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(54) **Iron-zinc alloy plated steel sheet having two plating layers and excellent in electropaintability and press-formability.**

(57) An iron-zinc alloy plated steel sheet having two plating layers and excellent in electropaintability and press-formability, which comprises; a steel sheet; an alloying-treated iron-zinc alloy dip-plating layer as a lower layer formed on at least one surface of the steel sheet; and an iron-zinc alloy electroplating layer as an upper layer, formed on the iron-zinc alloy dip-plating layer. The iron content in the iron-zinc alloy dip-plating layer is from 7 to 15 wt.%, and the plating weight of the iron-zinc alloy dip-plating layer is from 30 to 120 g/m^2 per surface of the steel sheet. The iron content in the iron-zinc alloy electroplating layer is at least 60 wt.%. The iron-zinc alloy electroplating layer has a plurality of dots of another iron-zinc alloy; the iron content in each of the plurality of dots of another iron-zinc alloy is under 60 wt.%; the total exposed area per unit area of the plurality of dots of another iron-zinc alloy is from 5 to 50% of the unit area of the iron-zinc alloy electroplating layer; the diameter of each of the plurality of dots of another iron-zinc alloy is from 1 to 100 µm; and the total plating weight of the iron-zinc alloy electroplating layer and the plurality of dots of another iron-zinc alloy is from 1 to 10 g/m^2 per surface of the steel sheet.

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REFERENCE TO PATENTS, APPLICATIONS AND PUBLICATIONS PERTINENT TO THE INVENTION

As far as we know, there are available the following prior art documents pertinent to the present invention:

(1) Japanese Patent Publication No. 58-15,554 dated March 26, 1983; and

(2) Japanese Patent Provisional Publication No. 2-66,148 dated March 6, 1990.

The contents of the prior art disclosed in the above-mentioned prior art documents will be discussed hereafter under the heading of "BACKGROUND OF THE INVENTION".

BACKGROUND OF THE INVENTION

(FIELD OF THE INVENTION)

The present invention relates to an iron-zinc alloy plated steel sheet having two plating layers and excellent in electropaintability and press-formability.

(RELATED ART STATEMENT)

An iron-zinc alloy plated steel sheet has many advantages such as excellent corrosion resistance and electropaintability and a low manufacturing cost, so that the iron-zinc alloy plated steel sheet is widely used as a steel sheet for an automobile body. There is a strong demand for the improvement of electropaintability and press-formability of such an iron-zinc alloy plated steel sheet.

A paint film is formed on the surface of an iron-zinc alloy plated steel sheet usually as follows: Subjecting the iron-zinc alloy plated steel sheet to a phosphating treatment to form a phosphate film on the surface of the iron-zinc alloy plating layer, and then subjecting same to a cation-type electropainting treatment to form a paint film having a prescribed thickness on the phosphate film.

However, when forming the paint film on the phosphate film on the surface of the iron-zinc alloy plating layer by means of the cation-type electropainting treatment, a hydrogen gas produced during the electropainting treatment and entangled into the paint film causes the production of crater-shaped pinholes in the paint film. The thus electropainted iron-zinc alloy plated steel sheet is further subjected to a finish painting to form a finish film on the above-mentioned paint film. The above-mentioned crater-shaped pinholes exert an adverse effect even on the finish paint film, thus deteriorating the quality of the painted iron-zinc alloy plated steel sheet.

As an iron-zinc alloy plated steel sheet solving the above-mentioned problem, Japanese Patent Publication No. 58-15,554 dated March 26, 1983 discloses an iron-zinc alloy plated steel sheet for a cation-type electropainting, having two plating layers, which comprises:

a steel sheet; an iron-zinc alloy plating layer as a lower layer formed on at least one surface of said steel sheet, the zinc content in said iron-zinc alloy plating layer as the lower layer being over 40 wt.% relative to said iron-zinc alloy plating layer as the lower layer; and an iron-zinc alloy plating layer as an upper layer formed on said iron-zinc alloy plating layer as the lower layer, the zinc content in said iron-zinc alloy plating layer as the upper layer being up to 40 wt.% relative to said iron-zinc alloy plating layer as the upper layer (hereinafter referred to as the "prior art 1").

The iron-zinc alloy plated steel sheet for an automobile body is subjected to a severe press-forming. The severe press-forming applied to the iron-zinc alloy plated steel sheet causes a powdery peeloff of the iron-zinc alloy plating layer, known as the "powdering" and a flaky peeloff of the iron-zinc alloy plating layer, known as the "flaking".

As an iron-zinc alloy plated steel sheet solving the above-mentioned problem, Japanese Patent Provisional Publication No. 2-66,148 dated March 6, 1990 discloses an iron-zinc alloy plated steel sheet having two plating layers and excellent in powdering resistance and flaking resistance, which comprises:

a steel sheet; an iron-zinc alloy plating layer as a lower layer formed on at least one surface of said steel sheet, the iron content in said iron-zinc alloy plating layer as the lower layer being up to 12 wt.% relative to said iron-zinc alloy plating layer as the lower layer; and an iron-zinc alloy plating layer as an upper layer formed on said iron-zinc alloy plating layer as the lower layer, the iron content in said iron-zinc alloy plating layer as the upper layer being at least 50 wt.% relative to said iron-zinc alloy plating layer as the upper layer, and the frictional coefficient of said iron-zinc alloy plating layer as the upper layer being up to 0.22 (hereinafter referred to as the "prior art 2").

According to the prior art 1, it is possible to prevent the production of the crater-shaped pinholes in the paint film, and according to the prior art 2, it is possible to prevent the occurrence of the powdering and the flaking of the iron-zinc alloy plating layer during the press-forming. In an iron-zinc alloy plated steel sheet having two plating layer such as that in the prior art 1 or 2, it is the usual practice to form a lower layer with an alloying-treated iron-zinc alloy dip-plating layer having a relatively large plating weight, and an upper layer with an iron-zinc alloy electroplating layer having a relatively small plating weight with a view to economically improve corrosion resistance.

