

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 488 408 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **91120596.1**(51) Int. Cl.⁵: **C23C 2/06, C25D 5/10,
C25D 5/26, C25D 5/36**(22) Date of filing: **29.11.91**(30) Priority: **30.11.90 JP 338838/90**(43) Date of publication of application:
03.06.92 Bulletin 92/23(84) Designated Contracting States:
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(54) **Iron-zinc alloy plated steel sheet having two plating layers and excellent in press-formability and electropaintability and method for manufacturing same.**

(57) An iron-zinc alloy plated steel sheet having two plating layers and excellent in press-formability and electropaintability, 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 alloy electroplating layer as an upper layer formed on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer. The alloying-treated iron-zinc alloy dip-plating layer as the lower layer, which has an iron content of 7 to 15 wt.% and a plating weight of 30 to 120 g/m² per surface of the steel sheet, is formed by subjecting the steel sheet to a conventional zinc dip-plating treatment followed by a conventional alloying treatment by heating. The iron alloy electroplating layer as the upper layer, which has an iron content of at least 60 wt.%, a content of silica particles of 0.01 to 2 wt.% and a plating weight of 1 to 10 g/l per surface of the steel sheet, is formed by electroplating the steel sheet, on which the alloying-treated iron-zinc alloy dip-plating layer has been formed, in an iron alloy electroplating bath containing silica particles of 0.1 to 10 g/l and nitric acid ions of 100 to 20,000 ppm.

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REFERENCE TO PATENT, 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 Provisional Publication No. 2-66,148 dated March 6, 1990; and
- (2) Japanese Patent Publication No. 58-15,554 dated March 26, 1983.

The contents of the prior art disclosed in the above-mentioned prior art documents will be discussed hereafter under the heading of the "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 press-formability and electropaintability and a method for manufacturing same.

(RELATED ART STATEMENT)

An iron-zinc alloy plated steel sheet having a relatively large plating weight has many advantages such as an excellent corrosion resistance and an excellent 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 and as a steel sheet for a home electrical appliance.

However, the iron-zinc alloy plated steel sheet has the problem of a low press-formability. More particularly, the iron-zinc alloy plated steel sheet has a large frictional resistance against a forming die during the press-forming thereof, resulting in a poor lubricity of the iron-zinc alloy plated steel sheet. As a result, a 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" or 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 1").

A paint film is usually formed on the surface of an iron-zinc alloy plated steel sheet 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 finishing painting treatment to form a finished paint film on the above-mentioned paint film. The above-mentioned crater-shaped pinholes exert an adverse effect even on the finished paint film, thus degrading the quality of the electropainted 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 having two plating layers, suitable for a cation-type electropainting, 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 2").

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

However, the prior arts 1 and 2 have the following problems. Application of a severe press-forming to the iron 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 alloy electroplating layer as the upper layer.

When applying a phosphating treatment to the iron-zinc alloy plated steel sheet, in which the above-mentioned cracks or the peeloffs have been produced in the plating layers, to form a phosphate film on the surface of the iron 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 surface of the cracks or the peeloffs of the plating layers.

When the paint film is baked after the electropainting thereof, therefore, a large amount of crystal water is released from the phosphate crystal grains of the phosphate film. The crystal water thus released is entangled 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 alloy electroplating layer as the upper layer. Production of these bubbles exerts an adverse effect even on the finished paint film, thus degrading the quality of the electropainted 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 and excellent in press-formability and electropaintability, in which the powdering or the flaking does not occur in the plating layers and such defects as the bubbles or the pinholes are not produced in the paint film even when subjected to a severe press-forming, and a method for manufacturing same, but an iron-zinc alloy plated steel sheet provided with such properties and a method for manufacturing same have 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 and excellent in press-formability and electropaintability, in which the powdering or the flaking does not occur in the plating layers and such defects as the bubbles or the pinholes are not produced in the paint film even when subjected to a severe press-forming, and a method for manufacturing same.

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 press-formability and electropaintability, 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/m² per surface of said steel sheet; and

an iron 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 alloy electroplating layer as the upper layer being at least 60 wt.% relative to said iron alloy electroplating layer;

wherein;

said iron alloy electroplating layer as the upper layer contains uniformly dispersed silica particles in an amount within a range of from 0.01 to 2 wt.% relative to said iron alloy electroplating layer; and

the plating weight of said iron alloy electroplating layer as the upper layer is within a range of from 1 to 10 g/m² per surface of said steel sheet.

