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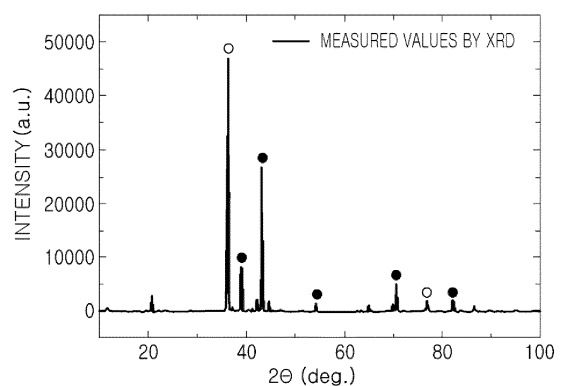
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(54) **ZINC ALLOY PLATED STEEL SHEET HAVING EXCELLENT BENDING WORKABILITY AND MANUFACTURING METHOD THEREFOR**

(57) Disclosed are: a zinc alloy plated steel sheet comprising a base steel sheet and a zinc alloy plated layer; and a method for manufacturing the same, the zinc alloy plated layer comprising a Zn single phase structure as a microstructure, and a Zn-Al-Mg-based intermetallic compound, wherein (0001) preferred orientation degree (f) of the Zn single phase structure, represented by the following relation formula 1, is 50% or higher. [Relation formula 1] $f(\%) = (I_{\text{basal}} / I_{\text{total}}) \times 100$ (wherein, I_{total} is defined as a value obtained by integrating diffraction peaks of all Zn single phases when an X-ray diffraction pattern is measured to 2 theta 10°-100° by using a Cu-K α source, and I_{basal} is defined as a value obtained by integrating diffraction peaks of Zn single phases related to a basal plane.)

【Figure 3】



Description

[Technical Field]

5 **[0001]** The present disclosure relates to a zinc alloy plated steel sheet having high bending workability and a method for manufacturing the zinc alloy plated steel sheet.

[Background Art]

10 **[0002]** A zinc plating method for suppressing the corrosion of iron by cathodic protection has high anti-corrosion efficiency and economic feasibility, and thus has been widely used in manufacturing steel materials having high corrosion resistance. Particularly, hot-dip zinc plated steel sheets, manufactured by dipping a steel material into molten zinc to form a plating layer, are obtainable through simple manufacturing processes and are relatively inexpensive, as compared to electro-zinc plated steel sheets, and thus, demand therefor has increased in a wide range of industries, such as the automotive industry, the home appliance industry, and the construction industry.

15 **[0003]** When a hot-dip zinc plated steel sheet is exposed to a corrosive environment, zinc having a lower oxidation-reduction potential than iron undergoes corrosion first, and thus, corrosion of the steel sheet is suppressed by sacrificial corrosion protection. Along with this, compact corrosion products are formed on the surface of the steel sheet as zinc of a plating layer is oxidized, thereby protecting the steel sheet from the corrosive environment and improving the corrosion resistance of the steel sheet.

20 **[0004]** However, air pollution and corrosive environments have increased with industrial advances, and regulations on resource and energy savings have been tightened. Therefore, the need to develop a steel material having higher corrosion resistance than existing zinc plated steel sheets has increased.

25 **[0005]** In this regard, research has been variously conducted into techniques for manufacturing zinc alloy-based plated steel sheets having corrosion resistance improved by adding elements such as aluminum (Al) and magnesium (Mg) to a zinc plating bath. Techniques for manufacturing a Zn-Al-Mg-based zinc alloy plated steel sheet, which is representative of zinc alloy-based plated steel sheets and manufactured by additionally adding magnesium (Mg) to a Zn-Al plating composition, have been actively researched.

30 **[0006]** However, such a Zn-Al-Mg-based zinc alloy plated steel sheet has poor bending workability. That is, the zinc alloy plated steel sheet includes large amounts of Zn-Al-Mg-based intermetallic compounds in a plating layer thereof as a result of thermodynamic reaction between zinc (Zn), aluminum (Al), and magnesium (Mg), and such intermetallic compounds may cause cracks in the plating layer during a bending process because of high hardness of the intermetallic compounds, thereby lowering the bending workability of the zinc alloy plated steel sheet.

35 [Disclosure]

[Technical Problem]

40 **[0007]** Aspects of the present disclosure may provide a zinc alloy plated steel sheet having high bending workability and a method for manufacturing the zinc alloy plated steel sheet.

[0008] The present disclosure is not limited to the above-mentioned aspects. Other aspects of the present disclosure are stated in the following description, and the aspects of the present disclosure will be clearly understood by those of ordinary skill in the art through the following description.

45 [Technical Solution]

[0009] According to an aspect of the present disclosure, a zinc alloy plated steel sheet may include a base steel sheet and a zinc alloy plating layer, wherein the zinc alloy plating layer may include a Zn single phase structure as a micro-structure and a Zn-Al-Mg-based intermetallic compound, and the Zn single phase structure may have a degree (f) of (0001) preferred orientation, expressed by Formula 1 below, within a range of 50% or greater,

[Formula 1]

$$55 \quad f(\%) = (I_{\text{basal}} / I_{\text{total}}) \times 100$$

where I_{total} refers to an integral of all diffraction peaks of the Zn single phase structure when an X-ray diffraction pattern is measured within a range of 2 theta from 10° to 100° using a Cu-K α source, and I_{basal} refers to an integral of diffraction

peaks of the Zn single phase structure relating to a basal plane.

