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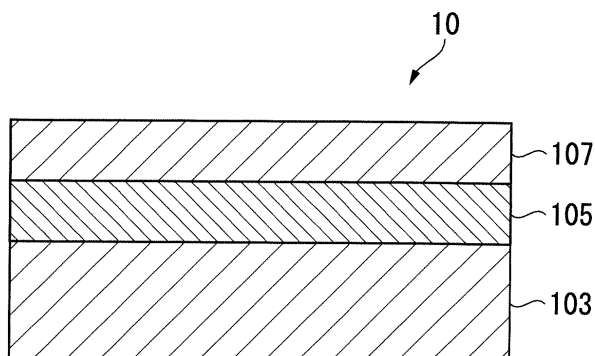
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(54) **CHEMICAL CONVERSION TREATED STEEL PLATE, AND METHOD FOR PRODUCING CHEMICAL CONVERSION TREATED STEEL PLATE**

(57) A chemical treatment steel sheet contains: a steel sheet; a plated layer containing Ni and formed on at least one surface of the steel sheet; a chemical treatment layer containing a Zr compound in which an amount of Zr contained therein is 1.0 to 150 mg/m², a phosphate compound in which an amount of P contained therein is 1.0 to 100 mg/m², and an Al compound in which an amount of Al contained therein is 0.10 to 30.0 mg/m².

The plated layer is a Ni-plated layer containing Ni in which an amount of Ni contained therein is 5.0 to 3000 mg/m² or a composite plated layer containing Ni in which an amount of Ni contained therein is 2.0 to 200 mg/m² and Sn in which an amount of Sn contained therein is 0.10 to 10.0 g/m² and having an island-shaped Sn-plated layer formed on a Fe-Ni-Sn alloy layer.

FIG. 1A



Description

[Technical Field]

5 **[0001]** The present invention relates to a chemical treatment steel sheet and a method for manufacturing a chemical treatment steel sheet.

[Related Art]

10 **[0002]** Corrosion is occurred when metals are continuously used in some cases. Various techniques have been proposed to prevent corrosion of metals. Examples of the proposed techniques include a technique of applying plating to a metal plate or a technique of performing various surface treatments on the surface of a metal plate of a plated surface.

15 **[0003]** For example, Patent Document 1 describes a technique of forming an organic resin film including a vanadium compound or at least one of a phosphate and phosphate-based compound,, a silane compound having at least one of an epoxy group and an amino group, and an organic resin including at least one of a water-soluble organic resin and a water-dispersible organic resin as main components on a surface of an Al-Zn-based alloy plated steel sheet used for building materials and home appliances.

20 **[0004]** On the other hand, when metal containers for the purpose of preserving beverages or foods are manufactured, Ni-plated steel sheets, Sn-plated steel sheets, Sn-based alloy plated steel sheets, or the like have been used. The Al-Zn-based alloy plated steel sheet described in Patent Document 1 is a so-called sacrificial protection steel sheet, whereas a Ni-plated steel sheet, a Sn-plated steel sheet, or a Sn-based alloy plated steel sheet is a so-called barrier plated steel sheet.

25 **[0005]** When a Ni-plated steel sheet, a Sn-plated steel sheet, or a Sn-based alloy plated steel sheet is used as a steel sheet for metal containers for the purpose of preserving beverages or foods (hereinafter referred to as a "steel sheet for containers"), the surface of the plated steel sheet is subjected to a chemical treatment using hexavalent chromium to secure adhesiveness and corrosion resistance between the steel sheet and a coating or a film in many cases. A chemical treatment using a solution containing a hexavalent chromium is referred to as a chromate treatment.

30 **[0006]** However, since hexavalent chromium used in a chromate treatment is harmful to the environment, a chemical treatment film such as a Zr-phosphate film has been developed as a replacement for the chromate treatment applied to a steel sheet for containers in the related art. For example, Patent Document 2 describes a steel sheet for containers having a chemical treatment film including Zr, a phosphate, a phenolic resin, and the like.

35 **[0007]** Examples of foods preserved in a metal container using a steel sheet for containers include meat, vegetables, and the like. Meat and vegetables contain various proteins, but these proteins contain amino acids containing sulfur (sulfur-containing amino acids represented by L-cysteine, L-methionine, and L-(-)-cystine) in some cases.

40 **[0008]** When foods containing sulfur-containing amino acids is heated during sterilization, S in the sulfur-containing amino acids binds to Sn, Fe, or the like in a steel sheet for containers, resulting in black discoloration. This phenomenon is referred to as "sulfide stain." Since the appearance of the inner surface of a metal container deteriorates when sulfide stain occurs, countermeasures have been sought to prevent the occurrence of sulfide stain.

45 **[0009]** In addition, Patent Document 3 describes a method for manufacturing a steel sheet for containers in which a Zr-containing film is formed on a surface of a steel sheet by immersing the steel sheet or performing an electrolytic treatment on the steel sheet in a solution containing Zr ions, and F ions, and at least one reaction accelerating component selected from the group consisting of Al ions, boric acid ions, Cu ions, Ca ions, Al metal, and Cu metal.

[Citation List]

[Patent Documents]

[0010]

50 [Patent Document 1]
 Japanese Unexamined Patent Application, First Publication No. 2005-290535
 [Patent Document 2]
 Japanese Unexamined Patent Application, First Publication No. 2007-284789
 [Patent Document 3]
 Japanese Unexamined Patent Application, First Publication No. 2012-62521

[Summary of Invention]

[Problems to be Solved by the Invention]

5 **[0011]** Since a film formed through a chromate treatment (hereinafter referred to as a "chromate film") is dense even when an adhered amount of film is small, a steel sheet for containers having a chromate film formed on its surface has excellent corrosion resistance and sulfide stain resistance. However, since hexavalent chromium is harmful to the environment as described above, a steel sheet for containers should preferably not contain hexavalent chromium as far as possible.

10 **[0012]** On the other hand, the organic resin film described in Patent Document 1 and the chemical treatment film described in Patent Document 2 do not contain hexavalent chromium and thus are appropriate for the environment. However, in the organic resin film described in Patent Document 1 and the chemical treatment film described in Patent Document 2, it is necessary to increase an adhered amount of film to form a dense film which can obtain appropriate sulfide stain resistance. An increase in adhered amount of film is not preferable because, when the adhered amount of film is increased, the adhesiveness between the film and a plated layer under the film decreases and the weldability decreases, which is not preferable. Furthermore, an increase in adhered amount of film is not economically preferable.

15 **[0013]** In the method for manufacturing a steel sheet for containers described in Patent Document 3, the Al content in the chemical treatment film is small. Thus, it is difficult to obtain an appropriate sulfide stain resistance in some cases.

20 **[0014]** The present invention was made in view of the above-described circumstances and an objective of the present invention is to provide a chemical treatment steel sheet which has excellent corrosion resistance and sulfide stain resistance even when an amount of chemical treatment layer adhered is small and a method for manufacturing the same.

[Means for Solving the Problem]

25 **[0015]** The present invention employs the following means to solve the above-described problems and achieve the above objective.

30 (1) A chemical treatment steel sheet according to an aspect of the present invention contains: a steel sheet; a plated layer which contains Ni and is formed on at least one surface of the steel sheet; a chemical treatment layer which is formed on the plated layer and contains a Zr compound in which an amount of Zr contained therein is 1.0 to 150 mg/m², a phosphate compound in which an amount of P contained therein is 1.0 to 100 mg/m², and an Al compound in which an amount of Al contained therein is 0.10 to 30.0 mg/m², wherein the plated layer is a Ni-plated layer which contains Ni in which an amount of Ni contained therein is 5.0 to 3000 mg/m² or a composite plated layer which contains Ni in which an amount of Ni contained therein is 2.0 to 200 mg/m² and Sn in which an amount of Sn contained therein is 0.10 to 10.0 g/m² and has an island-shaped Sn-plated layer formed on a Fe-Ni-Sn alloy layer.

35 (2) In the chemical treatment steel sheet according to (1), the chemical treatment layer may contain Al₂O₃ in which an amount of Al contained therein is 0.10 to 30.0 mg/m².

40 (3) In the chemical treatment steel sheet according to (1) or (2), the chemical treatment layer may contain: a Zr compound in which an amount of Zr contained therein is 1.0 to 120 mg/m²; a phosphate compound in which an amount of P contained therein is 2.0 to 70.0 mg/m²; and an Al compound in which an amount of Al contained therein is 0.20 to 20.0 mg/m².

(4) In the chemical treatment steel sheet according to any one of (1) to (3), the Ni-plated layer may contain Ni in which an amount of Ni contained therein may be 10.0 to 2000 mg/m².

45 (5) In the chemical treatment steel sheet according to any one of (1) to (3), the composite plated layer may contain: Ni in which an amount of Ni contained therein is 5.0 to 100 mg/m²; and Sn in which an amount of Sn contained therein may be 0.30 to 7.0 g/m².

(6) In the chemical treatment steel sheet according to any one of (1) to (5), a surface of the chemical treatment layer may not be covered with a film or a coating material.

50 (7) A method for manufacturing a chemical treatment steel sheet according to an aspect of the present invention contains: a plating process of forming a Ni-plated layer which contains Ni in which an amount of Ni contained therein is 5.0 to 3000 mg/m² or a composite plated layer which contains Ni in which an amount of Ni contained therein is 2.0 to 200 mg/m² and Sn in which an amount of Sn contained therein is 0.10 to 10.0 g/m² and has an island-shaped Sn-plated layer formed on a Fe-Ni-Sn alloy layer on a surface of a steel sheet; and an electrolytic treatment of forming a chemical treatment layer on the Ni-plated layer or the composite plated layer by performing an electrolytic treatment under the conditions of a current density of 1.0 to 100 A/dm² and an electrolytic treatment time of 0.20 to 150 seconds using a chemical treatment solution having a temperature of 5°C or higher and lower than 90°C and the chemical treatment solution contains 10 to 20,000 ppm of Zr ions, 10 to 20000 ppm of F ions, 10 to 3000 ppm of phosphate ions, a total amount of 100 to 30000 ppm of nitrate ions and sulfate ions, and 500 to 5000 ppm of Al

ions, in which a supply source of the Al ions is $(\text{NH}_4)_3\text{AlF}_6$.

(8) In the method for manufacturing a chemical treatment steel sheet according to (7), the chemical treatment solution may contain: 200 to 17000 ppm of Zr ions; 200 to 17000 ppm of F ions; 100 to 2000 ppm of phosphate ions; a total amount of 1000 to 23000 ppm of nitrate ions and sulfate ions; and 500 to 3000 ppm of Al ions.

[Effects of the Invention]

[0016] According to each aspect described above, a chemical treatment steel sheet having an excellent corrosion resistance and sulfide stain resistance even in a case in which an adhered amount of a chemical treatment layer is small and a method for manufacturing the chemical treatment steel sheet can be provided.

[Brief Description of Drawings]

[0017]

Fig. 1A is an explanatory drawing for schematically showing a layer structure of a chemical treatment steel sheet which has a Ni-plated layer formed on one surface of the steel sheet.