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

passing a steel sheet through a zinc dip-plating bath to apply a zinc dip-plating treatment to said steel sheet, so as to form a zinc dip-plating layer on at least one surface of said steel sheet; then

heating said steel sheet, on which said zinc dip-plating layer has been formed, to apply an alloying treatment to said zinc dip-plating layer and the surface portion of said steel sheet, so as to form, on at least one surface of said steel sheet, an alloying-treated iron-zinc alloy dip-plating layer as a lower layer, which has an iron content within a range of from 7 to 15 wt.% and a plating weight within a range of from 30 to 120 g/m² per surface of said steel sheet; and then

electroplating said steel sheet, on which said alloying-treated iron-zinc alloy dip-plating layer as the lower layer has been formed, in an iron alloy acidic electroplating bath containing silica particles in an amount within a range of from 0.1 to 10 g/l and nitric acid ions in an amount within a range of from 100 to 20,000 ppm, to form, on said alloying-treated iron-zinc alloy dip-plating layer as the lower layer, an iron alloy electroplating layer as an upper layer, containing uniformly dispersed silica particles in an amount within a range of from 0.01 to 2 wt.% and having an iron content of at least 60 wt.% and a plating weight within a range of from 1 to 10 g/m² per surface of said steel sheet.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 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 and excellent in press-formability and electropaintability, in which the powdering or the flaking does not occur in the plating layers and such defects as the bubbles or the pinholes are not produced in the paint film even when subjected to a severe press-forming, and a method for manufacturing same.

When applying a severe press-forming to an iron-zinc alloy plated steel sheet having two plating 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 alloy electroplating layer as an upper layer formed on the iron-zinc 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 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 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 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 be locally produced 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 causing the iron alloy electroplating layer as the upper layer to contain uniformly dispersed silica particles in a prescribed amount, fine cracks are produced in the iron alloy electroplating layer as the upper layer, starting from the silica particles, during the press-forming. As a result, the inner stress in the iron alloy electroplating layer as the upper layer is dispersed, thus leading to a reduced restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer. Therefore, even when the iron-zinc alloy plated steel sheet having these two plating layers is subjected to a severe press-forming, cracks or peeloffs are never produced in the alloying-treated iron-zinc alloy dip-plating layer as the lower layer. Consequently, bubbles are never produced in the paint film formed on the surface of the iron alloy electroplating layer as the upper layer.

In addition, by causing the iron alloy electroplating layer as the upper layer to contain uniformly dispersed silica particles in a prescribed amount, the silica particles reduce frictional resistance of the iron-zinc alloy plated steel sheet against the forming die during the press-forming, thus improving lubricity of the iron-zinc alloy plated steel sheet. Therefore, the powdering or the flaking never occurs in the plating layers even when the iron-zinc alloy plated steel sheet having these two plating layers is subjected to a severe press-forming.

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 press-formability and

electropaintability, and the method for manufacturing same, are described below.

The iron-zinc alloy plated steel sheet of the present invention 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 alloy electroplating layer as an upper layer, containing uniformly dispersed silica particles, formed on the iron-zinc alloy dip-plating layer as the lower layer.

The iron content in the alloying-treated iron-zinc alloy dip-plating layer 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. When the iron content in the iron-zinc alloy dip-plating layer as the lower layer is under 7 wt.% relative to the iron-zinc alloy dip-plating layer, corrosion resistance of the iron-zinc alloy dip-plating layer is degraded. When the iron content in the iron-zinc alloy dip-plating layer as the lower layer is over 15 wt.% relative to the iron-zinc alloy dip-plating layer, 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 as the lower layer should be limited within a range of from 30 to 120 g/m² per surface of the steel sheet. When the plating weight of the iron-zinc alloy dip-plating layer as the lower layer is under 30 g/m² per surface of the steel sheet, corrosion resistance of the iron-zinc alloy dip-plating layer is degraded. When the plating weight of the iron-zinc alloy dip-plating layer as the lower layer is over 120 g/m² per surface of the steel sheet, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded.

The iron content in the iron alloy electroplating layer as the upper layer should be limited to at least 60 wt.% relative to the iron alloy electroplating layer. When the iron content in the iron alloy electroplating layer as the upper layer is under 60 wt.% relative to the iron alloy electroplating layer, crater-shaped pinholes tend to be produced in the paint film formed on the surface of the iron alloy electroplating layer as the upper layer.

The iron alloy electroplating layer as the upper layer contains uniformly dispersed silica particles in a prescribed amount. The silica particles have a high hardness and a high melting point. Therefore, the silica particles contained in the iron alloy electroplating layer as the upper layer reduce frictional resistance of the iron-zinc alloy plated steel sheet against the forming die during the press-forming, thus improving lubricity of the iron-zinc alloy plated steel sheet. As a result, the powdering or the flaking never occurs in the plating layers even when the iron-zinc alloy plated steel sheet having these two plating layers is subjected to a severe press-forming.