The prior arts 1 and 2 have the following problems: Application of a severe press-forming to the iron-zinc alloy plated steel sheet of the prior art 1 or 2 causes the production of cracks or peeloffs in the alloying-treated iron-zinc alloy dip-plating layer as the lower layer and the iron-zinc alloy electroplating layer as the upper layer.

When applying a phosphating treatment to the iron-zinc alloy plated steal sheet, in which the cracks or the peeloffs have been produced in the plating layers, to form a phosphate film on the surface of the iron-zinc alloy electroplating layer as the upper layer, the steel sheet exposed by the cracks or the peeloffs accelerates dissolution of the lower and the upper plating layers into the phosphating solution. As a result, phosphate crystal grains of the phosphate film grow in an abnormally large amount even on the inner surfaces of the crack or the peeloff of the plating layers.

When the paint film is baked after the electropainting, therefore, a large amount of crystal water is released from the phosphate crystal grains of the phosphate film. The crystal water thus released is entrapped in the paint film and vaporized to produce bubbles in the paint film. Production of the bubbles in the paint film is considered to be rather accelerated by the iron-zinc alloy electroplating layer as the upper layer. Production of these bubbles exerts an adverse effect even on the finish paint film, thus deteriorating the quantity of the painted iron-zinc alloy plated steel sheet.

Under such circumstances, there is a demand for the development of an iron-zinc alloy plated steel sheet having two plating layers, in which such defects as bubbles and pinholes do not occur in the paint film even when subjected to a severe press-forming, and which is excellent in electropaintability and press-formability, but an iron-zinc alloy plated steel sheet provided with such properties has not as yet been proposed.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide an iron-zinc alloy plated steel sheet having two plating layers, in which such defects as bubbles and pinholes do not occur in the paint film even when subjected to a severe press-forming, and which is excellent in electropaintability and press-formability.

In accordance with one of the features of the present invention, there is provided an iron-zinc alloy plated steel sheet having two plating layers and excellent in electropaintability and press-formability, which comprises:

a steel sheet;

an alloying-treated iron-zinc alloy dip-plating layer as a lower layer, formed on at least one surface of said steel sheet, the iron content in said iron-zinc alloy dip-plating layer as the lower layer being within a range of from 7 to 15 wt.% relative to said iron-zinc alloy dip-plating layer, and the plating weight of said iron-zinc alloy dip-plating layer as the lower layer being within a range of from 30 to 120 g/m^2 per surface of said steel sheet; and

an iron-zinc alloy electroplating layer as an upper layer, formed on said alloying-treated iron-zinc alloy dip-plating layer as the lower layer, the iron content in said iron-zinc alloy electro-plating layer as the upper layer being at least 60 wt.% relative to said iron-zinc alloy electroplating layer;

characterized in that:

said iron-zinc alloy electroplating layer as the upper layer has a plurality of dots of another iron-zinc alloy;

the iron content in each of said plurality of dots of another iron-zinc alloy is under 60 wt.% relative to each of said plurality of dots of another iron-zinc alloy;

the total exposed area per unit area of said plurality of dots of another iron-zinc alloy is within a range of from 5 to 50% of the unit area of said iron-zinc alloy electroplating layer as the upper layer;

each of said plurality of dots of another iron-zinc alloy has a diameter within a range of from 1 to 100 μm; and

the total plating weight of said iron-zinc alloy electroplating layer as the upper layer and said plurality of dots of another iron-zinc alloy is within a range of from 1 to 10 g/m^2 per surface of said steel sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic plan view illustrating a first embodiment of the iron-zinc alloy plated steel sheet of the present invention;

Fig. 2 is a diagrammatic vertical sectional view illustrating the first embodiment of the iron-zinc alloy plated steel sheet of the present invention;

Fig. 3 is a diagrammatic plan view illustrating a second embodiment of the iron-zinc alloy plated steel sheet of the present invention;

Fig. 4 is a diagrammatic vertical sectional view illustrating the second embodiment of the iron-zinc alloy plated steel sheet of the present invention; and

Fig. 5 is a schematic vertical sectional view illustrating a draw-bead tester for testing press-formability of an iron-zinc alloy plated steel sheet.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

From the above-mentioned point of view, extensive studies were carried out to develop an iron-zinc alloy plated steel sheet having two plating layers, in which such defects as bubbles and pinholes do not occur in the paint film even when subjected to a severe press-forming, and which is excellent in electropaintability and press-formability.

When applying a severe press-forming to an iron-zinc alloy plated steel sheet having two palting layers, which comprises an alloying-treated iron-zinc alloy dip-plating layer as a lower layer formed on at least one surface of a steel sheet and an iron-zinc alloy electroplating layer as an upper layer formed on the iron-zinc alloy dip-plating layer as the lower layer, then subjecting same to a phosphating treatment to form a phosphate film on the surface of the iron-zinc alloy electroplating layer as the upper layer, and then subjecting same to an electropainting treatment to form a paint film on the phosphate film, bubbles are easily produced in the paint film. Causes of this phenomenon were first investigated. As a result, the followings were made clear.

The iron-zinc alloy electroplating layer as the upper layer, which is formed through the electro-precipitation of metals, has a considerable inner stress therein. On the other hand, the alloying-treated iron-zinc alloy dip-plating layer as the lower layer has almost no inner stress therein. Consequently, the iron-zinc alloy electroplating layer as the upper layer locally and strongly restrains the alloying-treated iron-zinc alloy dip-plating layer as the lower layer. When applying a severe press-forming to the iron-zinc alloy plated steel sheet having these two plating layers, therefore, cracks or peeloffs tend to occur in the alloying-treated iron-zinc alloy dip-plating layer as the lower layer. As a result, bubbles are produced in the paint film resulting from the vaporization of crystal water released from the phosphate crystal grains of the phosphate film, as described above.