Fig. 1B is an explanatory drawing for schematically showing a layer structure of a chemical treatment steel sheet which has Ni-plated layers formed on both surfaces of the steel sheet.

Fig. 2A is an explanatory drawing for schematically showing an example of a chemical treatment steel sheet which has a composite plated layer formed on one surface of the steel sheet.

Fig. 2B is an explanatory drawing for schematically showing an example of a chemical treatment steel sheet which has composite plated layers formed on both surfaces of the steel sheet.

Fig. 3 is a flowchart showing an example of a flow of a method for manufacturing a chemical treatment steel sheet according to an embodiment of the present invention.

Fig. 4 is a graph showing a result of Example 1.

[Embodiments of the Invention]

[0018] Exemplary embodiments of the present invention will be described in detail below with reference to the appended drawings. Note that, in the present embodiments, repeated description will be omitted by giving the same reference symbols to constituent elements having similar configurations.

<Regarding configuration of chemical treatment steel sheet>

[0019] First, a constitution of a chemical treatment steel sheet according to the present embodiment will be described in detail with reference to Figs. 1A to 2B. Figs. 1A and 1B are explanatory drawings for schematically showing a layer structure of the chemical treatment steel sheet according to the present embodiment.

[0020] As shown in Figs. 1A to 2B, a chemical treatment steel sheet 10 according to the present embodiment contains a steel sheet 103, any one of a Ni-plated layer 105 and a composite plated layer 106, and a chemical treatment layer 107. It should be noted that any one of the Ni-plated layer 105, the composite plated layer 106, and the chemical treatment layer 107 may be formed only on one surface of the steel sheet 103 as shown in Figs. 1A and 2A and may be formed on two opposite surfaces of the steel sheet 103 as shown in Figs. 1B and 2B.

[Regarding steel sheet 103]

[0021] The steel sheet 103 may be used as a base material of the chemical treatment steel sheet 10 according to the present embodiment. The steel sheet 103 used in the present embodiment is not particularly limited and a known steel sheet used as a steel sheet for containers can be used for the steel sheet 103. A manufacturing method and a material for the steel sheet 103 are not particularly limited and it is possible to use the steel sheet 103 manufactured through known processes such as hot rolling, acid cleaning, cold rolling, annealing, and temper rolling in a usual steel piece manufacturing process.

[0022] A plate thickness of the steel sheet 103 is preferably 0.05 to 1 mm in view of practicality and economic efficiency when the steel sheet 103 is used as a steel sheet for containers.

[Regarding plated layer]

[0023] Any one of the Ni-plated layer 105 and the composite plated layer 106 is formed on a surface of the steel sheet

103. Both of the Ni-plated layer 105 and the composite plated layer 106 are barrier plated layers which contain Ni. Here, a barrier plated layer is a plated layer in which the corrosion of the steel sheet 103 is suppressed by preventing a cause of corrosion from acting on the base material by means of forming a metal film of Ni or Sn on the surface of the steel sheet 103 using Ni or Sn which are metals more electrochemically noble than Fe constituting the steel sheet 103 as the base material.

[0024] On the other hand, a sacrificial protection layer has a function opposite to that of a barrier plated layer. In a sacrificial protection layer, the corrosion of the steel sheet 103 is suppressed by corroding a metal such as Zn constituting the plated layer earlier than Fe constituting the steel sheet 103 by mean of forming a metal film on the surface of the steel sheet 103 using a metal less electrochemically noble than Fe constituting the steel sheet 103 as the base material (for example Zn as in Patent Document 1).

[0025] The interaction between the barrier plated layer and the chemical treatment layer 107 is different from that between the sacrificial protection layer and the chemical treatment layer 107.

[0026] An example of the Ni-plated layer 105 and the composite plated layer 106 according to the present embodiment will be described in detail below with reference to Figs. 1A to 2B.

[Case in which Ni-plated layer 105 is formed on surface of steel sheet 103]

[0027] A case in which the Ni-plated layer 105 is formed on a surface of the steel sheet 103 will be described in detail with reference to Fig. 1A.

[0028] The Ni-plated layer 105 contains Ni and may be formed on one surface of the steel sheet 103 as shown in Fig. 1A and Ni-plated layers 105 may be formed on both surfaces of the steel sheet 103 as shown in Fig. 1B. In the Ni-plated layer 105, it is preferable that Ni be contained in a range of an amount of 5.0 to 3000 mg/m² per one surface.

[0029] Ni has excellent paint adhesiveness, film adhesiveness, corrosion resistance, and weldability. In order to achieve the above-described excellent effects, it is necessary to contain Ni of 5.0 mg/m² or more per one surface.

[0030] As an amount of Ni increases, the excellent effects of Ni are improved, but more than an amount of 3000 mg/m² of Ni per one surface is not economically preferable because the effects thereof is saturated. Therefore, an amount of Ni is set to an amount of 3000 mg/m² or less per one surface.

[0031] An amount of Ni in the Ni-plated layer is more preferably an amount of 10.0 mg/m² or more and 2000 mg/m² or less per one surface. The above-described effects are more remarkably exhibited when Ni is contained in an amount of 10.0 mg/m² or more per one surface. Furthermore, it is possible to further reduce the manufacturing costs of the Ni-plated layer 105 when an amount of Ni is set to an amount of 2000 mg/m² or less per one surface.

[0032] The amount of Ni contained in the Ni-plated layer 105 is 50 mass% or higher in a layer center portion of the Ni-plated layer 105. The amount of Ni contained in the Ni-plated layer 105 is preferably 70 mass% or higher in a layer center portion of the Ni-plated layer 105.

[0033] The Ni-plated layer 105 may contain Fe in an amount of 1.0 to 2000 mg/m² per one surface in addition to Ni described above. Furthermore, the Ni-plated layer 105 may contain inevitable impurities which may be mixed in the manufacturing process or the like.

[Case in which composite plated layer 106 is formed on surface of steel sheet 103]

[0034] A case in which the composite plated layer 106 containing Ni and Sn is formed on a surface of the steel sheet 103 will be described in detail with reference to Figs. 2A and 2B.

[0035] The composite plated layer 106 according to the present embodiment may be formed on one surface of the steel sheet 103 as shown in Fig. 2A and composite plated layers 106 may be formed on both surfaces of the steel sheet 103 as shown in Fig. 2B. The composite plated layer 106 has a Fe-Ni-Sn alloy layer 105d and an island-shaped Sn-plated layer 105e formed on the Fe-Ni-Sn alloy layer 105d.

[0036] In order to form the composite plated layer 106, a Ni-plated layer (not shown) is first formed on the steel sheet 103. The Ni-plated layer (not shown) contains a Ni or a Fe-Ni alloy and is formed to secure the corrosion resistance of the chemical treatment steel sheet 10.

[0037] The effect of improving the corrosion resistance of the chemical treatment steel sheet 10 using Ni is determined by an amount of Ni contained in the composite plated layer 106. The effect of improving the corrosion resistance using Ni is achieved if the amount of Ni in the composite plated layer 106 is an amount of 2 mg/m² or more per one surface.

[0038] On the other hand, when the amount of Ni in the composite plated layer 106 increases, the effect of improving the corrosion resistance increases. However, when the amount of Ni in the composite plated layer 106 exceeds an amount of 200 mg/m² per one surface, the effect of improving the corrosion resistance using Ni is saturated. Furthermore, since Ni is a high-cost metal the case in which the amount of Ni in the composite plated layer 106 exceeds an amount of 200 mg/m² per one surface is not economically preferable.

[0039] Therefore, the amount of Ni in the composite plated layer 106 is set to an amount of 2.0 mg/m² to 200 mg/m²

per one surface. The amount of Ni in the composite plated layer 106 is more preferably an amount of 5.0 mg/m² to 100 mg/m² per one surface. When the composite plated layer 106 contains Ni in an amount of 5.0 mg/m² or more per one surface, the effect of improving the corrosion resistance using Ni is effectively achieved. Furthermore, when the amount of Ni in the composite plated layer 106 is an amount of 100 mg/m² or less per one surface, it is possible to further reduce the manufacturing costs.

[0040] After the above-described Ni-plated layer (not shown) is formed, the Sn-plated layer (not shown) is formed. It should be noted that the Sn-plated layer (not shown) in the present embodiment may be constituted only of Sn or may contain impurities or trace elements in addition to Sn.

[0041] The Sn-plated layer (not shown) is formed to secure the corrosion resistance and the weldability of the chemical treatment steel sheet 10. Regarding Sn, not only does Sn itself having high corrosion resistance, but Sn alloys formed by a reflow treatment have excellent corrosion resistance and weldability.

[0042] When the Sn-plated layer (not shown) is formed and then is subjected to a reflow treatment, the Fe-Ni-Sn alloy layer 105d is formed on the steel sheet 103 and the island-shaped Sn-plated layer 105e is formed on the Fe-Ni-Sn alloy layer 105d.

[0043] In the island-shaped Sn-plated layer 105e, Sn is present in an island shape and the Fe-Ni-Sn alloy layer 105d in a lower portion is exposed in the sea. The film adhesiveness and the paint adhesiveness of the chemical treatment steel sheet 10 are secured by the island-shaped Sn-plated layer 105e.

[0044] In the heat treatment after film lamination or coating material application, the chemical treatment steel sheet 10 is heated to the melting point of Sn (232°C) or higher in some cases. In the case which is different from the present embodiment, when Sn covers the entire surface of the Fe-Ni-Sn alloy layer 105d, this is not preferable because Sn is melted or oxidized by the above-described heat treatment and thus the film adhesiveness and the paint adhesiveness of the chemical treatment steel sheet 10 are unlikely to be secured.

[0045] The composite plated layer 106 according to the present embodiment contains Sn in an amount of 0.10 to 10.0 g/m² per one surface.

[0046] Sn has excellent processability, weldability, and corrosion resistance, and by performing the reflow treatment after Sn plating, corrosion resistance of the chemical treatment steel sheet 10 can be further improved, and a surface appearance (mirror appearance) of the chemical treatment steel sheet 10 can be made more preferable. In order to achieve the above-described effects, it is necessary that the composite plated layer 106 contain Sn in an amount of 0.10 g/m² per one surface.

[0047] Also, when the amount of Sn in the composite plated layer 106 is high, the processability, the weldability, and the corrosion resistance of the chemical treatment steel sheet 10 is improved. However, when the amount of Sn exceeds 10.0 g/m² per one surface, the above-described effects using Sn are saturated. Furthermore, when the amount of Sn exceeds 10.0 g/m² per one surface, this is not economically preferable. For the above reasons, the amount of Sn in the composite plated layer 106 is set to 10.0 g/m² or less per one surface.

[0048] The more preferable amount of Sn in the composite plated layer 106 is 0.30 g/m² to 7.0 g/m² per one surface. When the composite plated layer 106 contains Sn in an amount of 0.30 g/m² or more per one surface, it is possible to more reliably achieve the above-described effects using Sn. Furthermore, when the composite plated layer 106 contains Sn in an amount of 7.0 g/m² or less per one surface, it is possible to further reduce the manufacturing costs.

