol, and so on.

Moreover, a coating weight per side of the chemical conversion treatment coating film may be determined appropriately depending on the application, including, but not limited to: 0.05 g/m² or more, where blackening resistance and corrosion resistance will not deteriorate; and 1.5 g/m² or less, where the amount of coating films formed will not increase and manufacturing cost will not increase significantly. As such, it is preferable that a coating weight per side of the chemical conversion treatment coating film is 0.05 to 1.5 g/m².

Then, a preferred method for manufacturing the coated steel sheet of the present invention will be described below.

[0024] For example, using continuous hot-dip Zn galvanizing production facilities, the steel sheet as the base plate is immersed in a hot-dip Zn-Al alloy molten bath and then removed therefrom and cooled to form a hot-dip Zn-Al alloy coating layer on a surface of the steel sheet.

The steel sheet used as the base plate has no particular limitation on its type and composition, and so may be selected appropriately from well-known hot-rolled steel sheets and cold-rolled steel sheets depending on the application.

[0025] Firstly, the steel sheet as the base plate is heated to a desired heating temperature using, for example, continuous hot-dip galvanizing production facilities. The heating temperature may be determined appropriately depending on the steel sheet used. Without limitation, according to the present invention, the temperature of the steel sheet (sheet temperature) should be controlled to a desired temperature when the steel sheet is immersed in a molten bath, at least such that a desired temperature of the steel sheet (sheet temperature) can be accomplished at the time of immersing the steel sheet in a molten bath.

[0026] The steel sheet heated to a predetermined temperature is immersed in a hot-dip Zn-Al alloy molten bath maintained with a predetermined composition and at a predetermined bath temperature.

The hot-dip Zn-Al alloy molten bath in which the steel sheet is immersed has a composition containing in mass %: Al: 3 to 6%; Mg: 0.2 to 1.0%; Ni: 0.01 to 0.10%; and the balance being Zn and incidental impurities. In addition, the

molten bath is to be at a bath temperature of 420°C to 520°C. If the molten bath is at a bath temperature below 420°C, the molten bath may be partially solidified since the bath temperature is extremely low, disabling a predetermined galvanizing process. On the other hand, if the molten bath is at a high temperature above 520°C, the molten bath is significantly oxidized and more dross will be generated. Thus, the molten bath is to be at a bath temperature limited within a range of 420°C to 520°C. Further, it is preferable that the molten bath is at a bath temperature within a range of 450 to 500°C.

- [0027] In addition, the temperature of the steel sheet to be immersed in the molten bath (sheet temperature) is controlled within a range of 420 to 600°C and equal to or higher than the bath temperature of the molten bath. If the sheet temperature of the steel sheet immersed is below 420°C or below the bath temperature, the bath temperature gradually decreases. Consequently, the viscosity of the molten bath increases and an operational failure will occur. On the other hand, if the sheet temperature is above 600°C, the bath temperature gradually rises and the fixation of galvanizing deteriorates. Thus, the temperature of the steel sheet to be immersed in the molten bath (sheet temperature) is limited within a range of 420 to 600°C and equal to or higher than the bath temperature of the molten bath.
- According to the present invention, the above-described molten bath is controlled at a bath temperature within the above-mentioned range, and the temperature of the steel sheet to be immersed in the molten bath (sheet temperature) is also controlled within a range of 420 to 600°C, and furthermore, the temperature of the steel sheet to be immersed in the molten bath (sheet temperature) is controlled so that it is equal to or higher than the bath temperature of the molten bath. This causes diffusion of alloy elements at an interface between the molten bath and a surface of the steel sheet, which facilitates the formation of a Ni-concentrated layer at an interface between the coating layer and the steel sheet (base plate). If a flaw reaching the base plate occurs in the coating layer due to the formation of a Ni-concentrated layer or if a crack occurs in the coating layer due to forming, corrosion resistance may still be maintained.