[0010] According to another aspect of the present disclosure, a method for manufacturing a zinc alloy plated steel sheet may include: preparing a zinc alloy plating bath including magnesium (Mg) and aluminum (Al); obtaining a zinc alloy plated steel sheet by dipping a base steel sheet into the zinc alloy plating bath to plate the base steel sheet; wiping the zinc alloy plated steel sheet with gas to adjust a plating weight; and after adjusting the plating weight of the zinc alloy plated steel sheet, cooling the zinc alloy plated steel sheet by spraying droplets of water or an aqueous solution onto the zinc alloy plated steel sheet and then using air, wherein when the droplets are sprayed, a droplet spray start temperature ranges from 405°C to 425°C, a droplet spray stop temperature ranges from 380°C to 400°C.

[Advantageous Effects]

[0011] According to one of various effects of the present disclosure, an embodiment of the present disclosure provides a zinc alloy plated steel sheet having high bending workability as well as high corrosion resistance.

[0012] In addition, according to one of various effects of the present disclosure, the zinc alloy plated steel sheet of the embodiment has high surface quality.

[0013] In addition, according to one of various effects of the present disclosure, the zinc alloy plated steel sheet of the embodiment has high scratch resistance.

[Description of Drawings]

[0014]

FIGS. 1A and 1B are views illustrating results of an observation of a surface microstructure of Inventive Sample 1 and an observation of a surface microstructure of Comparative Sample 5.

FIGS. 2A and 2B are views illustrating results of an observation of a cross-sectional microstructure of Inventive Sample 1 and an observation of a cross-sectional microstructure of Comparative Sample 5.

FIG. 3 is a view illustrating results of X-ray diffractometer (XRD) analysis of Inventive Sample 1.

[Best Mode]

[0015] Hereinafter, a zinc alloy plated steel sheet having high bending workability will be described in detail according to an aspect of the present disclosure.

[0016] According to the aspect of the present disclosure, the zinc alloy plated steel sheet includes a base steel sheet and a zinc alloy plating layer. In the present disclosure, the base steel sheet is not limited to a particular type. For example, a hot-rolled steel sheet or a cold-rolled steel sheet commonly used as a base steel sheet of a zinc alloy plated steel sheet may be used. However, hot-rolled steel sheets have a large amount of surface oxide scale that lowers plating adhesion and thus plating quality, and thus a hot-rolled steel sheet from which oxide scale has been previously removed using an acid solution may be used as the base steel sheet. In addition, the zinc alloy plating layer may be formed on one or each side of the base steel sheet.

[0017] The zinc alloy plating layer may include, by wt%, aluminum (Al): 0.5% to 3%, magnesium (Mg): 0.5% to 3%, and the balance of zinc (Zn) and inevitable impurities.

[0018] In the zinc alloy plating layer, magnesium (Mg) reacts with zinc (Zn) and aluminum (Al) and forms a Zn-Al-Mg-based intermetallic compound, thereby functioning as a key element improving the corrosion resistance of the zinc alloy plated steel sheet. If the content of magnesium (Mg) is excessively low, the Zn-Al-Mg-based intermetallic compound is not present in sufficient amounts in the microstructure of the zinc alloy plating layer, and thus corrosion resistance may not be sufficiently improved. Therefore, the amount of magnesium (Mg) in the zinc alloy plating layer may be 0.5 wt% or greater, preferably 1.0 wt% or greater. However, if the content of magnesium (Mg) is excessively high, the effect of improving corrosion resistance is saturated, and Mg oxide dross having a negative effect on platability may be formed in a plating bath. In addition, the Zn-Al-Mg-based intermetallic compound having high hardness may be formed in excessively large amounts in the microstructure of the zinc alloy plating layer, and thus bending workability may be lowered. Therefore, the amount of magnesium (Mg) in the zinc alloy plating layer may be 3 wt% or less, preferably 2.9 wt% or less.

[0019] Aluminum (Al) suppresses the formation of Mg oxide dross and reacts with zinc (Zn) and magnesium (Mg) to form the Zn-Al-Mg-based intermetallic compound in the zinc alloy plating layer, thereby functioning as a key element improving the corrosion resistance of the zinc alloy plated steel sheet. If the content of aluminum (Al) is excessively low, the formation of Mg dross is not sufficiently suppressed, and the Zn-Al-Mg-based intermetallic compound is not present in sufficient amounts in the microstructure of the zinc alloy plating layer, which may result in insufficient improvements in corrosion resistance. Therefore, the amount of aluminum (Al) in the zinc alloy plating layer may be 0.5 wt% or greater, preferably 0.6 wt% or greater. However, if the content of aluminum (Al) is excessively high, the effect of improving

corrosion resistance is saturated, and the durability of plating equipment may be negatively affected because of a high plating bath temperature. Moreover, the Zn-Al-Mg-based intermetallic compound having high hardness may be formed in excessively large amounts in the microstructure of the zinc alloy plating layer, and thus bending workability may be lowered. Therefore, the amount of aluminum (Al) in the zinc alloy plating layer may be 3 wt% or less, preferably 2.6 wt% or less.

[0020] According to an embodiment, the contents of magnesium (Mg) and aluminum (Al) in the zinc alloy plating layer may satisfy the following Formula 1. If [Mg]/[Al] is 1.0 or less, scratch resistance may deteriorate, and if [Mg]/[Al] is greater than 4.0, Mg-based dross may be formed in large amounts in a hot-dip plating bath to lower workability.

[Formula 1]

$$1.0 < [\text{Mg}] / [\text{Al}] \leq 4.0$$

where [Mg] and [Al] refer to the weight percentages (wt%) of corresponding elements, respectively.