[0049] A total amount of Ni and Sn contained in the composite plated layer 106 is 50 mass% or more of the composite plated layer 106. A total amount of Ni as Ni metal and an amount of Sn as Sn metal contained in the composite plated layer 106 is preferably 70 mass% or more of the composite plated layer 106.

[0050] The composite plated layer 106 may contain Fe in an amount of 1.0 to 3500 mg/m² per one surface in addition to Ni and Sn described above. Furthermore, the composite plated layer 106 may contain inevitable impurities which may be mixed in the manufacturing process or the like.

[0051] When the steel sheet 103 having the Ni-plated layer 105 or the composite plated layer 106 formed on its surface is used as a steel sheet for containers, even if a film is laminated on a surface of the Ni-plated layer 105 or the composite plated layer 106 or even if a coating material is applied thereon, it is difficult to prevent sulfide stain. The reason for this is thought to be the fact that S contained in beverages, foods, or the like which are the contents binds to Ni or Sn in the plated layer 105 to form black NiS, SnS, SnS₂, or the like.

[0052] Note that S is contained in beverages or foods as a constituent element of sulfur-containing amino acids such as L-cysteine, L-(γ)-cystine, and L-methionine.

[0053] In addition, when the Ni-plated layer 105 or the composite plated layer 106 is not densely formed, a part of the steel sheet 103 as the base material is exposed. In such a case, Fe in the steel sheet 103 binds to S contained in beverages, foods, or the like and black FeS, Fe₂S₃, or Fe₂S is formed in some cases.

[0054] In order to reduce the blackening caused by NiS, SnS, SnS₂, FeS, Fe₂S₃, Fe₂S, or the like described above, a chromate film is mainly formed on the surface of the Ni-plated layer 105 or the composite plated layer 106.

[0055] In the chemical treatment steel sheet 10 according to the present embodiment, in order to improve the sulfide stain resistance, the chemical treatment layer 107 which contains a Zr compound, a phosphate compound, and an Al

compound is formed on the surfaces of the Ni-plated layer 105 or the composite plated layer 106 as a substitute for a conventional chromate film.

[Regarding chemical treatment layer 107]

[0056] As illustrated in Figs. 1A to 2B, in the chemical treatment steel sheet 10 according to the present embodiment, the chemical treatment layer 107 is formed on the Ni-plated layer 105 or the composite plated layer 106. The chemical treatment layer 107 is a composite film layer which mainly contains a Zr compound and contains a Zr compound in which an amount of Zr contained therein is 1.0 to 150 mg/m² per one surface, a phosphate compound in which an amount of P contained therein is 1.0 to 100 mg/m² per one surface, and an Al compound in which an amount of Al contained therein is 0.10 to 30.0 mg/m² per one surface.

[0057] In the present embodiment, the composite film layer indicates a film layer in which the Zr compound, the phosphate compound, and the Al compound are present in a partially mixed state without being fully mixed.

[0058] When three films, i.e., a Zr film containing a Zr compound, a phosphate film containing a phosphate compound, and an Al film containing an Al compound stacked and are formed on the Ni-plated layer 105 or the composite plated layer 106, some degree of effects on the corrosion resistance and the adhesiveness can be obtained, but this is not practically sufficient. However, when a Zr compound, a phosphate compound, and an Al compound are present in a partially mixed state in the chemical treatment layer 107 as in the present embodiment, it is possible to obtain excellent corrosion resistance and adhesiveness as compared with when the three films are formed to be stacked as described above.

[0059] The Zr compound contained in the chemical treatment layer 107 according to the present embodiment has a function of improving corrosion resistance, adhesiveness, and process adhesiveness. Examples of the Zr compound according to the present embodiment include Zr oxides, Zr phosphates, Zr hydroxides, Zr fluorides, and the like and the chemical treatment layer 107 may contain a plurality of Zr compounds described above. Preferred combinations of Zr compounds are Zr oxides, Zr phosphates, and Zr fluorides.

[0060] When the amount of Zr contained in the Zr compound in the chemical treatment layer 107 is 1.0 mg/m² or more per one surface, appropriate corrosion resistance, adhesiveness, and process adhesiveness are secured for practical use.

[0061] On the other hand, when the amount of Zr contained in the Zr compound increases, corrosion resistance, adhesiveness, and process adhesiveness are improved. However, when the amount of Zr contained in the Zr compound exceeds 150 mg/m² per one surface, the chemical treatment layer 107 becomes too thick. In addition, the adhesiveness of the chemical treatment layer 107 with respect to the Ni-plated layer 105 or the composite plated layer 106 is reduced mainly due to cohesive failure as well as the electric resistance increasing and the weldability decreasing. Furthermore, when the amount of Zr contained in the Zr compound exceeds 150 mg/m², the appearance is inhomogeneous due to a unevenness adhered amount of the chemical treatment layer 107 in some cases.

[0062] Therefore, the amount of Zr contained in the Zr compound (that is, the Zr content) of the chemical treatment layer 107 according to the present embodiment is set to 1.0 mg/m² to 150 mg/m² per one surface. The more preferable amount of Zr contained in the Zr compound is 1.0 to 120 mg/m² per one surface. When the amount of Zr is set to 120 g/m² or less, it is possible to further reduce the manufacturing costs of the chemical treatment layer 107.

[0063] The chemical treatment layer 107 further contains one or more types of phosphate compounds in addition to the Zr compound described above.

[0064] The phosphate compound according to the present embodiment has a function of improving corrosion resistance, adhesiveness, and process adhesiveness. Examples of the phosphate compounds according to the present embodiment include iron phosphates, nickel phosphates, tin phosphates, zirconium phosphates, aluminium phosphates, and the like formed by the reaction of phosphate ions with the compounds contained in the steel sheet 103, the Ni-plated layer 105 or the composite plated layer 106, and the chemical treatment layer 107. The chemical treatment layer 107 may contain one of the above-described phosphate compounds or two or more thereof.

[0065] The higher the amount of phosphate compound in the chemical treatment layer 107, the better the corrosion resistance, the adhesiveness, and the process adhesiveness of the chemical treatment steel sheet 10. To be specific, when the amount of P contained in the phosphate compound in the chemical treatment layer 107 is 1.0 mg/m² or more, appropriate corrosion resistance, adhesiveness, and process adhesiveness are secured for practice use.

[0066] On the other hand, when the amount of P contained in phosphate compound increases, corrosion resistance, adhesiveness, and process adhesiveness are also improved. However, when the amount of P contained in the phosphate compound exceeds 100 mg/m² per one surface, the chemical treatment layer 107 becomes too thick. In addition, the adhesiveness of the chemical treatment layer 107 with respect to the Ni-plated layer 105 or the composite plated layer 106 is reduced mainly due to cohesive failure as well as the electric resistance increasing and the weldability decreasing. Furthermore, when the amount of P contained in phosphate compound exceeds 100 mg/m² per one surface, the appearance is inhomogeneous due to a unevenness adhered amount of the chemical treatment layer 107 in some cases.

[0067] Therefore, the amount of P contained in the phosphate compound in the chemical treatment layer 107 according to the present embodiment is set to 1.0 mg/m² to 100 mg/m² per one surface.

[0068] The more preferable amount of P contained in the phosphate compound in the chemical treatment layer 107 is 2.0 to 70.0 mg/m² per one surface. When the amount of P contained in the phosphate compound in the chemical treatment layer 107 is set to 2.0 mg/m² or more per one surface, it is possible to obtain a more preferable sulfide stain resistance. Furthermore, when the amount of P contained in the phosphate compound in the chemical treatment layer 107 is set to 70.0 mg/m² or less per one surface, it is possible to further reduce the manufacturing costs of the chemical treatment layer 107.

[0069] The chemical treatment layer 107 further contains an Al compound in addition to the Zr compound and the phosphate compound described above. The Al compound in the chemical treatment layer 107 exists mainly as an Al oxide in the chemical treatment layer 107. When an Al oxide reinforces film defects of the chemical treatment layer 107 having Zr as a main component, the chemical treatment steel sheet 10 can obtain excellent sulfide stain resistance.

[0070] Since the chemical treatment layer 107 having Zr as a main component is inherently an extremely uniform coating, an amount of Al contained in the Al compound added to the chemical treatment layer 107 to reinforce film defects may be 0.10 mg/m² or more per one surface. When the amount of Al contained in the Al compound is 0.10 mg/m² or more per one surface, it is possible to appropriately improve the sulfide stain resistance of the chemical treatment steel sheet 10.

[0071] On the other hand, when the amount of Al compound in the chemical treatment layer 107 increases, the sulfide stain resistance is also improved. However, when the amount of Al in the Al compound exceeds 30.0 mg/m² per one surface, the sulfide stain resistance is saturated and thus it is not economically preferable. For this reason, the amount of Al contained in the Al compound in the chemical treatment layer 107 is set to 30.0 mg/m² or less per one surface.

[0072] The more preferable amount of Al contained in the Al compound in the chemical treatment layer 107 is 0.20 to 20.0 mg/m² per one surface. When the amount of Al contained in the Al compound is set to 0.20 mg/m² or more per one surface, it is possible to appropriately improve the sulfide stain resistance. Furthermore, when the amount of Al contained in the Al compound is set to 20.0 mg/m² or less per one surface, it is possible to further reduce the manufacturing costs of the chemical treatment layer 107.

[0073] The preferable amount of Al in Al oxide (Al₂O₃) in the chemical treatment layer 107 is 0.10 to 30.0 mg/m². When the amount of Al oxide in the chemical treatment layer 107 is in the above-described range, it is possible to appropriately reinforce film defects of the chemical treatment layer 107 and to obtain excellent sulfide stain resistance.

[0074] Further, by including Al compounds in the chemical treatment layer 107, it is possible to reduce the content of phosphate compounds which improves the resistance to sulfide stain, as with Al.

[0075] When a large amount of zirconium phosphate generated by the reaction of the phosphate ions in the phosphate compound contained in the chemical treatment layer 107 with the Zr ions is present in a chemical treatment solution used when the chemical treatment layer 107 is formed, precipitation occurs and thus the chemical treatment solution becomes cloudy.

[0076] Here, the Al compound contributes to the improvement of the sulfide stain resistance more than the phosphate compound. For this reason, when the chemical treatment layer 107 contains the Al compound, it is possible to appropriately improve the sulfide stain resistance and to reduce the amount of phosphate compound which causes the clouding of the chemical treatment solution.

[0077] Also, when the amount of phosphate compound is reduced, it is possible to reduce an amount of F ions which inhibit the binding between Zr and phosphates and the binding between Al and phosphates. As a result, since Zr is precipitated more easily, it is possible to improve the electrolysis efficiency for forming the chemical treatment layer 107.

[0078] It should be noted that the chemical treatment layer 107 may contain inevitable impurities to be mixed in the manufacturing process or the like in addition to the Zr compound, the phosphate compound, and the Al compound described above. Furthermore, when the chemical treatment layer 107 contains Cr, the upper limit of the Cr content is 2.0 mg/m².

[0079] The chemical treatment steel sheet 10 according to the present embodiment accomplishes excellent sulfide stain resistance even when an amount of the chemical treatment layer 107 is reduced.