From these investigations, the following findings were obtained: By reducing the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer through dispersion of the inner stress in the iron-zinc alloy electroplating layer as the upper layer, the cracks or the peeloffs do not occur in the alloying-treated iron-zinc alloy dip-plating layer as the lower layer even when applying a severe press-forming to the iron-zinc alloy plated steel sheet having these two plating layers. As a result, bubbles are never produced in the paint film formed on the surface of the iron-zinc alloy electroplating layer as the upper layer.

The present invention was made on the basis of the above-mentioned findings. The iron-zinc alloy plated steel sheet of the present invention, having two plating layers and excellent in electropaintability and press-formability, is described below with reference to the drawings.

Fig. 1 is a diagrammatic plan view illustrating a first embodiment of the iron-zinc alloy plated steel sheet of the present invention, and Fig. 2 is a diagrammatic vertical sectional view illustrating the first embodiment of the iron-zinc alloy plated steel sheet of the present invention.

As shown in Figs. 1 and 2, the iron-zinc alloy plated steel sheet of the first embodiment of the present invention comprises a steel sheet 1, an alloying-treated iron-zinc alloy dip-plating layer 2 as a lower layer formed on at least one surface of the steel sheet 1, and an iron-zinc alloy electroplating layer 3 as an upper layer formed on the iron-zinc alloy dip-plating layer 2 as the lower layer, and the iron-zinc alloy electroplating layer 3 as the upper layer has a plurality of dots of another iron-zinc alloy 3a.

The iron content in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer should be limited within a range of from 7 to 15 wt.% relative to the iron-zinc alloy dip-plating layer 2. When the iron content in the iron-zinc alloy dip-plating layer 2 as the lower layer is under 7 wt.% relative to the iron-zinc alloy dip-plating layer 2, corrosion resistance of the iron-zinc alloy dip-plating layer 2 is degraded. When the iron content in the iron-zinc alloy dip-plating layer 2 as the lower layer is over 15 wt.% relative to the iron-zinc alloy dip-plating layer 2, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded.

The plating weight of the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer should be limited within a range of from 30 to 120 g/m^2 per surface of the steel sheet 1. When the plating weight of the iron-zinc alloy dip-plating layer 2 as the lower layer is under 30 g/m^2 per surface of the steel sheet 1, corrosion resistance of the iron-zinc alloy dip-plating layer 2 is degraded. When the plating weight of the iron-zinc alloy dip-plating layer 2 as the lower layer is over 120 g/m^2, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded.

The iron content in the iron-zinc alloy electroplating layer 3 as the upper layer should be limited to at least 60 wt.% relative to the iron-zinc alloy electroplating layer 3. The iron content in each of the plurality of dots of another iron-zinc alloy 3a present in the iron-zinc alloy electroplating layer 3 as the upper layer should be limited to under 60 wt.% relative to each of the plurality of dots of another iron-zinc alloy 3a.

The iron-zinc alloy electroplating layer 3 as the upper layer has the plurality of dots of another iron-zinc alloy 3a as described above. The structure of the iron-zinc alloy electroplating layer 3 as the upper layer is therefore non-uniform. Consequently, the inner stress in the iron-zinc alloy electroplating layer 3 as the upper layer is dispersed, and thus the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer is reduced. Even when a severe press-forming is applied to the iron-zinc slloy plated steel sheet having these two plating layers, therefore, cracks or peeloffs never occur in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer. As a result, bubbles are never produced in the paint film formed on the surface of the iron-zinc alloy electroplating layer 3 as the upper layer.

When the iron content in the iron-zinc alloy electroplating layer 3 as the upper layer is under 60 wt.% relative to the iron-zinc alloy electroplating layer 3, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 3.

When the iron content in each of the plurality of dots of another iron-zinc alloy 3a present in the iron-zinc alloy electroplating layer 3 as the upper layer is at least 60 wt.% relative to each of the plurality of dots of another iron-zinc alloy 3a, the inner stress in the iron-zinc alloy electroplating layer 3 as the upper layer cannot be dispersed. It is therefore impossible to reduce the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, and thus to prevent the production of the cracks or the peeloffs in the iron-zinc alloy dip-plating layer 2 during the press-forming.

The total exposed area per unit area of the plurality of dots of another iron-zinc alloy 3a present in the iron-zinc alloy electroplating layer 3 as the upper layer should be limited within a range of from 5 to 50% of the unit area of the iron-zinc alloy electroplating layer 3. When the total exposed area of the plurality of dots of another iron-zinc alloy 3a is under 5% of the unit area of the iron-zinc alloy electroplating layer 3, the inner stress in the iron-zinc alloy electroplating layer 3 cannot be fully dispersed. It is therefore impossible to reduce the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, and thus to prevent the production of the cracks or the peeloffs in the iron-zinc alloy dip-plating layer 2 during the press-forming. When the total exposed area of the plurality of dots of another iron-zinc alloy 3a is over 50% of the unit area of the iron-zinc alloy electroplating layer 3 as the upper layer, on the other hand, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 3.

The diameter of each of the plurality of dots of another iron-zinc alloy 3a present in the iron-zinc alloy electroplating layer 3 as the upper layer should be limited within a range of from 1 to 100 μm. When the diameter of each of the plurality of dots of another iron-zinc alloy 3a is under 1 μm, the inner stress in the iron-zinc alloy electroplating layer 3 cannot be fully dispersed. It is therefore impossible to reduce the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, and thus to prevent the production of the cracks or the peeloffs in the iron-zinc alloy dip-plating layer 2 during the press-forming. When the diameter of each of the plurality of dots of another iron-zinc alloy 3a is over 100 μm, on the other hand, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 3.