The silica particles contained in the iron alloy electroplating layer as the upper layer cause, furthermore, the production of fine cracks in the iron alloy electroplating layer as the upper layer, starting from the silica particles, during the press-forming. Consequently, the inner stress in the iron alloy electroplating layer as the upper layer is dispersed, and thus the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer is reduced. Even when the iron-zinc alloy plated steel sheet having these two plating layers is subjected to a severe press-forming, therefore, cracks or peeloffs are never produced in the alloying-treated iron-zinc alloy dip-plating layer as the lower layer. As a result, bubbles are never produced in the paint film formed on the surface of the iron alloy electroplating layer as the upper layer.

The content of silica particles in the iron alloy electroplating layer as the upper layer should be limited within a range of from 0.01 to 2 wt.% relative to the iron alloy electroplating layer. When the content of silica particles in the iron alloy electroplating layer as the upper layer is under 0.01 wt.% relative to the iron alloy electroplating layer, it is impossible to reduce frictional resistance of the iron-zinc alloy plated steel sheet against the forming die during the press-forming to sufficiently improve lubricity of the iron-zinc alloy plated steel sheet, and it is also impossible to disperse the inner stress in the iron alloy electroplating layer as the upper layer to reduce the restraining force acting on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer and thus to prevent the production of cracks or peeloffs in the iron-zinc alloy dip-plating layer during the press-forming. When the content of silica particles in the iron alloy electroplating layer as the upper layer is over 2 wt.% relative to the iron alloy electroplating layer, on the other hand, the production of fine cracks in the iron alloy electroplating layer as the upper layer, starting from the silica particles during the press-forming, becomes excessive, thus causing easy occurrence of the powdering in the iron alloy electroplating layer as the upper layer.

The particle size of the silica particles contained in the iron alloy electroplating layer as the upper layer should preferably be limited within a range of from 5 nm to 1 μm. When the particles size of the silica particles contained in the iron alloy electroplating layer as the upper layer is under 5 nm or over 1 μm, it becomes difficult to cause the silica particles to uniformly disperse in the iron alloy electroplating layer.

The plating weight of the iron alloy electroplating layer as the upper layer should be limited within a range of from 1 to 10 g/m² per surface of the steel sheet. When the plating weight of the iron alloy electroplating layer as the upper layer is under 1 g/m² per surface of the steel sheet, it is impossible to

reduce frictional resistance of the iron-zinc alloy plated steel sheet against the forming die during the press-forming to sufficiently improve lubricity of the iron-zinc alloy plated steel sheet, and crater-shaped pinholes tend to be produced in the paint film formed on the surface of the iron alloy electroplating layer as the upper layer. When the plating weight of the iron alloy electroplating layer as the upper layer is over 10 g/m² per surface of the steel sheet, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded.

The iron alloy electroplating layer as the upper layer should preferably comprise any one of an iron-zinc alloy containing zinc in an amount of under 40 wt.% and the silica particles, an iron-phosphorus alloy containing phosphorus in an amount within a range of from 0.0003 to 15 wt.% and the silica particles, an iron-boron alloy containing boron in an amount within a range of from 0.003 to 3 wt.% and the silica particles, and an iron alloy containing iron in an amount of at least 60 wt.%, at least two elements selected from the group consisting of zinc, phosphorus and boron in amounts within the above-mentioned respective ranges, and the silica particles.

The above-mentioned iron-zinc alloy plated steel sheet of the present invention is manufactured as follows.

A steel sheet, the both surfaces of which have been cleaned through degreasing in a heating furnace and reduction in a reducing furnace, is passed through a zinc dip-plating bath to subject the steel sheet to a zinc dip-plating treatment, so as to form a zinc dip-plating layer on at least one surface of the steel sheet. The above-mentioned zinc dip-plating treatment may be accomplished with the use of a conventional zinc dip-plating bath under conventional zinc dip-plating conditions.

Then, the thus zinc dip-plated steel sheet is heated to apply an alloying treatment to the zinc dip-plating layer and the surface portion of the steel sheet, so as to form, on at least one surface of the steel sheet, an alloying-treated iron-zinc alloy dip-plating layer as a lower layer, which has a plating weight within a range of from 30 to 120 g/m² per surface of the steel sheet. In the above-mentioned alloying treatment, the zinc dip-plated steel sheet is heated to a temperature within a range of from 470 to 520 °C to adjust the iron content in the alloying-treated iron-zinc alloy dip-plating layer as the lower layer within a range of from 7 to 15 wt.% relative to the iron-zinc alloy dip-plating layer.