[0080] For example, a coating material may be applied to a surface of the chemical treatment steel sheet 10, and then is baked, which results in forming a coating film. The chemical treatment steel sheet 10 having a coating film formed on its surface is placed as a lid and fixed on the mouth of a heat-resistant bottle which holds a 0.6 mass% L-cysteine liquid boiled for one hour and is subjected to heat treatment at 110°C for 30 minutes using a soaking furnace or the like. When an appearance of a portion in contact with the heat-resistant bottle is observed in the chemical treatment steel sheet 10 after the above-described heat treatment, blackening does not occur in 50% or more of an area of the contact portion when the chemical treatment steel sheet 10 according to the present embodiment is used.

[0081] As described above, the chemical treatment steel sheet 10 according to the present embodiment has excellent corrosion resistance and sulfide stain resistance. For this reason, it is possible to use the chemical treatment steel sheet 10 as a steel sheet for containers even when the surface of the chemical treatment layer 107 is not covered with a film

or a coating material.

<Regarding layer structure of chemical treatment steel sheet 10>

[0082] As described above, the chemical treatment steel sheet 10 has the Ni-plated layer 105 or the composite plated layer 106 on the steel sheet 103 and has the chemical treatment layer 107 on the Ni-plated layer 105 or the composite plated layer 106. That is to say, in the chemical treatment steel sheet 10, the steel sheet 103 is in contact with the Ni-plated layer 105 or the composite plated layer 106 and the steel sheet 103 does not have another layer between the steel sheet 103 and the Ni-plated layer 105 or the composite plated layer 106. Likewise, in the chemical treatment steel sheet 10, the Ni-plated layer 105 or the composite plated layer 106 is in contact with the chemical treatment layer 107 and the Ni-plated layer 105 or the composite plated layer 106 does not have another layer between the Ni-plated layer 105 or the composite plated layer 106 and the chemical treatment layer 107.

<Method for measuring component content>

[0083] Amounts of Ni and amounts of Sn in the Ni-plated layer 105 and the composite plated layer 106 can be measured using, for example, a fluorescent X-ray method. In this case, a calibration curve for an amount of Ni is created in advance using samples with a known amount of Ni and amounts of Ni are determined relatively using the created calibration curve. As for amounts of Sn, a calibration curve for an amount of Sn is created in advance using a sample with a known amount of Ni and amounts of Sn are relatively identified using the created calibration curve.

[0084] The amounts of Zr, P, and Al in the chemical treatment layer 107 can be measured using, for example, a quantitative analysis method such as fluorescent X-ray analysis. Furthermore, it is possible to determine the specific content of the compound present in the chemical treatment layer 107 by performing an analysis using X-ray photoelectron spectroscopy (XPS).

[0085] Also, in the case of the Al_2O_3 content in the chemical treatment layer 107, first peak intensity ratios of Al_2O_3 , Al metal, and other Al compounds are obtained using XPS. Then, as described above, the Al_2O_3 content in the chemical treatment layer 107 is calculated from a total amount of Al obtained using a quantitative analysis method such as fluorescent X-ray analysis and the peak intensity ratios obtained using XPS.

[0086] Note that a method for measuring each component is not limited to the above-described methods and it is possible to apply known measurement methods.

<Regarding method for manufacturing chemical treatment steel sheet 10>

[0087] A method for manufacturing the chemical treatment steel sheet 10 according to the present embodiment will be described in detail below with reference to Figs. 3. Fig. 3 is a flowchart showing an example of a flow of a method for manufacturing the chemical treatment steel sheet 10 according to the present embodiment.

[Pretreatment step]

[0088] In the method for manufacturing the chemical treatment steel sheet 10 according to the present embodiment, a known pretreatment is first performed on the steel sheet 103 if necessary (Step S101).

[Plating step]

[0089] Subsequently, any one of the Ni-plated layer 105 and the composite plated layer 106 is formed on the surface of the steel sheet 103 (Step S103).

[0090] When the Ni-plated layer 105 is formed on the surface of the steel sheet 103, it is possible to use a known technique such as an electroplating method and a vacuum evaporation method. It should be noted that heat treatment may be performed after the formation of the Ni-plated layer 105 to form a Fe-Ni diffusion layer (not shown) at an interface between the steel sheet 103 and the Ni-plated layer 105.

[0091] When the composite plated layer 106 having the Fe-Ni-Sn alloy layer 105d and the island-shaped Sn-plated layer 105e is formed on the surface of the steel sheet 103, the composite plated layer 106 is formed by forming an Ni-plated layer (not shown) including a Ni or Fe-Ni alloy on the surface of the steel sheet 103, and then forming the Sn-plated layer (not shown) on the Ni-plated layer (not shown), and subsequently performing a reflow treatment (reflow treatment) on them.

[0092] That is to say, Fe of the steel sheet 103, Ni of the Ni-plated layer (not shown), and Sn of a portion of the Sn-plated layer (not shown) are alloyed with a reflow treatment to form the Fe-Ni-Sn alloy layer 105d, the remaining Sn-plated layer has an island shape, and the island-shaped Sn-plated layer 105e is formed.

[0093] As a method for forming the Ni-plated layer (not shown) including Ni or a Fe-Ni alloy, it is possible to use a general electroplating method (for example, cathodic electrolysis method).

[0094] A method for forming the Sn-plated layer (not shown) is not limited. In addition, for example, it is possible to use a known electroplating method, a method for performing plating on the steel sheet 103 by immersing the steel sheet 103 in molten Sn, and the like.

[0095] When the Ni-plated layer (not shown) is formed by a diffusion plating method, the surface of the steel sheet 103 is subjected to Ni plating and then subjected to a diffusion treatment for forming a diffusion layer in an annealing furnace. A nitriding treatment may be performed before or after a diffusion treatment or simultaneously with a diffusion treatment. Even when a nitriding treatment is performed, the effect of Ni in the Ni-plated layer (not shown) in the present embodiment and the effect of a nitriding treatment can be achieved without interfering with each other.

[0096] After the Sn-plated layer (not shown) is formed, a reflow treatment (reflow treatment) is performed. The molten Sn, Fe of the steel sheet 103, and Ni in the Ni-plated layer (not shown) are alloyed by performing a reflow treatment and the Fe-Ni-Sn alloy layer 105d and the island-shaped Sn-plated layer 105e including Sn which is formed in an island shape are formed. The island-shaped Sn-plated layer 105e can be formed by appropriately controlling a reflow treatment.

[Electrolytic treatment step]

[0097] After forming any one of the Ni-plated layer 105 and the composite plated layer 106, the chemical treatment layer 107 is formed through an electrolytic treatment (Step S105).

[0098] The chemical treatment layer 107 is formed by an electrolytic treatment (for example, cathode electrolytic treatment). The chemical treatment solution used for forming the chemical treatment layer 107 through electrolytic treatment contains 10 ppm or more and 20000 ppm or less of Zr ions, 10 ppm or more and 20000 ppm or less of F ions, 10 ppm or more and 3000 ppm or less of phosphate ions, a total amount of 100 ppm or more and 30000 ppm or less of nitrate ions and sulfate ions, and 500 ppm or more and 5000 ppm or less of Al ions. Furthermore, $(\text{NH}_4)_3\text{AlF}_6$ is used as a supply source of Al ions in the chemical treatment solution.

[0099] It should be noted that nitrate ions and sulfate ions may be contained in the chemical treatment solution in a total amount of 10 ppm or more and 3000 ppm or less in both of the nitrate ions and the sulfate ions, both of the nitrate ions and the sulfate ions may be contained in the chemical treatment solution, and any one of the nitrate ions and the sulfate ions may be contained in the chemical treatment solution.

[0100] The chemical treatment solution preferably contains 200 ppm or more and 17000 ppm or less of Zr ions, 200 ppm or more and 17000 ppm or less of F ions, 100 ppm or more and 2000 ppm or less of phosphate ions, a total amount of 1000 ppm or more and 23000 ppm or less of nitrate ions and sulfate ions, and 500 ppm or more and 3000 or less of Al ions.

[0101] It is possible to more reliably prevent a decrease in an amount of Zr adhered when a concentration of Zr ions is set to 200 ppm or more. Furthermore, it is possible to more reliably prevent the clouding of the chemical treatment layer 107 accompanied by the precipitation of the phosphate when a concentration of F ions is set to 200 ppm or more.

[0102] Likewise, it is possible to more reliably prevent the clouding of the chemical treatment layer 107 accompanied by the precipitation of the phosphate when a concentration of phosphate ions is set to 100 ppm or more. Furthermore, it is possible to more reliably prevent the deterioration of the adhesion efficiency of the chemical treatment layer 107 when a concentration of nitrate ions or sulfate ions or a combination thereof is set to 1000 ppm or more. It is possible to more reliably achieve the effect of improving the sulfide stain resistance when a concentration of Al ions is set to 500 ppm or more.

[0103] It is possible to more reliably reduce the manufacturing costs of the chemical treatment layer 107 when the upper limit value of each component of the chemical treatment solution is set to the above-described value.

[0104] The temperature of the chemical treatment solution is preferably 5°C or higher and lower than 90°C. The temperature of the chemical treatment solution being lower than 5°C is not economically effective because the formation efficiency of the chemical treatment layer 107 is poor when the temperature of the chemical treatment solution is lower than 5°C. Furthermore, the temperature of the chemical treatment solution being 90°C or higher is not preferable because the structure of the formed chemical treatment layer 107 is inhomogeneous, defects such as cracks and micro-cracks are generated, and the defects become starting point of corrosion or the like when the temperature of the chemical treatment solution is 90°C or higher.

[0105] The temperature of the chemical treatment solution increases the reactivity of the chemical treatment solution at the interface and improves the adhesion efficiency of the chemical treatment layer 107 and is thus preferably higher than a temperature of the surface of the steel sheet 103 on which any one of the Ni-plated layer 105 and the composite plated layer 106 is formed.

[0106] The current density at the time of performing an electrolytic treatment is preferably 1.0 A/dm² or more and 100 A/dm² or less. The current density being less than 1.0 A/dm² is not preferable because an amount of the chemical treatment layer 107 adhered decreases and an electrolytic treatment time increases in some cases when the current density is less than 1.0 A/dm². Furthermore, the current density exceeding 100 A/dm² is not preferable because an

adhered amount of the chemical treatment layer 107 is excessive and a chemical treatment layer 107 which is inadequately adhered in the formed chemical treatment layer 107 is likely to be washed away (peeled off) in a washing step through washing with water or the like after the electrolytic treatment when the current density exceeds 100 A/dm^2 .

[0107] A time at which the electrolytic treatment is performed (electrolytic treatment time) is preferably 0.20 seconds or more and 150 seconds or less. The electrolytic treatment time being less than 0.20 seconds is not preferable because an amount of the chemical treatment layer 107 adhered decreases and the desired performance is not obtained when the electrolytic treatment time is less than 0.20 seconds. On the other hand, the electrolytic treatment time exceeding 150 seconds is not preferable because the adhered amount of the chemical treatment layer 107 is excessive and a chemical treatment layer 107 which is inadequately adhered in the formed chemical treatment layer 107 is likely to be washed away (peeled off) in a washing step through washing with water or the like after the electrolytic treatment when the electrolytic treatment time exceeds 150 seconds.