[0028] The steel sheet immersed in the molten bath is then removed from the molten bath and cooled. This cooling after the removal is performed at an

average cooling rate until 350°C of 1 to 100°C/sec in terms of a surface temperature of the steel sheet. If the average cooling rate until 350°C is below 1°C/sec, it takes longer to cool and thus productivity deteriorates. On the other hand, if the steel sheet is rapidly cooled at an average cooling rate above 100°C/sec, Zn-Al-Mg ternary eutectic alloys account for more than 50% of the surface by area ratio, which reduces the reactivity of chemical conversion treatment and the workability of the coating layer. As such, the cooling rate after removing the steel sheet from the molten bath is limited within a range of 1 to 100°C/sec, preferably 2 to 70°C/sec, on average until 350°C.

- 5 [0029] The steel sheet having the coating layer formed on the surface thereof is then subjected to chemical conversion treatment, whereby a chemical conversion treatment coating film is formed as an upper layer on the coating layer.

The chemical conversion treatment liquid used in the chemical conversion treatment according to the present invention is such a liquid that is obtained by adding molybdate to a solvent such as water and preferably adjusted to a pH of 2 to 6. It should be noted that the chemical conversion treatment liquid may contain, in addition to molybdate, any one, two, or more of: a chromic acid, a phosphate, a fluoride of Ti, Zr, V, Mn, Ni, Co or the like, a salt of Ti, Zr, V, Mn, Ni, Co or the like, a silane compound, a metal chelator, an aqueous resin and an oxide sol such as a silica sol.

- 20 [0030] In addition, if the chemical conversion treatment liquid has a pH of 2 or higher, it has suitable solubility in the surface of the coating layer and a chemical conversion treatment coating film is formed normally, without loss of fixation ability and corrosion resistance. On the other hand, if the liquid has a pH of 6 or lower, the stability of the chemical conversion treatment liquid will not deteriorate and adhesion ability and corrosion resistance will not be reduced. Thus, it is preferable that the chemical conversion treatment liquid is adjusted to a pH of 2 to 6, more preferably 4 to 5.

- 25 30 The above-described chemical conversion treatment liquid is applied to the surface of the coating layer at normal temperature, heated preferably to 60 to 120°C as the temperature of the steel sheet, and then dried to vaporize the solvent to form a chemical conversion treatment coating film as an upper layer on the

coating layer. Without limitation, the application method may use any continuous processing method, including roll coating, shower wringer and dip gas wiping, all of which are commonly-known application methods. In addition, the drying method may apply any of a hot air oven, electrically heated oven and
5 induction heating, all of which are commonly-known methods.

EXAMPLES

[0031] Cold-rolled steel sheets (sheet thickness: 0.8 mm, non-annealed) were used as base plates. Each of the base plates was heated to a temperature of the
10 steel sheet (sheet temperatures) at the time of immersion as shown in Table 1, then immersed in a hot-dip Zn-Al alloy molten bath having the composition and bath temperature as shown in Table 1, removed from the bath and cooled to form a hot-dip Zn-Al alloy coating layer having the composition and coating weight as shown in Table 2 on a surface of the base plate. Upon removal of each base
15 plate, the base plate was cooled at an average cooling rate until 350°C as shown in Table 1.

[0032] Then, a chemical conversion treatment liquid (liquid temperature: 25°C) was applied by roll coating to a surface of the coating layer of the resulting coated steel sheet, subsequently dried in a hot air oven at 220°C for 3 seconds,
20 and then subjected to chemical conversion treatment to form a chemical conversion treatment coating film in an amount of 0.6 g/m². It should be noted that the chemical conversion treatment liquids used were obtained by adding any one of molybdate, zirconate and titanate to the solvent (water) in an amount of 10 mass % in mass ratio so as to have the pH as shown in Table 1.

25 [0033] Each of the resulting hot-dip Zn-Al alloy coated steel sheets was first observed for the structure of a surface of the coating layer and subjected to a corrosion test. The test method will be described below.

(1) Observation for the structure of surfaces of the coating layers

A test specimen for structural observation was collected from each of the
30 resulting hot-dip Zn-Al alloy coated steel sheets, and was observed for the structure of a surface of the coating layer using a scanning electron microscope (magnified about 1000x). In addition, EPMA was used to analyze the surface of the coating layer for Mg and the results of analysis were subjected to image

analysis, where the image was converted to a black and white image to calculate the area ratio of Zn-Al-Mg ternary eutectic alloys from the histogram.