The total plating weight of the iron-zinc alloy electroplating layer 3 as the upper layer and the plurality of dots of another iron-zinc alloy 3a should be limited within a range of from 1 to 10 g/m^2 per surface of the steel sheet 1. With a total plating weight of under 1 g/m^2 per surface of the steel sheet 1, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 3 as the upper layer. With a total plating weight of over 10 g/m^2 per surface of the steel sheet 1, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded.

Fig. 3 is a diagrammatic plan view illustrating a second embodiment of the iron-zinc alloy plated steel sheet of the present invention, and Fig. 4 is a diagrammatic vertical sectional view illustrating the second embodiment of the iron-zinc alloy plated steel sheet of the present invention.

As shown in Figs. 3 and 4, the iron-zinc alloy plated steel sheet of the second embodiment of the present invention comprises a steel sheet 1, an alloying-treated iron-zinc alloy dip-plating layer 2 as a lower layer formed on at least one surface of the steel sheet 1, and an iron-zinc alloy electroplating layer 4 as an upper layer formed on the iron-zinc alloy dip-plating layer 2 as the lower layer, and the iron-zinc alloy electroplating layer 4 as the upper layer has a plurality of pores 4a.

The iron content in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer should be limited within a range of from 7 to 15 wt.% relative to the iron-zinc alloy dip-plating layer 2, and the plating weight of the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer should be limited within a range of from 30 to 120 g/m^2, under the same reasons just as those in the iron-zinc alloy plated steel sheet of the first embodiment of the present invention.

The iron content in the iron-zinc alloy electroplating layer 4 as the upper layer should be limited to at least 60 wt.% relative to the iron-zinc alloy electroplating layer 4. The iron-zinc alloy electroplating layer 4 as the upper layer has the plurality of pores 4a as described above. The structure of the iron-zinc alloy electroplating layer 4 as the upper layer is therefore non-uniform. Consequently, the inner stress in the iron-zinc alloy electroplating layer 4 as the upper layer is dispersed, and thus the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer is reduced. Even when a severe press-forming is applied to the iron-zinc alloy plated steel sheet having these two plating layers, therefore, cracks or peeloffs never occur in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer. As a result, bubbles are never produced in the paint film formed on the surface of the iron-zinc alloy electroplating layer 4 as the upper layer.

When the iron content in the iron-zinc alloy electroplating layer 4 as the upper layer is under 60 wt.% relative to the iron-zinc alloy electroplating layer 4, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 4.

The total opening area per unit area of the plurality of pores 4a present in the iron-zinc alloy electroplating layer 4 as the upper layer should be limited within a range of from 5 to 50% of the unit area of the iron-zinc alloy electroplating layer 4. When the total opening area of the plurality of pores 4a is under 5% of the unit area of the iron-zinc alloy electroplating layer 4, the inner stress in the iron-zinc alloy electroplating layer 4 cannot be fully dispersed. It is therefore impossible to reduce the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, and thus to prevent the production of the cracks or the peeloffs in the iron-zinc alloy dip-plating layer 2 during the press-forming. When the total opening area of the plurality of pores 4a is over 50% of the unit area of the iron-zinc alloy electroplating layer 4, on the other hand, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 4.

The diameter of each of the plurality of pores 4a present in the iron-zinc alloy electroplating layer 4 as the upper layer should be limited within a range of from 1 to 100 μm. When the diameter of each of the plurality of pores 4a is under 1 μm, the inner stress in the iron-zinc alloy electroplating layer 4 cannot be fully dispersed. It it therefore impossible to reduce the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, and thus to prevent the production of the cracks or the peeloffs in the iron-zinc alloy dip-plating layer 2 during the press-forming. When the diameter of each of the plurality of pores 4a is over 100 μm, on the other hand, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 4.

The plating weight of the iron-zinc alloy electroplating layer 4 as the upper layer should be limited within a range of from 1 to 10 g/m^2 per surface of the steel sheet 1. When the plating weight of the iron-zinc alloy electroplating layer 4 is under 1 g/m^2 per surface of the steel sheet 1, crater-shaped pinholes tend to occur in the paint film formed on the surface of the iron-zinc alloy electroplating layer 4 as the upper layer. When the plating weight of the iron-zinc alloy electroplating layer 4 is over 10 g/m^2 per surface of the steel sheet 1, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded.

The iron-zinc alloy plated steel sheet of the present invention having two plating layers and excellent in electropaintability and press-formability is manufactured as follows.

A steel sheet is passed through a zinc dip-plating bath to apply a zinc dip-plating treatment to the steel sheet to form a zinc plating layer on at least one surface of the steel sheet. Then, the zinc plated steel sheet is heated to alloy the zinc plating layer and the surface portion of the steel sheet together to convert the zinc plating layer into an iron-zinc alloy plating layer. The alloying-treated iron-zinc alloy dip-plating layer as a lower layer is thus formed on at least one surface of the steel sheet.

When forming the alloying-treated iron-zinc alloy dip-plating layer as the lower layer on at least one surface of the steel sheet by the above-mentioned conventional method, the heating of the zinc plated steel sheet for the alloying treatment is carried out at a temperature within a range of from 420 to 520 °C, which is lower than the usual heating temperature for the alloying treatment. As a result, columnar crystal grains (ζ-phase) are produced in the alloying-treated iron-zinc alloy dip-plating layer, so that fine irregularities are formed on the surface of the iron-zinc alloy dip-plating layer. Then, the steel sheet on the surface of which the iron-zinc alloy dip-plating layer having these fine irregularities has been formed, is subjected to a temper rolling to level the convexities of the surface of the iron-zinc alloy dip-plating layer. An alloying-treated iron-zinc alloy dip-plating layer having fine concavities is thus formed as a lower layer on at least one surface of the steel sheet.