Then, the steel sheet, on which the alloying-treated iron-zinc alloy dip-plating layer as the lower layer has been formed, is electroplated in an iron alloy acidic electroplating bath containing silica particles in an amount within a range of from 0.1 to 10 g/l and nitric acid ions in an amount within a range of from 100 to 20,000 ppm, to form, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, an iron alloy electroplating layer as an upper layer, containing silica particles in an amount within a range of from 0.01 to 2 wt.% and having an iron content of at least 60 wt.% and a plating weight within a range of from 1 to 10 g/m² per surface of the steel sheet.

The content of silica particles in the iron alloy acidic electroplating bath should be limited within a range of from 0.1 to 10 g/l. When the content of silica particles in the iron alloy acidic electroplating bath is under 0.1 g/l, the precipitation efficiency of the silica particles into the iron alloy electroplating layer as the upper layer decreases, thus making it impossible to make the iron alloy electroplating layer contain the silica particles in an amount within a range of from 0.01 to 2 wt.%. When the content of silica particles in the iron alloy acidic electroplating bath is over 10 g/l, on the other hand, it is impossible to uniformly disperse the silica particles into the plating bath. As a result, it is impossible to cause the silica particles to uniformly precipitate into the iron alloy electroplating layer as the upper layer, thus degrading the quality of the iron-zinc alloy plated steel sheet.

The particle size of the silica particles contained in the iron alloy acidic electroplating bath should preferably be limited within a range of from 5 nm to 1 μm. The reason is that, as described above, when the particle size of the silica particles is under 5 nm or over 1 μm, it becomes difficult to cause the silica particles to uniformly precipitate into the iron alloy electroplating layer as the upper layer.

The nitric acid ions contained in the iron alloy acidic electroplating bath have a function of accelerating the precipitation of the silica particles into the iron alloy electroplating layer as the upper layer. However, when the content of the nitric acid ions in the iron alloy acidic electroplating bath is under 100 ppm, a desired effect as described above is not available. When the content of the nitric acid ions in the iron alloy acidic electroplating bath is over 20,000 ppm, on the other hand, press-formability of the iron-zinc alloy plated steel sheet is degraded. The content of the nitric acid ions in the iron alloy acidic electroplating bath should therefore be limited within a range of from 100 to 20,000 ppm. As the nitric acid ions, there may be used nitric acid (HNO₃), sodium nitrate (NaNO₃), potassium nitrate (KNO₃) or zinc nitrate (Zn(NO₃)₂).

As the iron alloy acidic electroplating bath, there may be used a sulfuric acid plating bath, a chloride plating bath or a mixed plating bath of sulfuric acid and chloride, each of which contains any one of an iron-zinc alloy, an iron-phosphorus alloy, an iron-boron alloy, and an iron alloy comprising iron and at least two

elements selected from the group consisting of zinc, phosphorus and boron. A pH buffering agent, a complexing agent, a conductive assistant and a brightening agent may further be added as required to the above-mentioned basic plating bath.

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

EXAMPLES

Samples of an iron-zinc alloy plated steel sheet having two plating layers within the scope of the present invention as shown in Table 1 (hereinafter referred to as the "samples of the invention") Nos. 1 to 6 were prepared in accordance with the following method.

More specifically, the both surfaces of a cold-rolled steel sheet having a thickness of 0.8 mm were cleaned through degreasing in a heating furnace and reduction in a reducing furnace. Then, the thus cleaned steel sheet was subjected to a zinc dip-plating treatment and then an alloying treatment under the following conditions to form an alloying-treated iron-zinc alloy dip-plating layer as a lower layer on each of the both surfaces of the steel sheet:

(1) Chemical composition of plating bath:

Aluminum : 0.12 wt.%, and
the balance being zinc and incidental impurities,

(2) Plating bath temperature : 460°C,

(3) Temperature of the steel sheet passing through the
plating bath : 470°C,

(4) Alloying treatment temperature : 510°C,

(5) Alloying treatment time : adjusted so that
the plating layer has a prescribed iron content.

Then, the steel sheet, on each of the both surfaces of which the alloying-treated iron-zinc alloy dip-plating layer as the lower layer had been formed, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer containing uniformly dispersed silica particles, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby preparing the sample of the invention No. 1:

(1) Chemical composition of plating bath:

5 Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 380 g/l,

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 20 g/l,

Colloidal silica (particle size: 20 nm): 3 g/l,

10 and

Nitric acid ions (sodium nitrate) : 1,800 ppm,

15 (2) pH value of plating bath : 1.8,

(3) Plating bath temperature : 50°C,

(4) Plating electric current density : 70 A/dm².