Then, each of the resulting hot-dip Zn-Al alloy coated steel sheets was subjected to a blackening resistance test to evaluate its blackening resistance. The test

5 method is as follows:

[0034] (2) Blackening resistance test

A test specimen (flat plate: 50 × 50 mm) was collected from each of the resulting hot-dip Zn-Al alloy coated steel sheets, and was subjected to a test where the test specimen was held in a constant temperature and humidity tank at a temperature
10 of 80°C and a relative humidity of 95% for 24 hours. Then, luminosity L of the surface of the test specimen was measured before and after the test and a difference ΔL of luminosity L was determined to evaluate blackening resistance. Evaluation was made based on the following evaluation criteria:

- Grade 3: ΔL is 8 or less (with little blackening)
- 15 – Grade 2: ΔL is greater than 8 but less than 15 (with some blackening)
- Grade 1: ΔL is 15 or more (with significant blackening)

In addition, each of the resulting hot-dip Zn-Al alloy coated steel sheets was subjected to a corrosion resistance test after forming, whereby a formed portion was evaluated for its corrosion resistance. The test method is as follows:

20 [0035] (3) Corrosion resistance test of formed portion

A bend test specimen was collected from each of the resulting hot-dip Zn-Al alloy coated steel sheets, and was subjected to 180° bending (inner radius: 1.6 mmR) in accordance with JIS G 3317 standard, followed by a salt spray test under JIS Z 2371 standard. Salt spray conditions were as follows:

- 25 – liquid sprayed: a 5 mass % solution of sodium chloride
- temperature: 35°C
- test time: 2000 h

After the test, a surface of the test specimen was observed and imaged by a digital camera to determine a red rust occurrence ratio (area ratio) by image
30 processing, whereby a formed portion was evaluated for its corrosion resistance. Evaluation was made based on the following evaluation criteria:

- Grade 3: no red rust
- Grade 2: red rust occurred, red rust occurrence ratio is not more than 50%

– Grade 1: red rust occurred, red rust occurrence ratio is more than 50%

The obtained results are shown in Table 2.

[0036] [Table 1]

Steel No.	Sheet Temp. (immersed in molten bath) (°C)	molten bath						Difference between Sheet Temp. and Bath Temp. (°C)	Cooling After Removal	Chemical Conversion		Remarks
		Bath Temp. (°C)	Composition (mass %)				Type of Added Anti-rust Agent			pH (Liquid Temp.: 25°C)		
			Al	Mg	Ni	Zn						
1	500	460	4.5	0.5	0.05	balance	40	35	molybdate	4	Present Invention	
2	500	460	3.0	0.2	0.01	balance	40	35	molybdate	4	Present Invention	
3	500	460	6.0	1.0	0.10	balance	40	35	molybdate	4	Present Invention	
4	500	460	3.2	0.9	0.01	balance	40	35	molybdate	4	Present Invention	
5	500	460	5.5	0.3	0.08	balance	40	35	molybdate	4	Present Invention	
6	580	520	4.5	0.5	0.05	balance	60	50	molybdate	4	Present Invention	
7	580	440	4.5	0.5	0.05	balance	140	30	molybdate	4	Present Invention	
8	500	460	6.5	1.0	0.04	balance	40	35	molybdate	4	Comparative Example	
9	500	460	0.8	0.1	-	balance	40	35	molybdate	4	Comparative Example	
10	500	460	4.8	3.2	0.10	balance	40	35	molybdate	4	Comparative Example	
11	500	460	4.5	0.5	0.20	balance	40	35	molybdate	4	Comparative Example	
12	500	460	4.5	0.5	0.05	balance	40	35	titanate	8	Comparative Example	
13	500	460	4.5	0.5	0.05	balance	40	35	zirconate	8	Comparative Example	
14	500	440	4.5	0.5	0.05	balance	60	110	molybdate	4	Comparative Example	

*) Average from time of removal until 350°C

[0037] [Table 2]