Then, the steel sheet on the surface of which the alloying-treated iron-zinc alloy dip-plating layer having fine concavities has been formed, is electroplated with a prescribed electric current density in an acidic electroplating bath containing iron ions in a prescribed amount and zinc ions in a prescribed amount to form an iron-zinc alloy electroplating layer as an upper layer on the alloying-treated iron-zinc alloy dip-plating layer having fine concavities as the lower layer. In this treatment, it is more difficult for the plating electric current to flow through the concavities of the alloying-treated iron-zinc alloy dip-plating layer than through the flat portion thereof.

As a result, there is manufactured the iron-zinc alloy plated sheet of the first embodiment of the present invention as shown in Figs. 1 and 2, having two plating layers which comprises the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer formed on at least one surface of the steel sheet 1, and the iron-zinc alloy electroplating layer 3 as the upper layer formed on the iron-zinc alloy dip-plating layer 2 as the lower layer and having the plurality of dots of another iron-zinc alloy 3a, or there is manufactured the iron-zinc alloy plated steel sheet of the second embodiment of the present invention as shown in Figs. 3 and 4, having two plating layers which comprises the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer formed on at least one surface of the steel sheet 1, and the iron-zinc alloy electroplating layer 4 as the upper layer formed on the iron-zinc alloy dip-plating layer 2 as the lower layer and having the plurality of pores 4a.

Which of the iron-zinc alloy plated steel sheet of the first embodiment of the present invention and the iron-zinc alloy plated steel sheet of the second embodiment of the present invention is manufactured depends upon the plating electric current density applied when forming the iron-zinc alloy electroplating layer 3 or 4 as the upper layer on the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer and the quantity of the columnar crystal grains produced in the alloying-treated iron-zinc alloy dip-plating layer 2.

The iron content in the iron-zinc alloy electroplating layer 3 or 4 as the upper layer and the plating weight of the iron-zinc alloy electroplating layer 3 or 4 as the upper layer depend upon the chemical composition of the electroplating bath and the plating electric current density applied when forming the iron-zinc alloy electroplating layer 3 or 4.

The iron content, the diameter, and the total exposed area of the plurality of dots of another iron-zinc alloy 3a present in the iron-zinc alloy electroplating layer 3 as the upper layer depend upon the quantity of the columnar crystal grains produced in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, the reduction rate of the temper rolling of the steel sheet 1 on the surface of which the iron-zinc alloy dip-plating layer 2 has been formed, and the plating electric current density applied when forming the iron-zinc alloy electroplating layer 3 as the upper layer.

The diameter and the total opening area of the plurality of pores 4a present in the iron-zinc alloy electroplating layer 4 as the upper layer also depend upon the quantity of the columnar crystal grains produced in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, the reduction rate of the temper rolling of the steel sheet 1 on the surface of which the iron-zinc alloy dip-plating layer 2 has been formed, and the plating electric current density applied when forming the iron-zinc alloy electroplating layer 4 as the upper layer.

The iron content in the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer, and the plating weight of the iron-zinc alloy dip-plating layer 2 depend upon the chemical composition and the temperature of the zinc dip-plating bath used when forming the alloying-treated iron-zinc alloy dip-plating layer 2 as the lower layer on at least one surface of the steel sheet 1, the temperature of the steel sheet 1 passing through the zinc dip-plating bath, the alloying treatment temperature for alloying the zinc plating layer and the surface portion of the steel sheet 1 together, and the period of time for the alloying treatment.

The method for manufacturing the iron-zinc alloy plated steel sheet of the present invention is not limited to the above-mentioned one.

Now, the iron-zinc alloy plated steel sheet of the present invention having two plating layers and excellent in electropaintability and press-formability, is described below further in detail by means of examples while comparing with examples for comparison.

EXAMPLES

The both surfaces of each of cold-rolled steel sheets having a thickness of 0.8 mm were cleaned by means of a usual alkali degreasing and a usual electrolytic pickling. Then, the thus cleaned cold-rolled steel sheet was subjected to an alloying-treated iron-zinc alloy dip-plating under any one of three kinds of plating conditions A, B and C as shown in Table 1 to form an alloying-treated iron-zinc alloy dip-plating layer as a lower layer on each of the both surfaces of the cold-rolled steel sheet.

Then, the cold-rolled steel sheet on each surface of which the alloying-treated iron-zinc alloy dip-plating layers as the lower layers had been formed, was electroplated under any of five kinds of plating conditions a, b, c, d and e as shown in Table 2 to form an iron-zinc alloy electroplating layer as an upper layer on the iron-zinc alloy dip-plating layer. There were thus prepared samples of the iron-zinc alloy plated steel sheet of the first embodiment of the present invention (hereinafter referred to as the "samples of the invention") Nos. 1 to 10 as shown in Table 3, and samples of the iron-zinc alloy plated steel sheet of the second embodiment of the present invention (hereinafter referred to as the "samples of the invention) Nos. 11 to 20 as shown in Table 4, each having two plating layers within the scope of the present invention. For comparison purposes, there were prepared samples of the iron-zinc alloy plated steel sheet, each having two plating layers outside the scope of the present invention (hereinafter referred to as the "samples for comparison") Nos. 1 to 8 as shown in Table 5.