[0021] The zinc alloy plating layer may include a Zn single phase structure as a microstructure and the Zn-Al-Mg-based intermetallic compound. In the present disclosure, the Zn-Al-Mg-based intermetallic compound is not limited to a particular type. However, for example, the Zn-Al-Mg-based intermetallic compound may include at least one selected from the group consisting of a Zn/Al/MgZn₂ ternary eutectic structure, a Zn/MgZn₂ binary eutectic structure, a Zn-Al binary eutectic structure, and an MgZn₂ single phase structure.

[0022] The inventors have conducted in-depth research into improving the bending workability of zinc alloy plated steel sheets and found that if a Zn single phase structure having a hexagonal close packing (HCP) structure is grown in a (0001) orientation in the microstructure of the zinc alloy plating layer, ductility increases owing to easy slippage, and thus cracks are markedly reduced in a bending process.

[0023] In the present disclosure, to obtain this effect, the degree (f) of (0001) preferred orientation, expressed by the following formula 1, may preferably be adjusted to be 50% or greater, more preferably 60% or greater.

[Formula 1]

$$f(\%) = (I_{\text{basal}} / I_{\text{total}}) \times 100$$

where I_{total} refers to the integral of all diffraction peaks of the Zn single phase structure when an X-ray diffraction pattern is measured within the range of 2 theta from 10° to 100° using a Cu-K α source, and I_{basal} refers to the integral of diffraction peaks of the Zn single phase structure relating to a basal plane.

[0024] In addition, the inventors have found that if the Zn single phase structure coarsely formed in the zinc alloy plating layer is refined in size, it is also helpful to reduce cracking during a bending process.

[0025] To obtain this effect of the present disclosure, the average grain diameter of the Zn single phase structure may be preferably adjusted to be 15 μm or less, more preferably 12 μm or less, and even more preferably 10 μm or less.

The "average grain diameter" of the Zn single phase structure refers to the average of equivalent circular diameters of the Zn single phase structure measured by observing a thicknesswise cross-section of the zinc alloy plating layer. The zinc alloy plated steel sheet of the present disclosure has high corrosion resistance and bending workability as well.

[0026] According to an embodiment, the zinc alloy plated steel sheet of the present disclosure may have a good appearance. Specifically, the number of black spots per unit area may be equal to or less than 0.1/cm² on the surface of the zinc alloy plated steel sheet.

[0027] To obtain these effects of the present disclosure, the area fraction of the Zn single phase structure may preferably be 40% or less (excluding 0%) on the surface of the zinc alloy plating layer. That is, the appearance of the zinc alloy plated steel sheet may be improved by maximizing the fraction of the Zn-Al-Mg-based intermetallic compound present on the surface of the zinc alloy plating layer.

[0028] According to an embodiment, the zinc alloy plated steel sheet of the present disclosure may also have high scratch resistance.

[0029] According to results of research conducted by the inventors, if the area fractions of the Zn/MgZn₂ binary eutectic structure and the Zn/Al/MgZn₂ ternary eutectic structure which have a layer structure and are present on the surface of the zinc alloy plating layer are maximized, scratch resistance may be markedly improved.

[0030] To obtain this effect of the present disclosure, preferably, the sum of the area fractions of the Zn/MgZn₂ binary eutectic structure and the Zn/Al/MgZn₂ ternary eutectic structure may be 50% or greater (excluding 100%), and the area fraction of the MgZn₂ single phase structure may be 10% or less (including 0%). The MgZn₂ single phase structure has high hardness and thus causes cracks during a machining process, and thus the area fraction of the MgZn₂ single phase

structure may be adjusted to be as low as possible.

[0031] The zinc alloy plated steel sheet of the present disclosure may be manufactured by various methods without limitation. However, for example, when the zinc alloy plating layer solidifies from a molten state, the zinc alloy plating layer may be cooled by spraying droplets thereon and then cooled with air to obtain the above-described degree of preferred orientation and average grain diameter.

[0032] In this case, droplets may be sprayed by a charge spray method to attach the droplets by electrostatic attraction between the droplets and the zinc alloy plated steel sheet. This charge spray method may be helpful in forming fine, uniform droplets and reducing the amount of droplets colliding with and bouncing off the zinc alloy plated steel sheet after being sprayed on the zinc alloy plated steel sheet, thereby facilitating rapid cooling of the zinc alloy plating layer from the molten state and having a positive effect on the growth of the Zn single phase structure in the (0001) orientation and refinement of the Zn single phase structure.

[0033] The droplets may be droplets of a phosphate aqueous solution capable of rapidly cooling the zinc alloy plating layer from the molten state through an endothermic reaction and thus effective in growing the Zn single phase structure in the (0001) orientation and refining the Zn single phase structure. Examples of the phosphate aqueous solution may include an aqueous solution of ammonium hydrogen phosphate $((\text{NH}_4)_2\text{HPO}_4)$, an aqueous solution of sodium ammonium hydrogen phosphate $(\text{NaNH}_4\text{HPO}_4)$, an aqueous solution of zinc dihydrogen phosphate $(\text{Zn}(\text{H}_2\text{PO}_4)_2)$, and an aqueous solution of calcium phosphate $(\text{Ca}_3(\text{PO}_4)_2)$.

[0034] In addition, the content of the phosphate aqueous solution may be 1 wt% to 3 wt%. If the content of the phosphate aqueous solution is less than 1 wt%, the effect of the phosphate aqueous solution may not be sufficient. If the content of the phosphate aqueous solution is greater than 3 wt%, the effect of the phosphate aqueous solution is saturated, and nozzle clogging may occur in a continuous production process, lowering productivity.