Steel No.	Coating Layer				Surface Structure of Coating Layer	Chemical Conversion Treatment Coating Film		Blackening Resistance	Corrosion Resistance in Formed Portion	Remarks	
	Composition (mass %)					Coating weight (g/m ²)	Area Ratio of Zn-Al-Mg ternary eutectic alloys (area %)	Type of Added Anti-rust Agent	Coating Weight (g/m ²)		Grade
	Al	Mg	Ni	Zn							
1	4.5	0.5	0.05	balance	125	22	molybdate	0.6	3	Present Invention	
2	3.0	0.2	0.01	balance	125	15	molybdate	0.6	3	Present Invention	
3	6.0	1.0	0.10	balance	125	47	molybdate	0.6	3	Present Invention	
4	3.2	0.9	0.01	balance	125	18	molybdate	0.6	3	Present Invention	
5	5.5	0.3	0.08	balance	125	26	molybdate	0.6	3	Present Invention	
6	4.5	0.5	0.05	balance	125	22	molybdate	0.3	3	Present Invention	
7	4.5	0.5	0.05	balance	125	22	molybdate	1.5	3	Present Invention	
8	6.5	1.0	0.04	balance	125	75	molybdate	0.6	2	Comparative Example	
9	0.8	0.1	-	balance	125	<1	molybdate	0.6	2	Comparative Example	
10	4.8	3.2	0.10	balance	125	65	molybdate	0.6	1	Comparative Example	
11	4.5	0.5	0.20	balance	125	22	molybdate	0.6	3	Comparative Example	
12	4.5	0.5	0.05	balance	125	22	titanate	0.6	1	Comparative Example	
13	4.5	0.1	0.05	balance	125	22	zirconate	0.6	1	Comparative Example	
14	4.5	0.5	0.05	balance	125	52	molybdate	0.6	2	Comparative Example	

[0038] Each Example of the present invention represents a hot-dip Zn-Al alloy coated steel sheet that possesses superior blackening resistance as well as superior corrosion resistance in formed portions. In contrast, Comparative Examples outside the scope of the present invention are inferior in one or both of

5 blackening resistance and corrosion resistance in formed portions.

CLAIMS

1. A hot-dip Zn-Al alloy coated steel sheet comprising: a hot-dip Zn-Al alloy coating layer formed on at least one surface of the steel sheet; and further a
5 chemical conversion treatment coating film formed as an upper layer on the hot-dip Zn-Al alloy coating layer,

wherein the hot-dip Zn-Al alloy coating layer has a composition containing in mass %:

Al: 3.0 to 6.0%;

10 Mg: 0.2 to 1.0%;

Ni: 0.01 to 0.10%; and

the balance being Zn and incidental impurities,

wherein the coating layer has a surface structure containing a ternary eutectic of Zn-Al-Mg in an amount of 1 to 50% in area ratio, and

15 wherein the chemical conversion treatment coating film contains molybdate.

2. The hot-dip Zn-Al alloy coated steel sheet according to claim 1, wherein the chemical conversion treatment coating film containing molybdate has a coating weight per side of 0.05 to 1.5 g/m².

20

3. A method for manufacturing a hot-dip Zn-Al alloy coated steel sheet, the method comprising: immersing a steel sheet in a hot-dip Zn-Al alloy molten bath with a composition containing in mass %: Al: 3 to 6%; Mg: 0.2 to 1.0%; Ni: 0.01 to 0.10%; and the balance being Zn and incidental impurities; then removing
25 the steel sheet from the molten bath and cooling the steel sheet to form a hot-dip Zn-Al alloy coating layer on a surface of the steel sheet; and further subjecting the steel sheet to chemical conversion treatment to form a chemical conversion treatment coating film as an upper layer on the hot-dip Zn-Al alloy coating layer,

wherein the steel sheet is immersed in the hot-dip Zn-Al alloy molten bath,
30 while controlling the hot-dip Zn-Al alloy molten bath at a temperature within a range of 420 to 520°C, and controlling the steel sheet to be immersed in the hot-dip Zn-Al alloy molten bath at a temperature within a range of 420 to 600°C and being equal to or higher than the temperature of the hot-dip Zn-Al alloy molten

bath,

wherein the steel sheet is then removed from the hot-dip Zn-Al alloy molten bath and subsequently cooled at an average cooling rate until 350°C of 1 to 100°C/sec in terms of a surface temperature of the steel sheet, and

5 wherein the chemical conversion treatment is performed using a chemical conversion treatment liquid containing molybdate.

4. The method for manufacturing a hot-dip Zn-Al alloy coated steel sheet according to claim 3, wherein the chemical conversion treatment liquid has a pH
10 of 2 to 6.