[0108] A pH of the chemical treatment solution is preferably in a range of 3.1 to 3.7, more preferably about 3.5. In order to adjust the pH of the chemical treatment solution, nitric acid, ammonia, or the like may be added as necessary.

[0109] When the electrolytic treatment is performed under the above-described conditions, it is possible to form the chemical treatment layer 107 according to the present embodiment on a surface of any one of the Ni-plated layer 105 and the composite plated layer 106.

[0110] It should be noted that tannic acid may be further added to the chemical treatment solution used for the electrolytic treatment when forming chemical treatment layer according to the present embodiment. When tannic acid is added to the chemical treatment solution, tannic acid reacts with Fe in the steel sheet 103 to form a film made of iron tannate on the surface of the steel sheet 103. The film made of iron tannate is preferable for the purpose of improving rust resistance and the adhesiveness.

[0111] Examples of a solvent for the chemical treatment solution include deionized water, distilled water, and the like. The preferred electrical conductivity of the solvent for the chemical treatment solution is $10 \mu\text{S/cm}$ or less, more preferably $5 \mu\text{S/cm}$ or less, further more preferably $3 \mu\text{S/cm}$ or less. Here, the solvent for the chemical treatment solution is not limited thereto and it is possible to appropriately select the solvent for the chemical treatment solution in accordance with a material to be dissolved, a formation method, and the formation conditions or the like of the chemical treatment layer 107. Here, it is preferable to use deionized water or distilled water in view of industrial productivity, cost, and environment based on stable stability of an amount of each component adhered.

[0112] Examples of a supply source of Zr include a Zr complex such as H_2ZrF_6 . Zr in the Zr complex as described above is present in the chemical treatment solution as Zr^{4+} due to a hydrolysis reaction accompanied by an increase in pH at a cathode electrode interface. Such Zr ions form a compound such as ZrO_2 and $\text{Zr}_3(\text{PO}_4)_4$ through a dehydration condensation reaction with a hydroxyl group ($-\text{OH}$) present on a metal surface in the chemical treatment solution.

[0113] Also, in the chemical treatment solution, $(\text{NH}_4)_3\text{AlF}_6$ is used as a supply source of Al. When $(\text{NH}_4)_3\text{AlF}_6$ is used as the supply source of Al, Al is present in the chemical treatment solution in a state in which Al and F form a complex (hereinafter referred to as an "AlF complex"). Al in the AlF complex is precipitated together with Zr in the electrolytic treatment step to form the chemical treatment layer 107, thereby contributing to the sulfide stain resistance as described above.

[0114] Also, Al is present as a cation in the chemical treatment solution as in Zr. For this reason, when $(\text{NH}_4)_3\text{AlF}_6$ is used as a supply source of Al, it is possible to supply Al into the chemical treatment solution without increasing the concentration of phosphate ions in the chemical treatment solution.

[0115] On the other hand, when $\text{Al}_2(\text{SO}_4)_3$ is used as a supply source of Al as in Patent Document 3, an AlF complex is not formed. Therefore, Al is not appropriately precipitated during the electrolytic treatment step and thus the Al content in the chemical treatment layer 107 is very small. This case is not preferable because the chemical treatment layer 107 does not have appropriate sulfide stain resistance.

[Post treatment step]

[0116] After that, a known post treatment is performed on any one of the Ni-plated layer 105 and the composite plated layer 106 and the steel sheet 103 having the chemical treatment layer 107 formed thereon if necessary (Step S107).

[0117] The chemical treatment steel sheet 10 according to the present embodiment is manufactured by performing the treatment with the above-described flow.

[0118] Although a case in which the chemical treatment layer 107 is formed on the Ni-plated layer 105 or the composite plated layer 106 through the electrolytic treatment has been described in the above description, when a sufficient time for formation of the chemical treatment film is allowed, the chemical treatment layer 107 may be formed using an immersion time instead of electrolytic treatment.

[Examples]

[0119] A chemical treatment steel sheet and a method for manufacturing a chemical treatment steel sheet according to an embodiment of the present invention will be described in detail below while showing examples. Note that the following examples are examples of the chemical treatment steel sheet and the method for manufacturing the chemical treatment steel sheet according to the embodiment of the present invention and the chemical treatment steel sheet and the method for manufacturing the chemical treatment steel sheet according to the embodiment of the present invention are not limited to the following examples.

(Example 1)

[0120] In Example 1, how a sulfide stain resistance changes was examined by changing the amount of Al compound without changing the Zr compound and phosphate compound content in a chemical treatment layer.

[0121] In Example 1, steel sheets which are generally used as steel sheets for containers were used as base materials and a Ni-plated layer was formed as a plated layer. The amount of Ni contained in the Ni-plated layer was set at 1000 mg/m² per one surface in all samples. Furthermore, a chemical treatment layer is formed by changing a concentration of an Al compound in a chemical treatment layer for each sample to manufacture a plurality of samples. Here, in each sample, the amount of Zr contained in the Zr compound was 8 mg/m² per one surface and the amount of P contained in the phosphate compound was 3 mg/m² per one surface.

[0122] The sulfide stain resistance was evaluated as follows. First, a 0.6 mass% L-cysteine liquid boiled for one hour was put into a heat-resistant bottle and the samples (φ 40 mm) were placed and fixed as a lid to the mouth of the heat-resistant bottle. And then, a heat treatment (retort treatment) was performed on the heat-resistant bottle with the lid as described above in a soaking furnace at 110°C for 15 minutes. Subsequently, in each sample an appearance of a portion which contacted with the heat-resistant bottle was observed and evaluated as 10 levels on the basis of the following criteria. It should be noted that, in the following evaluation criteria, a sample in which the score is 5 points or more withstands actual use.

<Sulfide stain resistance evaluation criteria>

[0123] A ratio of an area which did not change to black with respect to a contact area between a sample and a 0.6 mass% L-cysteine liquid was scored from 1 to 10 points.

10 points: 100% to 90% or more

9 points: less than 90% to 80% or more

8 points: less than 80% to 70% or more

7 points: less than 70% to 60% or more

6 points: less than 60% to 50% or more

5 points: less than 50% to 40% or more

4 points: less than 40% to 30% or more

3 points: less than 30% to 20% or more

2 points: less than 20% to 10% or more

1 point: less than 10% to 0% or more

[0124] The obtained evaluation results are shown in Fig. 4. In Fig. 4, a horizontal axis indicates the amount of Al compound (amount of Al metal) in a chemical treatment layer in each sample and a vertical axis indicates the evaluation result of a sulfide stain resistance.

[0125] As shown in Fig. 4, when the amount of Al contained in Al compound is less than 0.1 mg/m² per one surface, the evaluation result of the sulfide stain resistance was scored at 1 point. On the other hand, when the amount of Al contained in Al compound is 0.1 mg/m² or more per one surface, the evaluation result of the sulfide stain resistance was scored at 7 or more points and it was revealed that the sample had very excellent sulfide stain resistance.

[0126] From the results, when an Al compound in a predetermined amount is contained in a chemical treatment layer, it was shown that the sulfide stain resistance of the chemical treatment steel sheet having the chemical treatment film is significantly improved.

(Example 2)

[0127] Next, how the sulfide stain resistance changes while a type of a plated layer and the amount of each component contained in a chemical treatment layer is changed was examined. In examples and comparative examples except for

Comparative Example a5, a plated layer is any one of a Ni-plated layer and a composite plated layer. On the other hand, in Comparative Example a5, a composite plated layer is formed on a Ni-plated layer (two plated layers are formed).

[0128] Also, $(\text{NH}_4)_3\text{AlF}_6$ was used as a supply source of Al ions in Examples A1 to A31 of the present invention and Comparative Examples a1 to a6, whereas $\text{Al}_2(\text{SO}_4)_3$ was used as a supply source of Al ions in Comparative Examples a7 and a8 to form a chemical treatment layer.

[0129] The amounts of Ni metal and Sn metal contained in a plated layer and the amounts of Zr, P, and Al contained in a chemical treatment layer were measured using a fluorescent X-ray analysis.

[0130] In the Al_2O_3 content in a chemical treatment layer, first, peak intensity ratios of Al_2O_3 , Al metal, and other Al compounds were obtained using an XPS. And then the Al_2O_3 content in the chemical treatment layer was calculated from a total amount of Al metals obtained through a quantitative analysis method such as a fluorescent X-ray analysis and the peak intensity ratios obtained through the XPS as described above.

[0131] The measurement results are shown in Table 1 which will be shown later.

[Table 1]

	Symbol	Chemical treatment steel sheet						
		Ni-plated layer	Composite plated layer		Chemical treatment layer			
		Amount of Ni as Ni metal (mg/m ²)	Amount of Ni (mg/m ²) as Ni metal	Amount of Sn as Si metal (g/m ²)	Amount of Zr as Zr metal (mg/m ²)	Amount of P (mg/m ²)	Total amount of Al (mg/m ²)	Amount of Al in Al ₂ O ₃ (mg/m ²)
Examples	A1	6.5	-	-	3.7	70	19	11
	A2	2938	-	-	105	63	16	11
	A3	571	-	-	1.2	58	3.2	2.8
	A4	2487	-	-	148	77	6.1	3.0
	A5	2861	-	-	55	1.3	4.7	2.7
	A6	1231	-	-	74	94	6.9	3.4
	A7	2854	-	-	52	36	0.12	0.11
	A8	1927	-	-	5.2	12	29	28
	A9	-	2.5	9.4	18	8.8	26	12
	A10	-	198	7.8	119	100	6.9	6.0
	A11	-	49	0.12	138	15	25	14
	A12	-	103	9.3	68	93	15	10
	A13	-	76	6.4	1.2	22	24	17
	A14	-	173	2.2	145	71	27	19
	A15	-	163	8.8	133	1.2	12	10
	A16	-	137	8.2	128	95	8.7	7.4
	A17	-	132	1.4	109	85	0.2	0.15
	A18	-	180	0.6	63	54	29	28
	A19	-	139	8.4	119	40	23	21
	A20	-	99	2.4	83	2.4	12	8.6

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(continued)

	Symbol	Chemical treatment steel sheet						
		Ni-plated layer	Composite plated layer		Chemical treatment layer			
		Amount of Ni as Ni metal (mg/m ²)	Amount of Ni (mg/m ²) as Ni metal	Amount of Sn as Si metal (g/m ²)	Amount of Zr as Zr metal (mg/m ²)	Amount of P (mg/m ²)	Total amount of Al (mg/m ²)	Amount of Al in Al ₂ O ₃ (mg/m ²)
	A21	-	187	7.7	19	69	14	6.2
	A22	-	110	7.1	67	67	0.2	0.18
	A23	-	29	5.4	89	45	19	18
	A24	11	-	-	133	20	19	16
	A25	1934	-	-	39	9.2	25	14
	A26	-	4.3	4.4	137	49	15	10
	A27	-	98	9.4	67	10	16	9.1
	A28	-	169	0.3	82	20	19	10
	A29	-	80	6.9	148	25	13	6.9
	A30	-	129	1.7	13	3.3	17	8.8
	A31	-	24	2.6	40	8.7	13	10
Comparative examples	a1	<u>2.3</u>	-	-	<u>243</u>	3.5	2.1	1.5
	a2	-	<u>0.1</u>	3.5	13	<u>230</u>	27	21
	a3	-	18	<u>0.03</u>	69	79	<u>50</u>	<u>38</u>
	a4	-	103	4.7	<u>0.5</u>	56	6.1	5.5
	a5	<u>5032</u>	68	1.8	23	<u>0.2</u>	20	9.4
	a6	-	<u>302</u>	<u>30</u>	72	23	<u>0.03</u>	<u>0.02</u>
	a7	23	-	-	2	3	<u>0.03</u>	<u>0.02</u>
	a8	-	112	3.3	43	12	<u>0.04</u>	<u>0.03</u>

<Corrosion resistance evaluation>

[0132] 3% acetic acid was used as a corrosion resistance test solution. A piece with a diameter of 35 mm was cut out of a steel sheet and placed and fixed to the mouth of a heat-resistant bottle into which the corrosion resistance test solution is put. After a heat treatment is performed at 121 °C for 60 minutes, the corrosion resistance was evaluated using a ratio of a corrosion area with respect to an area in which the corrosion resistance test solution contacted with a Ni-plated steel sheet (an area of the mouth of the heat-resistant bottle) was evaluated.