[0035] In addition, when the droplets may be sprayed at a droplet spray start temperature of 405°C to 425°C, and more preferably 410°C to 420°C. Here, the term "droplet spray start temperature" refers to a surface temperature of the zinc alloy plated steel sheet at the start time of droplet spraying. If the droplet spray start temperature is less than 405°C, solidification of the Zn single phase structure may have already started, and thus black spots may be formed on the surface of the zinc alloy plated steel sheet. Conversely, if the droplet spray start temperature is greater than 425°C, droplets may not effectively undergo an endothermic reaction, and thus it may be difficult to obtain an intended structure.

[0036] In addition, the droplets may be sprayed at a droplet spray stop temperature of 380°C to 400°C, and more preferably 390°C to 400°C. Here, the term "droplet spray stop temperature" refers to a surface temperature of the zinc alloy plated steel sheet at a point in time at which spraying of droplets stops. If the droplet spray stop temperature is greater than 400°C, an endothermic reaction by the droplets may occur ineffectively, and thus it may be difficult to obtain an intended structure. Conversely, if the droplet spray stop temperature is less than 380°C, a $\text{Mg}_2\text{Zn}_{11}$ phase may be formed due to over cooling while the Zn/MgZn₂ binary eutectic phase and the Zn/Al/MgZn₂ ternary phase start to solidify, and thus many black spots may be formed, decreasing the degree of (0001) preferred orientation of the Zn single phase structure.

[0037] In addition, the difference between the droplet spray start temperature and the droplet spray stop temperature may be 15°C or greater. If the difference is less than 15°C, the droplets may not undergo an effective endothermic reaction, and thus it may be difficult to obtain an intended structure.

[0038] In addition, the droplets may be sprayed in an amount of 50 g/m² to 100 g/m². If the spraying amount of the droplets is less than 50 g/m², the effect of the droplets may be insufficient, and if the spraying amount of the droplets is greater than 100 g/m², the effect of the droplets may be saturated.

[Mode for Invention]

[0039] Hereinafter, the present disclosure will be described more specifically through examples. However, the following examples should be considered in a descriptive sense only and not for purpose of limitation. The scope of the present invention is defined by the appended claims, and modifications and variations reasonably made therefrom.

(Example 1)

[0040] Low carbon cold-rolled steel sheets each having a thickness of 0.8 mm, a width of 100 mm, and a length of 200 mm were prepared as base steel sheets for plating test samples, and then foreign substances such as rolling oil were removed from the surfaces of the base steel sheets by dipping the base steel sheets into acetone and washing the base steel sheets with ultrasonic waves. Thereafter, a 750°C reducing atmosphere heat treatment commonly performed to guarantee mechanical characteristics of steel sheets in the hot-dipping plating field was performed on the base steel sheets, and then the base steel sheets were dipped into plating baths (bath temperature: 460°C) having compositions shown in Table 1 below to fabricate zinc alloy plated steel sheets. Thereafter, each of the zinc alloy plated steel sheets was wiped with gas to adjust a plating weight to be 70 g/m² on each side. Then, the zinc alloy plated steel

sheets were cooled under the conditions shown in Table 1 below and were cooled with air. Although not shown in Table 1 below, Comparative Sample 5 was prepared by performing a gas wiping process on a zinc alloy plated steel sheet fabricated using the same plating bath as that used to fabricate Inventive Sample 1 to adjust a plating weight to be 70 g/m² on each side, and then cooling the zinc alloy plated steel sheet using a general cooling device at an average cooling rate of 12°C/sec until the plating layer of the zinc alloy plated steel sheet was completely solidified (at about 300°C or less).

[0041] Then, the microstructures of the fabricated zinc alloy plated steel sheets were observed using an FE-SEM (SUPRA-55VP, Zeiss) as illustrated in FIGS. 1 and 2, and the average grain diameter of a Zn single phase structure of each of the zinc alloy plated steel sheets was measured as shown in Table 2 below.

[0042] Thereafter, the degree (f) of (0001) preferred orientation of the Zn single phase structure was measured using the following Formula 1, and results thereof are shown in Table 2 below.

[Formula 1]

$$f(\%) = (I_{\text{basal}} / I_{\text{total}}) \times 100$$

where I_{total} refers to the integral of all diffraction peaks of the Zn single phase structure when an X-ray diffraction pattern was measured within the range of 2 theta from 10° to 100° using a Cu-K α source, and I_{basal} refers to the integral of diffraction peaks of the Zn single phase structure relating to a basal plane.

[0043] Thereafter, the bending workability of each of the zinc alloy plated steel sheets was evaluated, and results thereof are shown in Table 2 below.

[0044] Corrosion resistance was evaluated as follows.

[0045] A salt spray test (based on KS-C-0223) was performed on each of the zinc alloy plated steel sheets to facilitate corrosion, and then the time taken until the area fraction of red rust on the surface of each plating layer was 5% was measured.

[0046] Bending workability was evaluated as follows.

[0047] 3T bending was performed on each of the zinc alloy plated steel sheets, and a 1-mm length of the apex of each bent portion was observed using an SEM to measure the area fraction of bending cracks using an image analysis system.