Table 1

Kind	Chemical composition of plating bath (wt.%)		Plating bath temperature (°C)	Temperature of steel sheet passing through plating bath (°C)	Alloying treatment temperature (°C)	Alloying treatment time
	Aℓ	Zn and incidental impurities				
A	0.12	Balance	460	462	490	Adjusting so that plating layer has prescribed iron content
B	0.14	Balance	460	470	510	
C	0.12	Balance	460	462	520	

Table 2

Kind	Chemical composition of plating bath (g/ℓ)		pH Value of plating bath	Plating bath temperature (°C)	Plating electric current density (A/dm²)
	$FeSO_4 \cdot 7H_2O$	$ZnSO_4 \cdot 7H_2O$			
a	380	20	1.8 - 2.0	50	70
b	380	20	1.8 - 2.0	50	120
c	340	60	1.8 - 2.0	50	70
d	340	60	1.8 - 2.0	50	120
e	320	80	1.8 - 2.0	50	70

Table 3

No.		Alloying-treated Fe-Zn alloy dip-plating layer (lower layer): Plating condition	Chemical composition (wt.%) Fe	Chemical composition (wt.%) Zn etc.	Plating weight (g/m^2)	Reduction rate of temper rolling (%)	Fe-Zn alloy electroplating layer (upper layer): Plating condition	Chemical composition (wt.%) Fe	Chemical composition (wt.%) Zn	Dots of Fe-Zn alloy: Chemical composition (wt.%) Fe	Dots of Fe-Zn alloy: Chemical composition (wt.%) Zn	Dots of Fe-Zn alloy: Total exposed area (%)	Dots of Fe-Zn alloy: Diameter (µm)	Total plating weight (g/m^2)	Electro-paint-ability: Production of bubbles	Electro-paint-ability: Production of crater-shaped pinholes	Press-formability (g/m^2)
Sample of the invention	1	A	8.5	91.5	118	0.4	a	85	15	58	42	40	30	4	○	○	11.0
	2	A	8.5	91.5	118	0.8	c	75	25	55	45	20	50	4	○	○	11.0
	3	A	9.7	90.3	68	0.4	a	85	15	58	42	40	20	5	○	○	5.3
	4	A	9.7	90.3	68	0.8	c	75	25	55	45	20	40	7	○	○	5.7
	5	A	9.7	90.3	68	1.2	a	85	15	58	42	10	20	10	○	○	5.8
	6	B	10.2	89.8	56	0.4	a	85	15	58	42	35	10	4	○	○	3.2
	7	B	10.2	89.8	56	0.8	c	75	25	55	45	15	15	4	○	○	3.0
	8	B	11.2	89.8	56	1.2	a	85	15	58	42	35	5	5	○	○	3.6
	9	B	11.8	88.2	45	0.4	c	75	25	55	45	15	20	7	○	○	1.6
	10	B	11.8	88.2	45	0.8	a	85	15	58	42	5	25	10	○	○	1.5

Table 4

No.		Alloying-treated Fe-Zn alloy dip-plating layer (lower layer)					Fe-Zn alloy electroplating layer (upper layer)						Electro-paint-ability		Press-formability
		Plating condition	Chemical composition (wt.%)		Plating weight	Reduction rate of temper rolling	Plating condition	Chemical composition (wt.%)		Total open area of pores	Pore diameter	Plating weight	Production of bubbles	Production of crater-shaped pinholes	
			Fe	Zn etc.	(g/m^2)	(%)		Fe	Zn	(%)	(μm)	(g/m^2)			(g/m^2)
Sample of the invention	11	A	8.5	91.5	118	0.4	b	85	15	40	45	3	○	○	11.0
	12	A	8.5	91.5	118	0.8	d	75	25	25	20	3	○	○	11.0
	13	A	9.7	90.3	68	0.4	b	85	15	40	60	2	○	○	5.2
	14	A	9.7	90.3	68	0.8	d	75	25	20	15	3	○	○	5.8
	15	A	9.7	90.3	68	1.2	b	85	15	10	10	3	○	○	5.7
	16	B	10.2	89.8	56	0.4	b	85	15	35	25	4	○	○	3.2
	17	B	10.2	89.8	56	0.8	d	75	25	20	20	4	○	○	3.1
	18	B	10.2	89.8	56	1.2	b	85	15	35	10	3	○	○	3.5
	19	B	11.8	88.2	45	0.4	d	75	25	15	30	3	○	○	1.6
	20	B	11.8	88.2	45	0.8	b	85	15	5	20	3	○	○	1.4

Table 5

No.	Alloying-treated Fe-Zn alloy dip-plating layer (lower layer): Plating condition	Chemical composition (wt.%): Fe	Chemical composition (wt.%): Zn etc.	Plating weight (g/m²)	Reduction rate of temper rolling (%)	Fe-Zn alloy electroplating layer (upper layer): Plating condition	Chemical composition (wt.%): Fe	Chemical composition (wt.%): Zn	Dots of Fe-Zn alloy: Chemical composition (wt.%): Fe	Dots of Fe-Zn alloy: Chemical composition (wt.%): Zn	Dots of Fe-Zn alloy: Total exposed area (%)	Dots of Fe-Zn alloy: Diameter (µm)	Total plating weight (g/m²)	Electropaintability: Production of bubbles	Electropaintability: Production of crater-shaped pinholes	Press-formability (g/m²)
Sample for comparison 1	C	13.0	87.0	65	0.4	e	55	45	45	55	30	40	5	○	X	5.2
2	A	9.7	90.3	68	0.4	a	85	15	65	35	40	45	5	X	○	5.3
3	C	13.5	86.5	65	1.2	a	85	15	58	42	1	15	5	X	○	7.5
4	A	8.5	91.5	65	0.4	a	80	20	45	55	55	40	5	○	X	4.5
5	B	10.2	89.8	55	1.2	a	85	15	57	43	10	0.5	6	X	○	5.1
6	A	9.6	90.4	63	0.4	c	75	25	55	45	35	150	4	○	X	6.0
7	C	10.5	89.5	62	0.8	d	75	25	56	44	40	20	0.5	○	X	5.5
8	C	10.5	89.5	62	0.8	a	85	15	59	41	5	10	20	X	○	12.5

For each of the samples of the invention Nos. 1 to 20 and the samples for comparison Nos. 1 to 8 prepared as described above, electropaintability and press-formability were investigated through the following performance tests. The results of these tests are shown in Tables 3, 4 and 5.