20 A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer containing uniformly dispersed silica particles, on the alloying-treated iron-zinc dip-plating layer as the lower layer, thereby preparing the sample of the invention No. 2:

30 (1) Chemical composition of plating bath:

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 340 g/l,

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 60 g/l,

35 Colloidal silica (particle size: 20 nm): 3 g/l,

and

40 Nitric acid ions (sodium sulfate) : 1,200 ppm,

(2) pH value of plating bath : 2.0,

(3) Plating bath temperature : 50°C,

45 (4) Plating electric current density : 50 A/dm².

50 A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-phosphorus alloy electroplating layer as an upper layer containing uniformly dispersed silica particles, on the alloying-treated iron-zinc dip-plating layer as the lower layer, thereby preparing each of the samples of the invention Nos. 3 and 4:

(1) Chemical composition of plating bath:

5	Ferrous chloride (FeCl_2)	: 150 g/l,
	Potassium chloride (KCl)	: 200 g/l,
	Citric acid	: 10 g/l,
10	Sodium dihydrogen phosphate (NaH_2PO_2)	: 2 g/l,
	Colloidal silica (particle size: 20 nm):	2 g/l,
	and	
15	Nitric acid ions (sodium nitrate)	: 900 ppm,
	(2) pH value of plating bath	: 3.0,
20	(3) Plating bath temperature	: 50°C,
	(4) Plating electric current density	: 50 A/dm ² .

25 The samples of the invention Nos. 3 and 4 were different from each other in the plating weight of the iron-phosphorus alloy electroplating layer as the upper layer resulting from the difference in the electroplating time.

A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention
 30 No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-boron alloy electroplating layer as an upper layer containing uniformly dispersed silica particles, on the alloying-treated iron-zinc dip-plating layer as the lower layer, thereby preparing the sample of the invention No. 5:

(1) Chemical composition of plating bath:

35	Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	: 380 g/l,
	Basic acid	: 20 g/l,
40	Colloidal silica (particle size: 20 nm):	1 g/l,
	and	
45	Nitric acid ions (sodium nitrate)	: 1,100 ppm,
	(2) pH value of plating bath	: 2.0,
	(3) Plating bath temperature	: 50°C,
50	(4) Plating electric current density	: 60 A/dm ² .

A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention
 55 No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-boron alloy electroplating layer as an upper layer containing uniformly dispersed silica particles, on the alloying-treated iron-zinc dip-plating layer as the lower layer, thereby preparing the sample of the invention No. 6:

(1) Chemical composition of plating bath:

5 Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 380 g/l,

10 Boric acid : 20 g/l,

Colloidal silica (particle size: 20 nm): 0.5 g/l,

and

15 Nitric acid ions (sodium nitrate) : 1,000 ppm,

(2) pH value of plating bath : 2.0,

(3) Plating bath temperature : 50°C,

20 (4) Plating electric current density : 50 A/dm².

25 Then, for comparison purposes, samples of an iron-zinc alloy plated steel sheet having two plating layers outside the scope of the present invention as shown in Table 1 (hereinafter referred to as the "samples for comparison") Nos. 1 to 8 were prepared in accordance with the following method.

30 More specifically, a cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer containing no silica particles, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby preparing the sample for comparison No. 1:

35 (1) Chemical composition of plating bath:

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 380 g/l,

40 and

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 20 g/l,

45 (2) pH value of plating bath : 1.8,

(3) Plating bath temperature : 50°C,

50 (4) Plating electric current density : 70 A/dm².

55 A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer having a small iron content outside the scope of the present invention, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby preparing the sample for comparison No. 2:

(1) Chemical composition of plating bath:

5 Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 320 g/l,

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 80 g/l,

Colloidal silica (particle size: 20 nm): 2 g/l,

10 and

Nitric acid ions (sodium nitrate) : 1,000 ppm,

(2) pH value of plating bath : 2.0,

15 (3) Plating bath temperature : 50°C,

(4) Plating electric current density : 50 A/dm².

20 A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer having a large content of silica particles outside the scope of the
25 present invention, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby preparing the sample for comparison No. 3:

30 (1) Chemical composition of plating bath:

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 380 g/l,

Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 20 g/l,

35 Colloidal silica (particle size: 20 nm): 13 g/l,

and

40 Nitric acid ions (sodium nitrate) : 1,000 ppm,

(2) pH value of plating bath : 2.0,

(3) Plating bath temperature : 50°C,

45 (4) Plating electric current density : 50 A/dm².