[Table 1]

No.	Composition of plating bath (wt%)		Droplet spray start temperature (°C)	Droplet spray stop temperature (°C)	Droplets	Spraying amount (g/m ²)	Notes
	Al	Mg					
1	1.6	1.6	410	390	Aqueous solution of ammonium hydrogen phosphate, 2 wt%	70	*IS 1
2	1.6	1.6	420	400	Aqueous solution of ammonium hydrogen phosphate, 2 wt%	70	IS 2
3	1.6	1.6	<u>430</u>	400	Aqueous solution of ammonium hydrogen phosphate, 2 wt%	70	**CS 1
4	1.6	1.6	<u>400</u>	390	Aqueous solution of ammonium hydrogen phosphate, 2 wt%	70	CS 2
5	1.6	1.6	420	<u>405</u>	Aqueous solution of ammonium hydrogen phosphate, 2 wt%	70	CS 3
6	1.6	1.6	410	<u>375</u>	Aqueous solution of ammonium hydrogen phosphate, 2 wt%	70	CS 4
*IS: Inventive Sample, **CS: Comparative Sample							

[Table 2]

No.	Average grain diameter of Zn single phase structure (μm)	f(%)	Red rust occurrence time (h)	Area fraction of bending cracks (%)	Notes
1	8	63	650	8	*IS 1
2	10	62	645	9	IS 2
3	12	49	640	25	**CS 1
4	14	47	630	38	CS 2
5	15	46	620	40	CS 3
6	16	44	610	42	CS 4
7	18	42	600	45	CS 5
*IS: Inventive Sample, **CS: Comparative Sample					

[0048] Referring to Table 2, Inventive Samples 1 and 2 satisfying conditions proposed in the present disclosure had high bending workability.

[0049] However, although Comparative Samples 1 to 5 had high corrosion resistance, Comparative Samples 1 to 5 had poor bending workability because the (f) values thereof were less than 50%.

[0050] FIG. 1A and 1B are views illustrating results of an observation of a surface microstructure of Inventive Sample 1 of the present disclosure and an observation of a surface microstructure of Comparative Sample 5, and FIGS. 2A and 2B are views illustrating results of an observation of a cross-sectional microstructure of Inventive Sample 1 of the present disclosure and an observation of a cross-sectional microstructure of Comparative Sample 5.

[0051] FIG. 3 is a view illustrating results of X-ray diffractometer (XRD) analysis of Inventive Sample 1. In FIG. 1, peaks denoted with "○" and "●" are all diffraction peaks of the Zn single phase structure, and the peaks denoted with "○" are diffraction peaks of the Zn single phase structure relating to a basal plane.

(Example 2)

[0052] Low carbon cold-rolled steel sheets each having a thickness of 0.8 mm, a width of 100 mm, and a length of 200 mm were prepared as base steel sheets for plating test samples, and then foreign substances such as rolling oil were removed from the surfaces of the base steel sheets by dipping the base steel sheets into acetone and washing the base steel sheets with ultrasonic waves. Thereafter, a 750°C reducing atmosphere heat treatment commonly performed to guarantee mechanical characteristics of steel sheets in the hot-dipping plating field was performed on the base steel sheets, and then the base steel sheets were dipped into plating baths having compositions shown in Table 3 below to fabricate zinc alloy plated steel sheets. Thereafter, each of the zinc alloy plated steel sheets was wiped with gas to adjust a plating weight to be 70 g/m² on each side. Then, the zinc alloy plated steel sheets were cooled under the same conditions as Inventive Sample 1 of Example 1.

[0053] Thereafter, the fractions of microstructures observed on the surface of each of the zinc alloy plated steel sheets were measured, and the number of black spots on the surface of each of the zinc alloy plated steel sheets was measured. Results thereof are shown in Tables 3 and 4.

[0054] Thereafter, a friction test (linear friction test) was performed by rubbing the surface of each of the zinc alloy plated steel sheets 20 times with a tool head at a constant pressure. In the friction test, a target load was 333.3 kgf, a pressure was 3.736 MPa, the tool head traveled 200 mm per rub, and the speed of the tool head was 20 mm/s.

[0055] After the friction test, a stripping test was performed on each of the zinc alloy plated steel sheets. Specifically, cellophane adhesive tape (NB-1 by Ichiban) was attached to a bent portion of each of the zinc alloy plated steel sheets subjected to a 10R bending process, and then the cellophane tape was momentarily separated. Then, the number of plating layer defects was measured using an optical microscope (magnification: 50 times). Results of the measurement were evaluated as "○" when the number of plating layer defects was 5/m² or less, and "X" when the number of plating layer defects was greater than 5/m². Evaluation results are shown in Table 4 below.

[0056] In addition, after the friction test, each of the zinc alloy plated steel sheets was inserted into a salt spray tester, and the time taken until the occurrence of red rust was measured according to international standard ASTM B117-11. In that time, a 5% salt solution (35°C, pH 6.8) was sprayed at a rate of 2 ml/80 cm² per hour. When the time taken until red rust was present on a sample was 500 hours or greater, the sample was evaluated as "○", and when the time taken until red rust was present on a sample was less than 500, the sample was evaluated as "X." Results of the evaluation

are shown in Table 4 below.

[Table 3]

No.	Alloy composition (wt%)			Area fractions of surface structures (area%)						Notes
	Al	Mg	Mg/Al	Zn	Zn/MgZn ₂	Zn/Al/MgZn ₂	MgZn ₂	Zn/Al	Zn/Al/MgZn ₂ + Zn/MgZn ₂	
1	0.6	2.3	3.83	28	41	31	0	0	72	*IS A
2	1.5	2.8	1.87	20	57	21	1	1	78	IS B
3	2	2.9	1.45	8	63	28	1	0	91	IS C
4	2.2	2.7	1.23	4	58	34	2	2	92	IS D
5	2.6	2.9	1.12	4	39	51	3	3	90	IS E
6	0	0	-	100	0	0	0	0	0	**CS A
7	1.4	1	0.71	82	7	11	0	0	18	CS B
8	2.5	1.2	0.48	6	21	26	46	1	47	CS C
9	5	0	0.00	76	0	0	0	24	0	CS D
10	5	1	0.20	59	9	11	0	21	20	CS E
11	8	3	0.38	13	7	13	18	49	20	CS F
12	55	0	0.00	14	0	0	0	86	0	CS G
Here, surface structures refer to microstructures observed on the surfaces of zinc alloy plating layers.										
*IS: Inventive Sample, **CS: Comparative Sample										