(1) Electropaintability test:

(a) Production of bubbles in paint film:

Each sample was subjected to an immersion-type phosphating treatment in a phosphating solution to form a phosphate film on each of the both surfaces of each sample, then subjected to a cation-type electropainting treatment to form a paint film having a thickness of 20 μm on each phosphate film under the following conditions:

Impressed voltage	260 V,
Paint temperature	27 °C,
Ratio of sample surface/anode surface	1/1,
Baking temperature	270 °C, and
Baking time	10 minutes.

Production of bubbles in the paint film thus formed on each sample was investigated through the visual inspection, and was evaluated in accordance with the following criteria:

○ : No bubbles are produced in the paint film;
Δ : one to ten bubbles are produced in the paint film;
X : over ten bubbles are produced in the paint film.

(b) Production of crater-shaped pinholes in paint film:

Each sample was subjected to an immersion-type phosphating treatment in a phosphating solution to form a phosphate film on each of the both surfaces of each sample, and then subjected to a cation-type electropainting treatment to form paint film having a thickness of 20 μm on the phosphate film under the following conditions:

Impressed voltage	280 V,
Paint temperature	27 °C,
Ratio of sample surface/anode surface	1/1,
Baking temperature	170 °C, and
Baking time	25 minutes.

Production of crater-shaped pinholes in the paint film thus formed on each sample was investigated through the visual inspection, and was evaluated in accordance with the following criteria:

○ : up to 20 crater-shaped pinholes are produced in the paint film;
Δ : from over 20 to up to 100 crater-shaped pinholes are produced in the paint film;
X : over 100 crater-shaped pinholes are produced in the paint film.

(2) Press-formability test:

Press-formability of each sample was investigated by the use of a draw-bead tester as shown in the schematic vertical sectional view of Fig. 5.

As shown in Fig. 5, the draw-bead tester comprises a male die 5 having a substantially horizontal projection 6 with a prescribed height, and a female die 7 having a groove 8 with a prescribed depth facing the projection 6 of the male die 5. While the male die 5 is stationarily secured, the female die 7 is horizontally movable toward the male die 5 by means of a hydraulic cylinder not shown. A tip 6a of the projection 6 of the male die 5 has a radius of 0.5 mm. A shoulder 8a of the groove 8 of the female die 7 has a radius of 1 mm. The projection 6 of the male die 5 and the groove 8 of the female die 7 have a width of 40 mm.

A test piece 9 (i.e., each of the samples of the invention Nos. 1 to 20 and the samples for comparison Nos. 1 to 8) having a width of 30 mm was vertically inserted into the gap between the male die 5 and the female die 7 of the above-mentioned draw-bead tester, and by operating the hydraulic cylinder not shown, the test piece 9 was pressed against the projection 6 of the male die 5 and the shoulders 8a of the groove 8 of the female die 7 under a pressure of 500 Kgf/cm^2. Then, the test piece 9 was pulled out upward as shown by the arrow in Fig. 5 to squeeze same. Then, an adhesive tape was stuck to the iron-zinc alloy electroplating layer as the upper layer of the thus squeezed test piece 9, and then the adhesive tape was peeled off. The amount of peeloff of the iron-zinc alloy electroplating layer was measured and press-formability was evaluated from the thus measured amount of peeloff.

As is clear from Table 5, the sample for comparison No. 1, in which the iron content in the iron-zinc alloy electroplating layer as the upper layer was low outside the scope of the present invention, showed the production of many crater-shaped pinholes in the paint film, resulting in a poor electropaintability. The sample for comparison No. 2, in which the iron content in each of the plurality of dots of another iron-zinc alloy present in the iron-zinc alloy electroplating layer as the upper layer was high outside the scope of the present invention, showed the production of many bubbles in the paint film, revealing a low electropaintability.

The sample for comparison No. 3, in which the total exposed area per unit area of the plurality of dots of another iron-zinc alloy present in the iron-zinc alloy electroplating layer as the upper layer was small outside the scope of the present invention, showed the production of many bubbles in the paint film, leading to a low electropaintability. The sample for comparison No. 4, in which the total exposed area per unit area of the plurality of dots of another iron-zinc alloy was large outside the scope of the present invention, showed the production of many crater-shaped pinholes in the paint film, revealing a low electropaintability.

The sample for comparison No. 5, in which the diameter of each of the plurality of dots of another iron-zinc alloy present in the iron-zinc alloy electroplating layer as the upper layer was small outside the scope of the present invention, showed the production of many bubbles in the paint film, resulting in a low electropaintability. The sample for comparison No. 6, in which the diameter of each of the plurality of dots of another iron-zinc alloy was large outside the scope of the present invention, showed the production of many crater-shaped pinholes in the paint film, revealing a low electropaintability.

The sample for comparison No. 7, in which the total plating weight of the iron-zinc alloy electroplating layer as the upper layer and the plurality of dots of another iron-zinc alloy was small outside the scope of the present invention, showed the production of many crater-shaped pinholes in the paint film, leading to a low electropaintability. The sample for comparison No. 8, in which the above-mentioned total plating weight was large outside the scope of the present invention, showed the production of many bubbles in the paint film, thus revealing a low electropaintability, and showed a poor press-formability.

In contrast, the samples of the invention Nos. 1 to 20 were excellent in electropaintability and press-formability, as is clear from Tables 3 and 4.

According to the present invention, as described above in detail, it is possible to provide an iron-zinc alloy plated steel sheet having two plating layers, in which such defects as bubbles and pinholes do not occur in the paint film even when subjected to a severe press-forming, and which is excellent in electropaintability and press-formability, thus providing industrially useful effects.