50 A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer having a large content of silica particles outside the scope of the
present invention, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby
55 preparing the sample for comparison No. 4:

(1) Chemical composition of plating bath:

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 380 g/l,
 Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 20 g/l,
 Colloidal silica (particle size: 20 nm): 0.08 g/l,
 and
 Nitric acid ions (sodium nitrate) : 1,000 ppm,

(2) pH value of plating bath : 2.0,

(3) Plating bath temperature : 50°C,

(4) Plating electric current density : 70 A/dm².

A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-zinc alloy electroplating layer as an upper layer having a plating weight outside the scope of the present invention, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby preparing each of the samples for comparison Nos. 5 and 6:

(1) Chemical composition of plating bath:

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) : 380 g/l,
 Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) : 20 g/l,
 Colloidal silica (particle size: 20 nm): 3 g/l,
 and
 Nitric acid ions (sodium nitrate) : 1,800 ppm,

(2) pH value of plating bath : 1.8,

(3) Plating bath temperature : 50°C,

(4) Plating electric current density : 70 A/dm².

Due to the difference in the electroplating time, the sample for comparison No. 5 had a high plating weight of the iron-zinc alloy electroplating layer as the upper layer outside the scope of the present invention, whereas the sample for comparison No. 6 had a low plating weight of the iron-zinc alloy electroplating layer as the upper layer outside the scope of the present invention.

A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-phosphorus alloy electroplating layer as an upper layer having a high content of silica particles outside the scope of the present invention, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby preparing the sample for comparison No. 7:

(1) Chemical composition of plating bath:

	Ferrous chloride (FeCl_2)	: 150 g/l,
5	Potassium chloride (KCl)	: 200 g/l,
	Citric acid	: 10 g/l,
10	Sodium dihydrogen phosphate (NaH_2PO_2)	: 2 g/l,
	Colloidal silica (particle size: 20 nm):	12 g/l,
	and	
15	Nitric acid ions (sodium sulfate)	: 1,200 ppm,
	(2) pH value of plating bath	: 2.0,
20	(3) Plating bath temperature	: 50°C,
	(4) Plating electric current density	: 50 A/dm ² .

25 A cold-rolled steel sheet, on each of the both surfaces of which an alloying-treated iron-zinc alloy dip-plating layer as a lower layer had been formed under the same conditions as in the sample of the invention No. 1, was subjected to an electroplating treatment under the following conditions to form an iron-boron alloy electroplating layer as an upper layer having a low content of silica particles outside the scope of the present invention, on the alloying-treated iron-zinc alloy dip-plating layer as the lower layer, thereby
30 preparing the sample for comparison No. 8:

(1) Chemical composition of plating bath:

35		
	Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	: 380 g/l,
40	Boric acid	: 20 g/l,
	Colloidal silica (particle size: 20 nm):	0.08 g/l,
45	and	
	Nitric acid ion (sodium sulfate)	: 1,200 ppm,
	(2) pH value of plating bath	: 2.0,
50	(3) Plating bath temperature	: 50°C,
	(4) Plating electric current density	: 50 A/dm ² .

55

No.	Alloying-treated Fe-Zn alloy dip-plating layer (lower layer)			Fe alloy electroplating layer (upper layer)							Frictional coefficient	Press-formability (g/m ²)	Electropaintability	
	Chemical composition (wt.%)		Plating weight (g/m ²)	Chemical composition (wt.%)					Plating weight (g/m ²)	Production of bubbles			Production of crater-shaped pinholes	
	Fe	Zn and others		Fe	Zn	P	B	SiO ₂ particles						
Sample of the invention	1	10.3	89.7	65	83.0	15.0	-	-	2.0	3	0.11	2.6	○	○
	2	10.3	89.7	65	65.0	33.0	-	-	2.0	3	0.11	2.7	○	○
	3	10.3	89.7	65	97.0	-	2.0	-	1.0	4	0.10	3.4	○	○
	4	10.3	89.7	65	97.0	-	2.0	-	1.0	8	0.10	3.9	○	○
	5	10.5	89.5	45	99.5	-	-	0.1	0.4	3	0.10	2.1	○	○
	6	10.5	89.5	45	99.82	-	-	0.10	0.08	3	0.12	2.5	○	○
Sample for comparison	1	10.3	89.7	63	85.0	15.0	-	-	-	3	0.15	7.5	×	○
	2	10.0	90.0	60	55.0	44.0	-	-	1.0	3	0.12	3.5	○	×
	3	10.5	89.5	65	83.0	12.0	-	-	5.0	3	0.10	5.5	△	○
	4	10.5	89.5	65	83.000	16.995	-	-	0.005	3	0.15	6.5	×	○
	5	10.5	89.5	65	83.0	15.0	-	-	2.0	15	0.11	12.3	×	○
	6	10.5	89.5	65	83.0	15.0	-	-	2.0	0.5	0.17	5.7	○	×
	7	10.3	89.7	65	95.0	-	2.0	-	3.0	4	0.11	5.8	△	○
	8	10.3	89.7	65	99.895	-	-	0.100	0.005	3	0.15	6.3	×	○

For each of the samples of the invention Nos. 1 to 6 and the samples for comparison Nos. 1 to 8 prepared as described above, frictional coefficient was measured, and press-formability and electropaintability were investigated through the following performance tests. The results of the measurement of frictional coefficient and these tests are shown also in Table 1.