[Table 4]

No.	Number of black spots (/cm ²)	Results of stripping test after friction test		Results of salt spray test after friction test		Notes
		Number of defects (/m ²)	Evaluation results	Separated area (%)	Evaluation results	
1	0.05	3	○	520	○	*IS A
2	0.08	2	○	550	○	IS B
3	0.04	4	○	600	○	IS C
4	0.08	3	○	650	○	IS D
5	0.04	2	○	580	○	IS E
6	1.2	2	○	120	X	**CS A
7	0.8	3	○	230	X	CS B
8	0.05	23	X	620	○	CS C
9	1.1	3	○	350	X	CS D
10	0.6	2	○	420	X	CS E
11	0.06	15	X	650	○	CS F
12	0.05	11	X	200	X	CS G
*IS: Inventive Sample, **CS: Comparative Sample						

[0057] Referring to Table 4, Inventive Samples A to E satisfying conditions proposed in the present disclosure had

good appearance and high scratch resistance.

[0058] However, each of Comparative Samples A, B, D, and E had poor appearance because the area fraction of a Zn single phase structure present on the surface of a plating layer was excessively high, and each of Comparative Samples A to G had poor scratch resistance because the area fractions of a Zn/MgZn₂ binary eutectic structure and a Zn/Al/MgZn₂ ternary eutectic structure are excessively low.

Claims

1. A zinc alloy plated steel sheet comprising a base steel sheet and a zinc alloy plating layer, wherein the zinc alloy plating layer comprises a Zn single phase structure as a microstructure and a Zn-Al-Mg-based intermetallic compound, and the Zn single phase structure has a degree (f) of (0001) preferred orientation, expressed by Formula 1 below, within a range of 50% or greater,

[Formula 1]

$$f(\%) = (I_{\text{basal}} / I_{\text{total}}) \times 100$$

where I_{total} refers to an integral of all diffraction peaks of the Zn single phase structure when an X-ray diffraction pattern is measured within a range of 2 theta from 10° to 100° using a Cu-K α source, and I_{basal} refers to an integral of diffraction peaks of the Zn single phase structure relating to a basal plane.

2. The zinc alloy plated steel sheet of claim 1, wherein the Zn single phase structure has a degree (f) of (0001) preferred orientation, expressed by Formula 1, within a range of 60% or greater.
3. The zinc alloy plated steel sheet of claim 1, wherein the Zn-Al-Mg-based intermetallic compound comprises at least one selected from the group consisting of a Zn/MgZn₂ binary eutectic structure, a Zn/Al binary eutectic structure, an MgZn₂ single phase structure, and a Zn/Al/MgZn₂ ternary eutectic structure.
4. The zinc alloy plated steel sheet of claim 1, wherein an area fraction of the Zn single phase structure on a surface of the zinc alloy plating layer is 40% or less (excluding 0%).
5. The zinc alloy plated steel sheet of claim 1, wherein a total area fraction of a Zn/MgZn₂ binary eutectic structure and a Zn/Al/MgZn₂ ternary eutectic structure is 50% or greater (excluding 100%) on a surface of the zinc alloy plating layer.
6. The zinc alloy plated steel sheet of claim 1, wherein an area fraction of an MgZn₂ single phase structure on a surface of the zinc alloy plating layer is 10% or less (excluding 0%).
7. The zinc alloy plated steel sheet of claim 1, wherein an average grain diameter of the Zn single phase structure observed on a cross-section of the zinc alloy plating layer taken in a sheet thickness direction is 15 μm or less (excluding 0 μm).
8. The zinc alloy plated steel sheet of claim 1, wherein the zinc alloy plating layer comprises, by wt%, aluminum (Al): 0.5% to 3%, magnesium (Mg): 0.5% to 3%, and a balance of zinc (Zn) and inevitable impurities.
9. The zinc alloy plated steel sheet of claim 1, wherein the zinc alloy plating layer satisfies Formula 1 below:

[Formula 1]

$$1.0 < [\text{Mg}] / [\text{Al}] \leq 4.0$$

where [Mg] and [Al] refer to weight percentages (wt%) of corresponding elements, respectively.

10. The zinc alloy plated steel sheet of claim 1, wherein a number of black spots per unit area is 0.1/cm² or less on a

surface of the zinc alloy plated steel sheet.

11. A method for manufacturing a zinc alloy plated steel sheet, the method comprising:

5 preparing a zinc alloy plating bath comprising magnesium (Mg) and aluminum (Al);
obtaining a zinc alloy plated steel sheet by dipping a base steel sheet into the zinc alloy plating bath to plate the base steel sheet;
wiping the zinc alloy plated steel sheet with gas to adjust a plating weight; and
10 after adjusting the plating weight of the zinc alloy plated steel sheet, cooling the zinc alloy plated steel sheet by spraying droplets of water or an aqueous solution onto the zinc alloy plated steel sheet and then using air, wherein when the droplets are sprayed, a droplet spray start temperature ranges from 405°C to 425°C, a droplet spray stop temperature ranges from 380°C to 400°C.

12. The method of claim 11, wherein when the droplets are sprayed, a difference between the droplet spray start temperature and the droplet spray stop temperature is 15°C or greater.

13. The method of claim 11, wherein the droplets are sprayed by a charge spray method to attach the droplets by electrostatic attraction between the droplets and the zinc alloy plated steel sheet.