[0133] To be more specific, the ratio of a corrosion area with respect to an area in which a test piece contacted with a test solution was scored from 1 to 10 points. It should be noted that, in the following evaluation criteria, a sample in which the score is 5 points or more withstands actual use.

[0134]

10 points: 100% to 90% or more

9 points: less than 90% to 80% or more

8 points: less than 80% to 70% or more

7 points: less than 70% to 60% or more

6 points: less than 60% to 50% or more

5 points: less than 50% to 40% or more

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4 points: less than 40% to 30% or more

3 points: less than 30% to 20% or more

2 points: less than 20% to 10% or more

1 point: less than 10% to 0% or more

[0135] In items of corrosion resistance evaluation, 10 points to 9 points are labeled as "very good," 8 points to 5 points are labeled as "good," and 4 points or less are labeled as "not good."

<Sulfide stain resistance evaluation>

[0136] A sulfide stain resistance evaluation was performed as follows. A 0.6 mass% L-cysteine liquid boiled for one hour was put into a heat-resistant bottle and the samples (<p 40 mm) were placed and fixed as a lid to the mouth of the heat-resistant bottle. A heat treatment (retort treatment) was performed on the heat-resistant bottle with the sample as a lid at 110°C for 15 minutes in a soaking furnace. Subsequently, an appearance of a portion in each sample which contacted with the heat-resistant bottle was observed and evaluated in 10 levels on the basis of the same criteria as above. In Table 2 which will be shown later, 10 points to 8 points are labeled as "very good," 7 points to 5 points are labeled as "good," and 4 points or less are labeled as "not good."

[0137] The obtained results are Table 2 which will be shown later.

[Table 2]

	Symbol	Characteristic evaluation	
		Corrosion resistance	Sulfide stain resistance
Examples	A1	Good	Very Good
	A2	Very Good	Very Good
	A3	Very Good	Good
	A4	Very Good	Very Good
	A5	Very Good	Good
	A6	Very Good	Very Good
	A7	Very Good	Good
	A8	Very Good	Very Good
	A9	Good	Very Good
	A10	Very Good	Very Good
	A11	Good	Very Good
	A12	Very Good	Very Good
	A13	Very Good	Good
	A14	Very Good	Very Good
	A15	Very Good	Good
	A16	Very Good	Very Good
	A17	Very Good	Good
	A18	Very Good	Very Good
	A19	Very Good	Very Good
	A20	Very Good	Very Good
	A21	Very Good	Very Good
	A22	Very Good	Very Good
	A23	Very Good	Very Good
	A24	Very Good	Very Good

(continued)

	Symbol	Characteristic evaluation	
		Corrosion resistance	Sulfide stain resistance
	A25	Very Good	Very Good
	A26	Very Good	Very Good
	A27	Very Good	Very Good
	A28	Very Good	Very Good
	A29	Very Good	Very Good
	A30	Very Good	Very Good
	A31	Very Good	Very Good
Comparative examples	a1	Not Good	Very Good
	a2	Not Good	Very Good
	a3	Not Good	Very Good
	a4	Very Good	Not Good
	a5	Very Good	Not Good
	a6	Very Good	Not Good
	a7	Very Good	Not Good
	a8	Very Good	Not Good

[0138] As shown in Table 2, Examples A1 to A31 of the present invention all have excellent corrosion resistance and sulfide stain resistance. On the other hand, either one of corrosion resistance and sulfide stain resistance of Comparative Examples a1 to a8 deteriorated. In Comparative Examples a7 and a8 in which $\text{Al}_2(\text{SO}_4)_3$ was used as the supply source of Al ions, amounts of Al and Al_2O_3 were significantly small and the sulfide stain resistance was also "not good."

(Example 3)

[0139] Next, how the sulfide stain resistance changes according to a type of plated layer and the each component contained in a chemical treatment layer was examined.

[0140] For each sample having a Ni-plated layer or a composite plated layer shown in Table 3, a chemical treatment was performed under the conditions shown in Table 4 (conditions for a chemical treatment solution and conditions for an electrolytic treatment). Table 5 shows the amounts of Zr, P, Al, and Al_2O_3 included in a chemical treatment layer formed on a plated layer of each sample.

[0141] Also, for each sample having a plated layer and a chemical treatment layer, corrosion resistance and sulfide stain resistance were evaluated as in Example 2. The results are shown in Table 5.

[0142] $(\text{NH}_4)_3\text{AlF}_6$ was used as a supply source of Al ions in Examples B1 to B31 of the present invention and Comparative Examples b1 to b8, whereas $\text{Al}_2(\text{SO}_4)_3$ was used as a supply source of Al ions in Comparative Examples b9 and b10 to form a chemical treatment layer.

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[Table 3]

	Symbol	Ni-plated layer	Composite plated layer	
		Amount of Ni as Ni metal (mg/m ²)	Amount of Ni as Ni metal (mg/m ²)	Amount of Sn as Sn metal (g/m ²)
Examples	B1	1203	-	-
	B2	1664	-	-
	B3	563	-	-
	B4	1896	-	-
	B5	358	-	-
	B6	1452	-	-
	B7	1344	-	-
	B8	1352	-	-
	B9	-	52	5.4
	B10	-	199	4.9
	B11	-	28	7.6
	B12	-	141	8.4
	B13	-	145	1.5
	B14	-	22	6.8
	B15	-	74	8.3
	B16	-	146	2.4
	B17	-	67	4.9
	B18	-	155	2.7
	B19	2322	-	-
	B20	893	-	-
	B21	1716	-	-
	B22	1709	-	-
	B23	1333	-	-
	B24	1618	-	-
	B25	2584	-	-
	B26	-	16	9.5
	B27	-	83	5.7
	B28	-	166	0.8
	B29	-	187	4.1
	B30	-	104	8.6
	B31	-	45	0.6

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(continued)

	Symbol	Ni-plated layer	Composite plated layer	
		Amount of Ni as Ni metal (mg/m ²)	Amount of Ni as Ni metal (mg/m ²)	Amount of Sn as Sn metal (g/m ²)
Comparative examples	b1	2771	-	-
	b2	1902	-	-
	b3	2151	-	-
	b4	-	167	5.3
	b5	-	4	3.9
	b6	-	192	9.1
	b7	-	154	0.13
	b8	-	56	7.7
	b9	1702	-	-
	b10	-	46	5.3

[Table 4]

Chemical treatment											
Symbol	Chemical treatment solution										
	Zr ions (ppm)	F ions (ppm)	Phosphate ions (ppm)	Nitrate ions (ppm)	Sulfate ions (ppm)	Al ions (ppm)	Supply source of Al ions	Bath temperature (°C)	Electrolytic treatment		
									Current (A/dm ²)	Time (sec)	
Examples	B1	13	12277	1936	4921	18830	4506	(NH ₄) ₃ AlF ₆	56	41	66
	B2	19323	4730	2601	6852	8827	4485	(NH ₄) ₃ AlF ₆	58	35	14
	B3	14993	12	145	6861	12906	1339	(NH ₄) ₃ AlF ₆	55	89	59
	B4	12986	19653	1634	4674	18624	4348	(NH ₄) ₃ AlF ₆	68	84	61
	B5	1951	6595	122	15304	12584	3477	(NH ₄) ₃ AlF ₆	46	49	60
	B6	8743	8980	2984	8002	20831	732	(NH ₄) ₃ AlF ₆	15	75	138
	B7	938	12003	667	112	-	1697	(NH ₄) ₃ AlF ₆	18	91	125
	B8	804	2848	1985	29843	-	2924	(NH ₄) ₃ AlF ₆	85	17	13
	B9	12993	11644	1284	-	112	3592	(NH ₄) ₃ AlF ₆	56	10	124
	B10	2962	10320	244	-	29484	940	(NH ₄) ₃ AlF ₆	17	99	133
	B11	16174	14341	1075	5440	19183	532	(NH ₄) ₃ AlF ₆	63	97	60
	B12	8936	7132	2929	13378	11910	4985	(NH ₄) ₃ AlF ₆	67	69	41
	B13	16350	4690	2788	6499	22336	2120	(NH ₄) ₃ AlF ₆	6	97	149
	B14	18054	11783	227	8323	17533	4615	(NH ₄) ₃ AlF ₆	89	73	112
	B15	1949	12852	1979	6982	139	3334	(NH ₄) ₃ AlF ₆	19	1.3	93
	B16	5004	7048	1815	6269	9938	3492	(NH ₄) ₃ AlF ₆	53	98	29
	B17	18806	6927	2530	9931	453	1914	(NH ₄) ₃ AlF ₆	76	72	0.23
	B18	4213	4005	1274	6071	15839	3444	(NH ₄) ₃ AlF ₆	48	42	147
	B19	232	14704	835	4439	14788	734	(NH ₄) ₃ AlF ₆	29	18	4.5
	B20	16382	12122	2386	3365	22816	3800	(NH ₄) ₃ AlF ₆	47	70	101
	B21	18680	236	164	7089	16070	3208	(NH ₄) ₃ AlF ₆	75	85	144

(continued)