(1) 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. 1.

As shown in Fig. 1, the draw-bead tester comprises a male die 1 having a substantially horizontal projection 2 with a prescribed height, and a female die 3 having a groove 4 with a prescribed depth, which groove faces the projection 2 of the male die 1. While the male die 1 is stationarily secured, the female die 3 is horizontally movable toward the male die 1 by means of a hydraulic cylinder not shown. A tip 2a of the projection 2 of the male die 1 has a radius of 0.5 mm. Each shoulder 4a of the groove 4 of the female die 3 has a radius of 1 mm. The projection 2 of the male die 1 and the groove 4 of the female die 3 have a width of 40 mm.

A test piece 5 (i.e., each of the samples of the invention Nos. 1 to 6 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 1 and the female die 3 of the above-mentioned draw-bead tester, and by operating the hydraulic cylinder not shown, the test piece 5 was pressed against the projection 2 of the male die 1 and the shoulders 4a of the groove 4 of the female die 3 under a pressure of 500 kgf/cm². Then, the test piece 5 was pulled out upward as shown by the arrow in Fig. 1 to squeeze same. Then, an adhesive tape was stuck to the iron alloy electroplating layer as the upper layer of the thus squeezed test piece 5, and then the adhesive tape was peeled off. The amount of peeloff of the plating layer was measured and press-formability was evaluated from the thus measured amount of peeloff.

(2) 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, and then subjected to a cation-type electropainting treatment to form a paint film having a thickness of 20 μm on the 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;
- △: one to ten bubbles are produced in the paint film; and
- 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 a 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 this 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; and

x : over 100 crater-shaped pinholes are produced in the paint film.

As is clear from Table 1, the sample for comparison No. 1, in which the iron-zinc alloy electroplating layer as the upper layer contained no silica particles, had a high frictional coefficient, resulting in a poor press-formability, and showed the production of many bubbles in the paint film, leading to a poor electropaintability. The sample for comparison No. 2, 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.

Both of the sample for comparison No. 3, in which the content of silica particles in the iron-zinc alloy electroplating layer as the upper layer was high outside the scope of the present invention, and the sample for comparison No. 7, in which the content of silica particles in the iron-phosphorus alloy electroplating layer as the upper layer was high outside the scope of the present invention, were poor in press-formability and showed the production of bubbles in the paint film, leading to a poor electropaintability.

Both of the sample for comparison No. 4, in which the content of silica particles in the iron-zinc alloy electroplating layer as the upper layer was low outside the scope of the present invention, and the sample for comparison No. 8, in which the content of silica particles in the iron-boron alloy electroplating layer as the upper layer was low outside the scope of the present invention, had a high frictional coefficient, resulting in a poor press-formability, and showed the production of many bubbles in the paint film, leading to a poor electropaintability.

The sample for comparison No. 5, in which the plating weight of the iron-zinc alloy electroplating layer as the upper layer was high outside the scope of the present invention, was poor in press-formability, and showed the production of many bubbles in the paint film, resulting in a poor electropaintability. The sample for comparison No. 6, in which the plating weight of the iron-zinc alloy electroplating layer as the upper layer was low outside the scope of the present invention, had a high frictional coefficient, resulting in a low press-formability, and showed the production of many crater-shaped pinholes in the paint film, leading to a poor electropaintability.

In contrast, as is clear from Table 1, all the samples of the invention Nos. 1 to 6 had a low frictional coefficient and were excellent in press-formability and electropaintability.

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 and excellent in press-formability and electropaintability, in which the powdering or the flaking does not occur in the plating layers and such defects as the bubbles or the pinholes are not produced in the paint film even when subjected to a severe press-forming, and a method for manufacturing same, thus providing industrially useful effects.

Claims

1. An iron-zinc alloy plated steel sheet having two plating layers and excellent in press-formability and electropaintability, 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/m² per surface of said steel sheet; and

an iron 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 alloy electroplating layer as the upper layer being at least 60 wt.% relative to said iron alloy electroplating layer;

wherein:

said iron alloy electroplating layer as the upper layer contains uniformly dispersed silica particles in an amount within a range of from 0.01 to 2 wt.% relative to said iron alloy electroplating layer; and

the plating weight of said iron alloy electroplating layer as the upper layer is within a range of from 1 to 10 g/m² per surface of said steel sheet.