14. The method of claim 11, wherein the droplets are sprayed in an amount of 50 g/m² to 100 g/m².

15. The method of claim 11, wherein the aqueous solution is a phosphate aqueous solution.

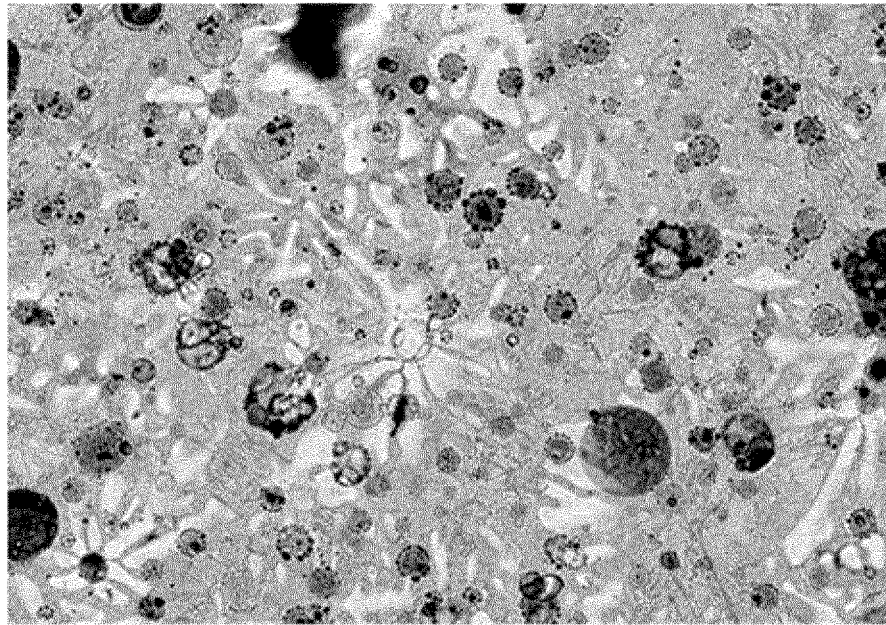
16. The method of claim 15, wherein the phosphate aqueous solution comprises at least one selected from the group consisting of an aqueous solution of ammonium hydrogen phosphate ((NH₄)₂HPO₄), an aqueous solution of sodium ammonium hydrogen phosphate (NaNH₄HPO₄), an aqueous solution of zinc dihydrogen phosphate (Zn(H₂PO₄)₂), and an aqueous solution of calcium phosphate (Ca₃(PO₄)₂).

17. The method of claim 15, wherein the phosphate aqueous solution has a concentration of 0.5 wt% to 5 wt%.

18. The method of claim 11, wherein the zinc alloy plating bath comprises, by wt%, aluminum (Al): 0.5% to 3%, magnesium (Mg): 0.5% to 3%, and a balance of zinc (Zn) and inevitable impurities.

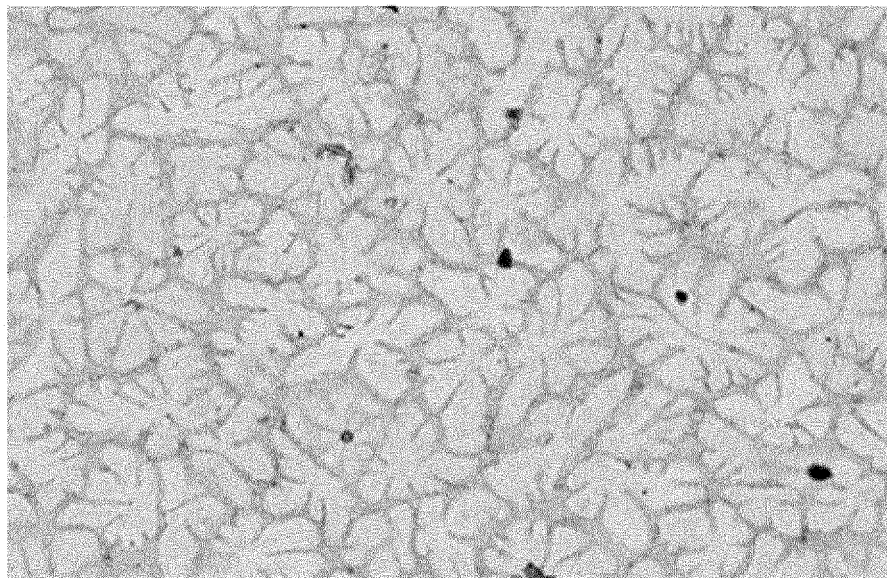
【Figure 1】

(a)



10 μm

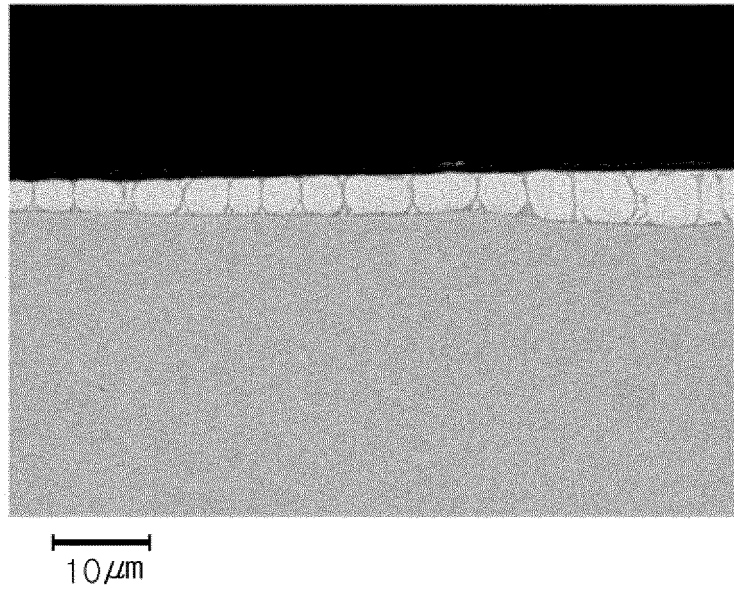
(b)