	Symbol	Chemical treatment									
		Chemical treatment solution								Electrolytic treatment	
		Zr ions (ppm)	F ions (ppm)	Phosphate ions (ppm)	Nitrate ions (ppm)	Sulfate ions (ppm)	Al ions (ppm)	Supply source of Al ions	Bath temperature (°C)		
	B22	18091	17468	437	17432	4749	531	(NH ₄) ₃ AlF ₆	51	70	146
	B23	3994	15961	115	13281	10137	2022	(NH ₄) ₃ AlF ₆	27	66	91
	B24	17731	11516	1938	3297	4740	1431	(NH ₄) ₃ AlF ₆	6.7	21	57
	B25	14666	10731	506	1192	-	2368	(NH ₄) ₃ AlF ₆	57	71	131
	B26	19227	8897	2254	22938	-	926	(NH ₄) ₃ AlF ₆	75	66	109
	B27	15114	15954	69	-	1029	4161	(NH ₄) ₃ AlF ₆	40	29	107
	B28	19837	17323	2264	-	22973	736	(NH ₄) ₃ AlF ₆	7.5	90	106
	B29	14412	1090	2278	2913	14327	2938	(NH ₄) ₃ AlF ₆	89	66	114
	B30	10741	6088	1594	23206	296	3173	(NH ₄) ₃ AlF ₆	80	40	38
	B31	11921	15848	42	19783	4945	1063	(NH ₄) ₃ AlF ₆	67	55	22
Comparative examples	b1	4	3	2315	30392	30302	4646	(NH ₄) ₃ AlF ₆	7	39	31
	b2	32984	40393	5029	2467	4417	833	(NH ₄) ₃ AlF ₆	36	100	68
	b3	18608	4938	4	9843	9868	3837	(NH ₄) ₃ AlF ₆	14	70	94
	b4	11174	9218	2538	12	63	6054	(NH ₄) ₃ AlF ₆	38	89	57
	b5	11586	16949	716	2018	26326	112	(NH ₄) ₃ AlF ₆	97	71	103
	b6	12729	227	2910	17217	276	2456	(NH ₄) ₃ AlF ₆	2	132	130
	b7	15053	19771	1546	6903	20580	848	(NH ₄) ₃ AlF ₆	19	0.4	170
	b8	12839	13209	2905	20539	4706	4177	(NH ₄) ₃ AlF ₆	36	6	0.1
	b9	19283	2004	1837	2932	523	3465	Al ₂ (SO ₄) ₃	15	12	24
	b10	3829	3283	1232	23533	6545	624	Al ₂ (SO ₄) ₃	25	2	23

[Table 5]

	Symbol	Chemical treatment layer				Characteristic evaluation	
		Amount of Zr as Zr metal (mg/m ²)	Amount of P (mg/m ²)	Total amount of Al (mg/m ²)	Amount of Al in Al ₂ O ₃ (mg/m ²)	Corrosion resistance	Sulfide stain resistance
Examples	B1	26	17	5.1	4.5	Very Good	Good
	B2	4.5	2.9	0.9	0.4	Very Good	Very Good
	B3	52	35	8.6	6.4	Very Good	Very Good
	B4	42	33	8.5	6.9	Very Good	Good
	B5	26	19	5.9	4.2	Very Good	Good
	B6	88	59	17	7.4	Very Good	Very Good
	B7	113	63	20	14	Very Good	Good
	B8	1.9	1.2	0.4	0.3	Very Good	Very Good
	B9	13	7.6	2.1	1.8	Very Good	Good
	B10	123	79	24	21	Very Good	Very Good
	B11	50	32	10	7.5	Very Good	Good
	B12	27	17	5.2	4.7	Very Good	Very Good
	B13	129	82	28	19	Very Good	Good
	B14	71	48	13	10	Very Good	Very Good
	B15	1.1	1.4	0.5	0.4	Very Good	Good
	B16	29	18	4.8	2.5	Very Good	Very Good
	B17	1.3	3.2	0.5	0.4	Very Good	Good
	B18	54	37	11	5.3	Very Good	Very Good
	B19	13	8.4	0.2	0.1	Very Good	Very Good
	B20	59	39	13	6.7	Very Good	Very Good
	B21	99	75	23	10	Very Good	Very Good
	B22	86	65	20	15	Very Good	Very Good
	B23	49	38	10	7.7	Very Good	Very Good
	B24	11.5	7.4	2.4	1.3	Very Good	Very Good
	B25	88	61	18	13	Very Good	Very Good
	B26	59	43	13	5.6	Very Good	Very Good
	B27	27	19	4.9	2.1	Very Good	Very Good
	B28	89	61	16	13	Very Good	Very Good
	B29	71	47	12	10	Very Good	Very Good
	B30	14	8.4	2.5	1.5	Very Good	Very Good
	B31	10	7.3	2.1	1.6	Very Good	Very Good

(continued)

	Symbol	Chemical treatment layer				Characteristic evaluation	
		Amount of Zr as Zr metal (mg/m ²)	Amount of P (mg/m ²)	Total amount of Al (mg/m ²)	Amount of Al in Al ₂ O ₃ (mg/m ²)	Corrosion resistance	Sulfide stain resistance
Comparative examples	b1	<u>0.8</u>	6.7	2.3	1.2	Very Good	Not Good
	b2	<u>0.3</u>	34	13	11	Very Good	Not Good
	b3	56	<u>0.8</u>	12	6.3	Very Good	Not Good
	b4	<u>0.7</u>	33	8.1	3.7	Very Good	Not Good
	b5	59	2.1	<u>0.05</u>	<u>0.04</u>	Very Good	Not Good
	b6	<u>0.4</u>	<u>0.4</u>	4.7	3.1	Very Good	Not Good
	b7	<u>0.7</u>	7.3	0.4	0.3	Very Good	Not Good
	b8	<u>0.1</u>	1.3	0.6	0.3	Very Good	Not Good
	b9	23	12	<u>0.03</u>	<u>0.02</u>	Very Good	Not Good
	b10	14	4	<u>0.04</u>	<u>0.03</u>	Very Good	Not Good

[0143] As shown in Table 5, each sample of Examples B1 to B31 of the present invention manufactured by the method for manufacturing the chemical treatment steel sheet according to the present embodiment had excellent corrosion resistance and sulfide stain resistance. On the other hand, each sample of Comparative Examples b1 to b10 had excellent corrosion resistance, but the sulfide stain resistance was poor. In Comparative Examples b9 and b10 using Al₂(SO₄)₃ as the supply source of Al ions, the amounts of Al and Al₂O₃ was significantly small and had "not good" in sulfide stain resistance.

[0144] While the preferred embodiments of the present invention have been described in detail above with reference to the appended drawings, the present invention is not limited to such examples. It is apparent that various changed examples and modified examples could have been conceived by those of ordinary skill in the art to which the present invention pertains without departing from the gist of the technical ideas described in the claims. In addition, it is understood that the changed examples and modified examples also naturally belong to the technical scope of the present invention.

[Industrial Applicability]

[0145] According to the above-described embodiment, it is possible to provide a chemical treatment steel sheet and a method for manufacturing a chemical treatment steel sheet which have excellent corrosion resistance and sulfide stain resistance even when an amount of chemical treatment layer adhered is small.

[Brief Description of the Reference Symbols]

[0146]

- 10 Chemical treatment steel sheet
- 103 Steel sheet
- 105 Ni-plated layer
- 105d Fe-Ni-Sn alloy layer
- 105e Island-shaped Sn-plated layer
- 106 Composite plated layer
- 107 Chemical treatment layer

Claims

1. A chemical treatment steel sheet comprising:

a steel sheet;

a plated layer which contains Ni and is formed on at least one surface of the steel sheet;

a chemical treatment layer which is formed on the plated layer and contains a Zr compound in which an amount of Zr contained therein is 1.0 to 150 mg/m², a phosphate compound in which an amount of P contained therein is 1.0 to 100 mg/m², and an Al compound in which an amount of Al contained therein is 0.10 to 30.0 mg/m², wherein the plated layer is :

a Ni-plated layer which contains Ni in which an amount of Ni contained therein is 5.0 to 3000 mg/m²; or
a composite plated layer which contains Ni in which an amount of Ni contained therein is 2.0 to 200 mg/m² and Sn in which an amount of Sn contained therein is 0.10 to 10.0 g/m² and has an island-shaped Sn-plated layer formed on a Fe-Ni-Sn alloy layer.

2. The chemical treatment steel sheet according to claim 1, wherein the chemical treatment layer contains Al₂O₃ in which an amount of Al contained therein is 0.10 to 30.0 mg/m².

3. The chemical treatment steel sheet according to claim 1 or 2, wherein the chemical treatment layer contains:

the Zr compound in which an amount of Zr contained therein 1.0 to 120 mg/m²;
the phosphate compound in which an amount of P contained therein is 2.0 to 70.0 mg/m²; and
the Al compound in which an amount of Al contained therein is 0.20 to 20.0 mg/m².

4. The chemical treatment steel sheet according to any one of claims 1 to 3, wherein the Ni-plated layer contains Ni in which an amount of Ni contained therein is 10.0 to 2000 mg/m².

5. The chemical treatment steel sheet according to any one of claims 1 to 3, wherein the composite plated layer contains:

Ni in which an amount of Ni contained therein is 5.0 to 100 mg/m²; and
Sn in which an amount of Sn contained therein is 0.30 to 7.0 g/m².

6. The chemical treatment steel sheet according to any one of claims 1 to 5, wherein a surface of the chemical treatment layer is not covered with a film or a coating material.

7. A method for manufacturing a chemical treatment steel sheet, the method comprising:

a plating process of forming a Ni-plated layer or a composite plated layer on a surface of a steel sheet,
an electrolytic treatment process of forming a chemical treatment layer on the Ni-plated layer or the composite plated layer by performing an electrolytic treatment under the conditions of a current density of 1.0 to 100 A/dm² and an electrolytic treatment time of 0.20 to 150 seconds using a chemical treatment solution having a temperature of 5 °C or higher and lower than 90°C,

wherein the Ni Plated layer contains Ni in which an amount of Ni contained therein is 5.0 to 3000 mg/m²,
the composite plated layer contains Ni in which an amount of Ni contained therein is 2.0 to 200 mg/m² and Sn in which an amount of Sn contained therein is 0.10 to 10.0 g/m² and has an island-shaped Sn-plated layer is formed on a Fe-Ni-Sn alloy layer, and

the chemical treatment solution contains 10 to 20000 ppm of Zr ions, 10 to 20000 ppm of F ions, 10 to 3000 ppm of phosphate ions, a total amount of 100 to 30000 ppm of nitrate ions and sulfate ions, and 500 to 5000 ppm of Al ions, in which a supply source of the Al ions is (NH₄)₃AlF₆.

8. The method for manufacturing a chemical treatment steel sheet according to claim 7, wherein the chemical treatment solution contains:

200 to 17000 ppm of the Zr ions;
200 to 17000 ppm of the F ions;
100 to 2000 ppm of the phosphate ions;
the total amount of 1000 to 23000 ppm of the nitrate ions and the sulfate ions; and
500 to 3000 ppm of the Al ions.