2. An iron-zinc alloy plated steel sheet as claimed in claim 1, wherein:

said silica particles have a particle size within a range of from 5 nm to 1 μ m.

3. An iron-zinc alloy plated steel sheet as claimed in Claim 1, wherein:

said iron alloy electroplating layer as the upper layer comprises any one of an iron-zinc alloy, an iron-phosphorus alloy, and an iron-boron alloy respectively containing said silica particles.

4. A method for manufacturing an iron-zinc alloy plated steel sheet having two plating layers and excellent in press-formability and electropaintability, which comprises the steps of:

passing a steel sheet through a zinc dip-plating bath to apply a zinc dip-plating treatment to said steel sheet, so as to form a zinc dip-plating layer on at least one surface of said steel sheet; then

heating said steel sheet, on which said zinc dip-plating layer has been formed, to apply an alloying treatment to said zinc dip-plating layer and the surface portion of said steel sheet, so as to form, on at least one surface of said steel sheet, an alloying-treated iron-zinc alloy dip-plating layer as a lower layer, which has an iron content within a range of from 7 to 15 wt.% and a plating weight within a range of from 30 to 120 g/m² per surface of said steel sheet; and then

electroplating said steel sheet, on which said alloying-treated iron-zinc alloy dip-plating layer as the lower layer has been formed, in an iron alloy acidic electroplating bath containing silica particles in an amount within a range of from 0.1 to 10 g/l and nitric acid ions in an amount within a range of from 100 to 20,000 ppm, to form, on said alloying-treated iron-zinc alloy dip-plating layer as the lower layer, an iron alloy electroplating layer as an upper layer, containing uniformly dispersed silica particles in an amount within a range of from 0.01 to 2 wt.% and having an iron content of at least 60 wt.% and a plating weight within a range of from 1 to 10 g/m² per surface of said steel sheet.

5. A method as claimed in Claim 4, wherein:

said silica particles have a particle size within a range of from 5 nm to 1 μ m:

6. A method as claimed in Claim 4, wherein:

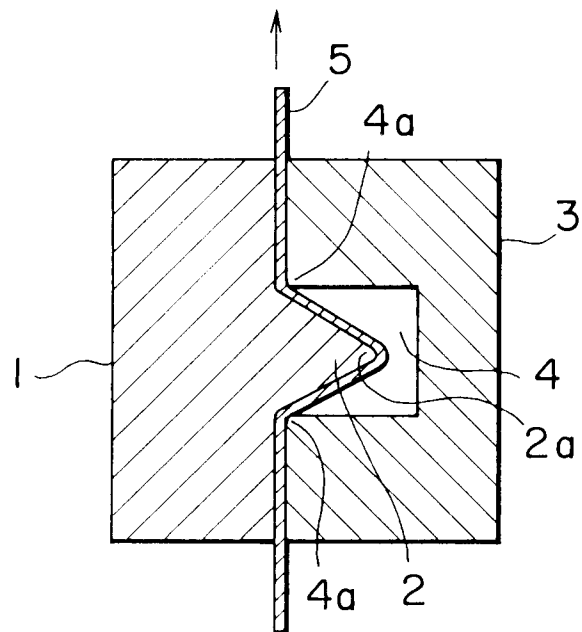
said alloying treatment comprises the steps of:

heating said steel sheet, on which said zinc dip-plating layer has been formed, to a temperature within a range of from 470 to 520 °C to adjust the iron content in said alloying-treated iron-zinc alloy dip-plating layer as the lower layer within a range of from 7 to 15 wt.%.

7. A method as claimed in Claim 4, wherein:

said iron alloy electroplating layer as the upper layer comprises any one of an iron-zinc alloy, an iron-phosphorus alloy, and an iron-boron alloy respectively containing said silica particles.

FIG. 1





European Patent
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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 91120596.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 14, no. 246, May 25, 1990 THE PATENT OFFICE JAPANESE GOVERNMENT page 78 C 722 * Kokai-no. 2-66 148 *	1-7	C 23 C 2/06 C 25 D 5/10 C 25 D 5/26 C 25 D 5/36
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A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 9, no. 12, January 18, 1985 THE PATENT OFFICE JAPANESE GOVERNMENT page 61 C 261 * Kokai-no. 59-162 294 *	1-7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 23 C C 25 D
	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 12, no. 128, April 20, 1988 THE PATENT OFFICE JAPANESE GOVERNMENT page 78 C 489 * Kokai-no. 62-247 097 *	1-7	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 11-02-1992	Examiner HAUK
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			