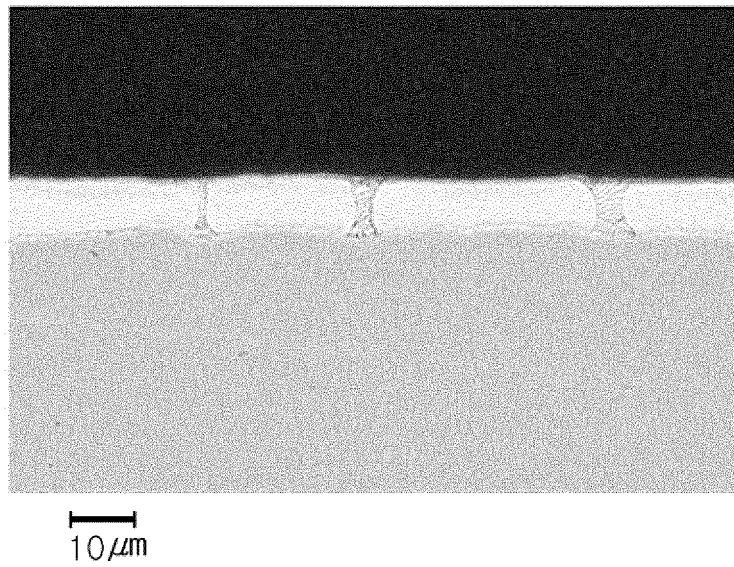
20 μm

【Figure 2】

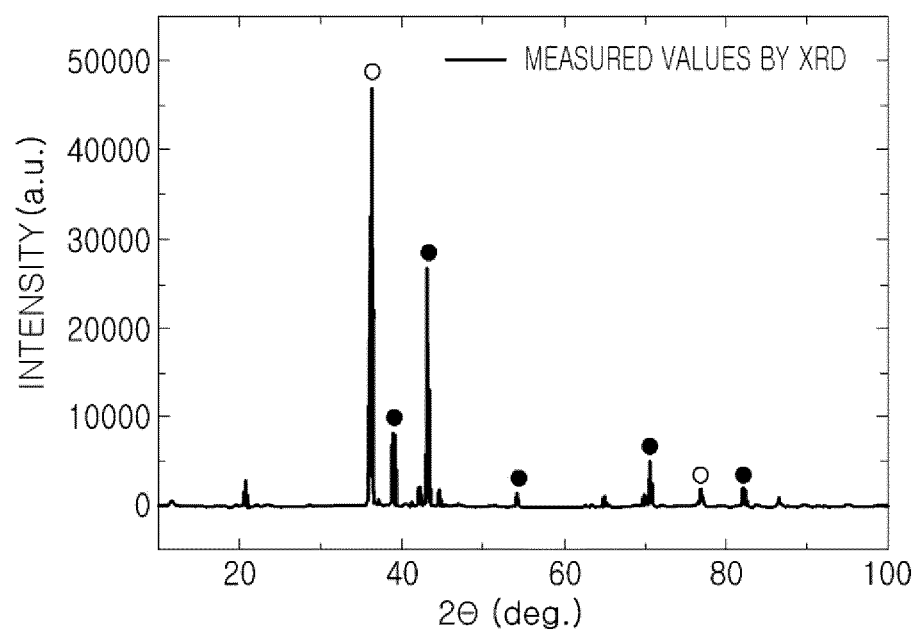
(a)



(b)



【Figure 3】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2016/012098

A. CLASSIFICATION OF SUBJECT MATTER

C23C 2/06(2006.01)i, C23C 2/40(2006.01)i, C23C 2/26(2006.01)i, C23C 2/14(2006.01)i, C23C 2/16(2006.01)i,
C23C 2/18(2006.01)i, C23C 2/20(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C 2/06; C23C 2/16; C23C 2/26; C23C 2/40; C23C 2/14; C23C 2/18; C23C 2/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models: IPC as above

Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & Keywords: zinc alloy plating layer, substrate steel plate, Zn single phase structure, preferred orientation degree, compound, steel plate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2012-0075235 A (POSCO) 06 July 2012 See paragraphs [0018]-[0047]; claims 1-14; and figures 1-3.	11-18
Y		1-10
Y	PISTOFIDIS, N. et al., "A Combined Microscopical and XRD Study of Zinc Coatings", Solid State Phenomena vol. 163 (2010), 07 June 2010, pages 93-97. See page 93-96; and figure 1.	1-10
A	KR 10-2015-0052376 A (POSCO) 14 May 2015 See paragraphs [0024]-[0053]; claim 1; and figures 1-2.	1-18
A	JP 3212977 B2 (NIPPON STEEL CORP.) 25 September 2001 See paragraphs [0004]-[0020]; and claims 1-4.	1-18
A	KR 10-1500043 B1 (POSCO) 06 March 2015 See paragraphs [0023]-[0042]; claims 1-2; and figures 1-4.	1-18

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

26 JANUARY 2017 (26.01.2017)

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INTERNATIONAL SEARCH REPORT
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International application No.

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Form PCT/ISA/210 (patent family annex) (January 2015)