Claims

1. An iron-zinc alloy plated steel sheet having two plating layers and excellent in electropaintability and press-formability, which comprises:

a steel sheet;

an alloying-treated iron-zinc alloy dip-plating layer as a lower layer, formed on at least one surface of said steel sheet, the iron content in said iron-zinc alloy dip-plating layer as the lower layer being within a range of from 7 to 15 wt.% relative to said iron-zinc alloy dip-plating layer, and the plating weight of said iron-zinc alloy dip-plating layer as the lower layer being within a range of from 30 to 120 g/m^2 per surface of said steel sheet; and

an iron-zinc alloy electroplating layer as an upper layer, formed on said alloying-treated iron-zinc alloy dip-plating layer as the lower layer, the iron content in said iron-zinc alloy electroplating layer as the upper layer being at least 60 wt.% relative to said iron-zinc alloy electroplating layer;

characterized in that:

said iron-zinc alloy electroplating layer as the upper layer has a plurality of dots of another iron-zinc alloy;

the iron content in each of said plurality of dots of another iron-zinc alloy is under 60 wt.% relative to each of said plurality of dots of another iron-zinc alloy;

the total exposed area per unit area of said plurality of dots of another iron-zinc alloy is within a range of from 5 to 50% of the unit area of said iron-zinc alloy electroplating layer as the upper layer;

each of said plurality of dots of another iron-zinc alloy has a diameter within a range of from 1 to 100 μm; and

the total plating weight of said iron-zinc alloy electroplating layer as the upper layer and said plurality of dots of another iron-zinc alloy is within a range of from 1 to 10 g/m^2 per surface of said steel sheet.

2. An iron-zinc alloy plated steel sheet having two plating layers and excellent in electropaintability and press-formability, which comprises:

a steel sheet;

an alloying-treated iron-zinc alloy dip-plating layer as a lower layer, formed on at least one surface of said steel sheet, the iron content in said iron-zinc alloy dip-plating layer as the lower layer being within a range of from 7 to 15 wt.% relative to said iron-zinc alloy dip-plating layer, and the plating weight of said iron-zinc alloy dip-plating layer as the lower layer being within a range of from 30 to 120 g/m^2 per surface of said steel sheet; and

an iron-zinc alloy electroplating layer as an upper layer, formed on said alloying-treated iron-zinc alloy dip-plating layer as the lower layer, the iron content in said iron-zinc alloy electroplating layer as the upper layer being at least 60 wt.% relative to said iron-zinc alloy electroplating layer;

characterized in that:

said iron-zinc alloy electroplating layer as the upper layer has a plurality of pores;

the total opening area per unit area of said plurality of pores is within a range of from 5 to 50% of the unit area of said iron-zinc alloy electroplating layer as the upper layer;

each of said plurality of pores has a diameter within a range of from 1 to 100 μm; and

the plating weight of said iron-zinc alloy electroplating layer as the upper layer is within a range of from 1 to 10 g/m^2 per surface of said steel sheet.

FIG. 1

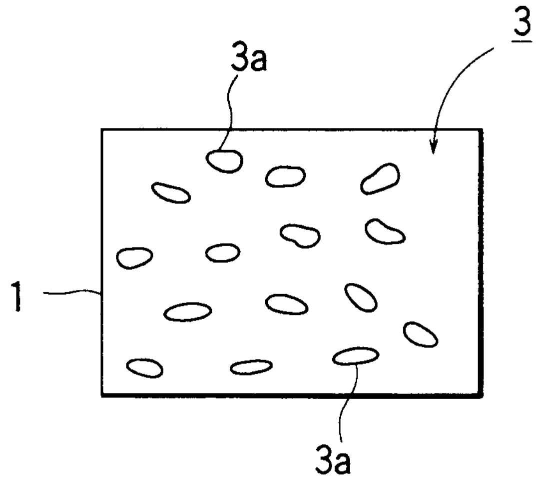

FIG. 2

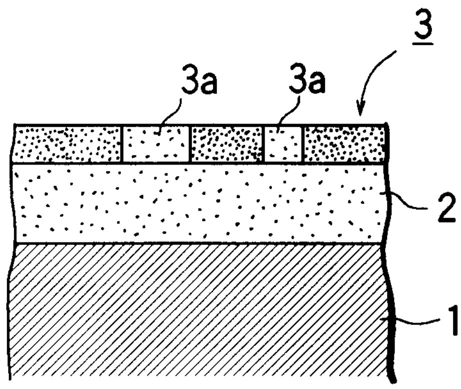

FIG. 3

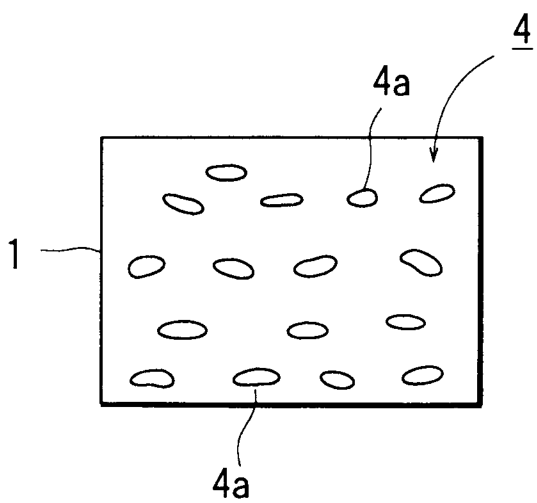

FIG. 4

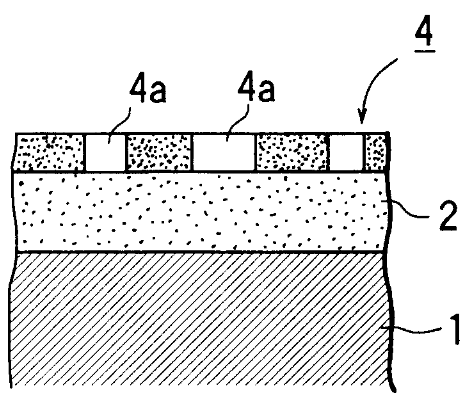

FIG. 5