FIG. 1A

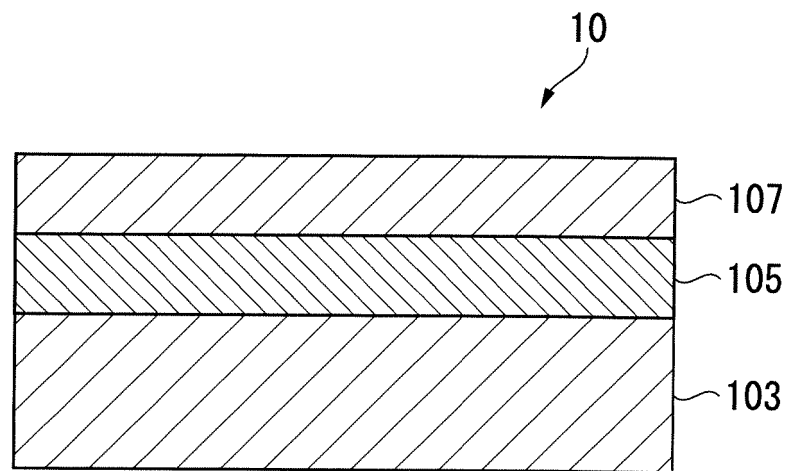


FIG. 1B

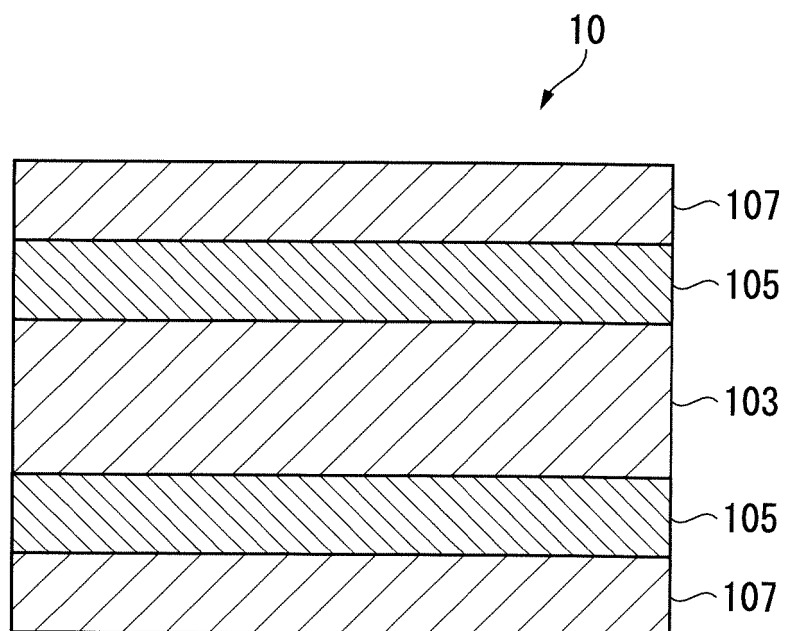


FIG. 2A

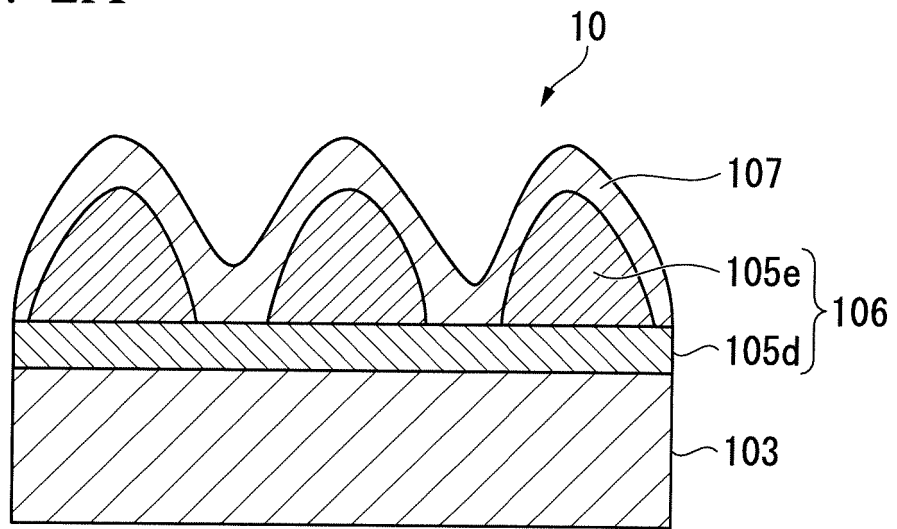


FIG. 2B

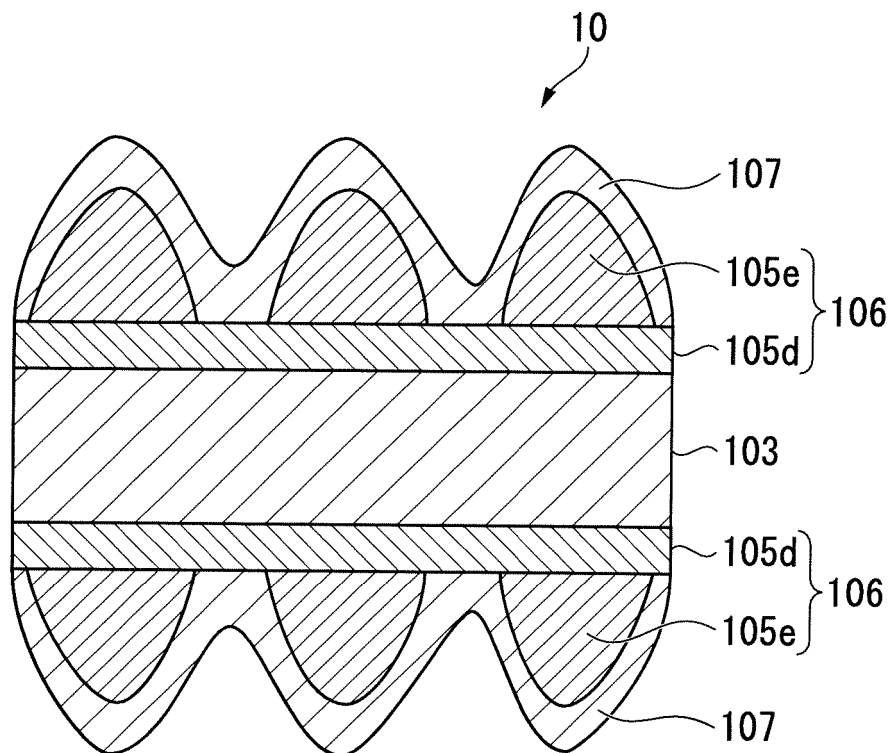


FIG. 3

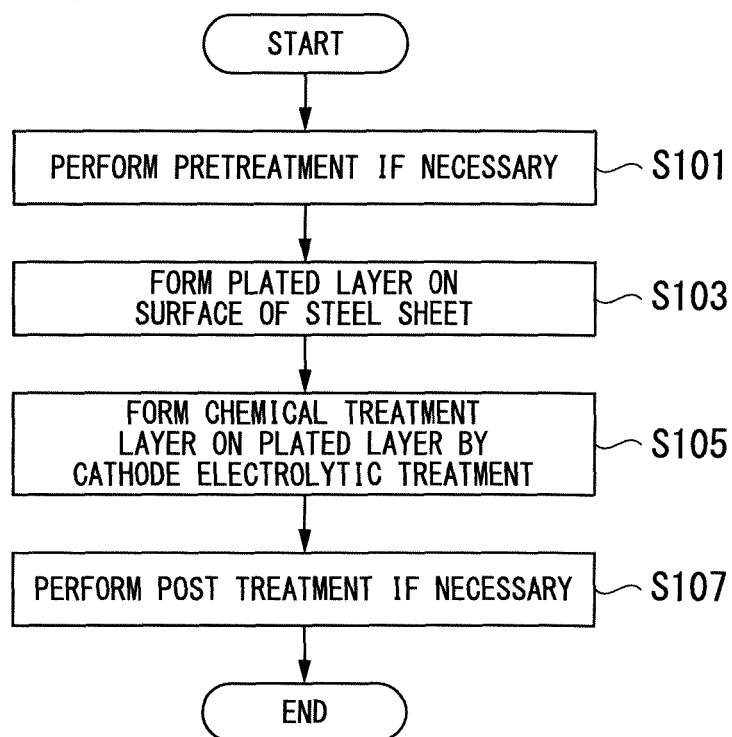
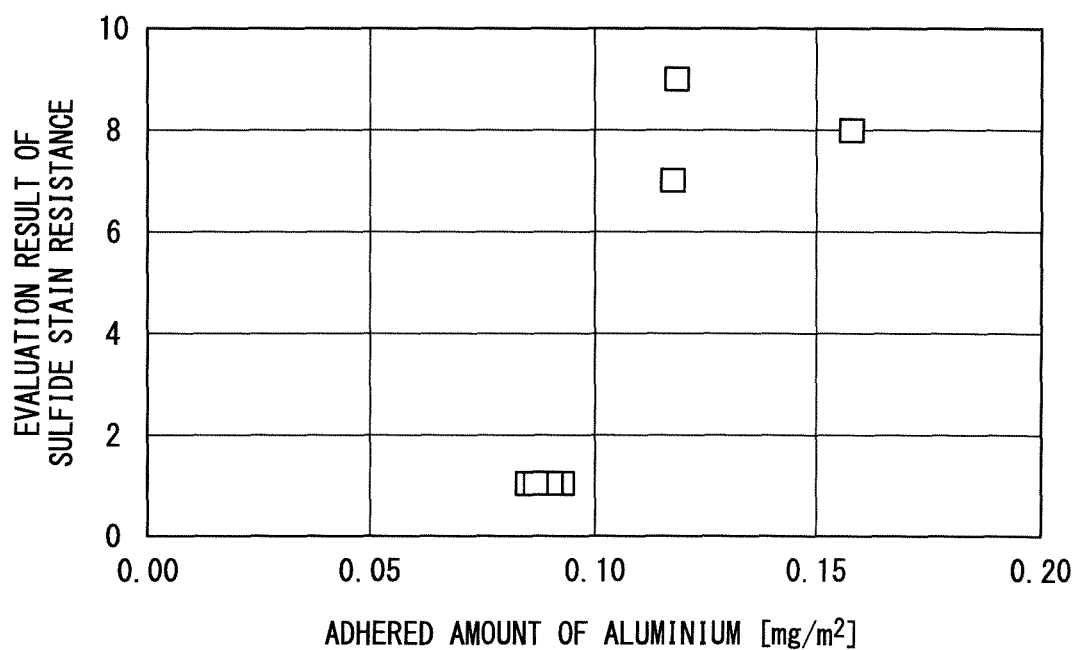


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/058899

A. CLASSIFICATION OF SUBJECT MATTER

C25D9/08(2006.01)i, C23C22/36(2006.01)i, C23C28/00(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D9/08, C23C22/36, C23C28/00

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-062521 A (JFE Steel Corp.), 29 March 2012 (29.03.2012), claims; paragraphs [0018] to [0051] & US 2013/0216714 A1 claims; paragraphs [0019] to [0073] & WO 2012/036201 A1 & TW 201223752 A & CN 103108991 A & CO 6690787 A	1-8
A	WO 2014/189081 A1 (Nippon Steel & Sumitomo Metal Corp.), 27 November 2014 (27.11.2014), claims & EP 3000917 A claims & CN 105283584 A & TW 201504034 A & KR 10-2015-0143828 A	1-8

☒ Further documents are listed in the continuation of Box C.
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Date of the actual completion of the international search
08 June 2016 (08.06.16)Date of mailing of the international search report
21 June 2016 (21.06.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/058899

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-231404 A (Toyo Seikan Kaisha, Ltd.), 17 November 2011 (17.11.2011), claims (Family: none)	1-8

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2012062521 A [0010]