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(54) **STOCK COLD-ROLLED STEEL SHEET WITH FE-BASED COATING FILM, METHOD FOR PRODUCING STOCK COLD-ROLLED STEEL SHEET WITH FE-BASED COATING FILM, METHOD FOR PRODUCING COLD-ROLLED STEEL SHEET WITH FE-BASED COATING FILM, METHOD FOR PRODUCING HOT-DIPPED GALVANIZED STEEL SHEET, AND METHOD FOR PRODUCING ALLOYED HOT-DIPPED GALVANIZED STEEL SHEET**

(57) There is provided a raw material cold-rolled steel sheet with Fe-based coating film excellent in primary rust prevention property or plating appearance. The raw material cold-rolled steel sheet with Fe-based coating film comprises: a base steel sheet having a chemical composition containing C of 0.80 mass% or less, Si of 0.10 mass% or more and 3.00 mass% or less, Mn of 1.50 mass% or more and 3.50 mass% or less, P of 0.100 mass% or less; S of 0.0300 mass% or less, Al of 0.100

mass% or less, with a remaining part consisting of Fe and inevitable impurities; and a P-adhered Fe-based coating film containing an Fe-based coating film disposed on at least one surface of the base steel sheet and a P-containing substance adhered to a surface of the Fe-based coating film, and an adhesion amount of the P-containing substance in terms of P is 0.2 mg/m² or more.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a raw material cold-rolled steel sheet with Fe-based coating film, a method for producing a raw material cold-rolled steel sheet with Fe-based coating film, a method for producing a cold-rolled steel sheet with Fe-based coating film, a method for producing a hot-dip galvanized steel sheet, and a method for producing an alloyed hot-dip galvanized steel sheet.

10 BACKGROUND ART

[0002] In recent years, from the viewpoint of global environmental conservation, improvement in the fuel efficiency of automobiles has become important.

15 **[0003]** For this reason, there is a growing trend to reduce the weight of an automobile body by making a steel sheet as the raw material of an automobile member stronger and thinner.

[0004] However, since an increase in the strength of a steel sheet causes deterioration in formability, it is desirable to develop a steel sheet having both high strength and high formability. From the viewpoint of improving the rust prevention performance of a vehicle body, a hot-dip galvanized steel sheet including a hot-dip galvanized layer on a surface thereof is desired.

20 **[0005]** In order to improve the formability of the steel sheet, for example, it is effective to add a solid solution element such as Si, Mn, or Cr into the steel sheet. A steel sheet used for an automobile component is generally subjected to an annealing treatment after rolling for structure control. This annealing treatment is performed under a reducing atmosphere in which Fe is not oxidized, but the solid solution element such as Si, Mn, or Cr is more easily oxidized than Fe, and thus oxides are formed on the surface of the steel sheet even under such reducing atmosphere. These oxides may deteriorate wettability between the hot-dip galvanizing bath solution and the steel sheet, resulting in plating defects (a portion where a hot-dip galvanizing layer is not formed).

25 **[0006]** In view of such a problem, a technique is known, in which an Fe-based coating film is formed by subjecting the surface of a steel sheet to an Fe-based electroplating treatment before an annealing treatment in a reducing atmosphere to improve wettability with a hot-dip galvanizing bath solution (see Patent Literatures 1 and 2).

30

CITATION LIST

PATENT LITERATURE

35 **[0007]**

Patent Literature 1: JP S57-79160 A

Patent Literature 2: JP 2011-214102 A

40 SUMMARY OF INVENTION

TECHNICAL PROBLEMS

45 **[0008]** However, when the steel sheet after the Fe-based electroplating treatment is left for a certain period of time until the annealing treatment in the next step for the reason of transportation or the like, rust may occur on the surface of the Fe-based coating film. In this case, the primary rust prevention property of the steel sheet is insufficient.

[0009] The rust occurring on the surface of the Fe-based coating film may cause plating defects.

50 **[0010]** That is, when the steel sheet in which the rust occurred on the surface of the Fe-based coating film is subjected to the annealing treatment, and then subjected to a hot-dip galvanizing treatment (alternatively, a hot-dip galvanizing treatment and an alloying treatment), a portion where a hot-dip galvanizing layer (alternatively, an alloyed hot-dip galvanizing layer) is not formed, that is, plating defects may occur. In this case, the plating appearance (the appearance of the hot-dip galvanizing layer or alloyed hot-dip galvanizing layer formed after the annealing treatment) is not good.

[0011] The present invention has been made in view of the above points, and an object of the present invention is to provide a raw material cold-rolled steel sheet with Fe-based coating film excellent in primary rust prevention property or plating appearance.

55 **[0012]** Another object of the present invention is to provide a method for producing the raw material cold-rolled steel sheet with Fe-based coating film, a method for producing a cold-rolled steel sheet with Fe-based coating film using the raw material cold-rolled steel sheet with Fe-based coating film, a method for producing a hot-dip galvanized steel sheet,

and a method for producing an alloyed hot-dip galvanized steel sheet.

SOLUTION TO PROBLEMS

5 **[0013]** The present inventors have found that the above objects are achieved by adopting the following configuration, and have completed the present invention.

[0014] That is, the present invention provides [1] to [11] below.

10 [1] A raw material cold-rolled steel sheet with Fe-based coating film comprising: a base steel sheet having a chemical composition containing, C in an amount of 0.80 mass% or less, Si in an amount of 0.10 mass% or more and 3.00 mass% or less, Mn in an amount of 1.50 mass% or more and 3.50 mass% or less, P in an amount of 0.100 mass% or less; S in an amount of 0.0300 mass% or less, Al in an amount of 0.100 mass% or less, with a remaining part consisting of Fe and inevitable impurities; and a P-adhered Fe-based coating film comprising an Fe-based coating film disposed on at least one surface of the base steel sheet and a P-containing substance adhered to a surface of the Fe-based coating film, wherein an adhesion amount of the P-containing substance in terms of P is 0.2 mg/m² or more.

[2] The raw material cold-rolled steel sheet with Fe-based coating film according to [1], wherein a coating amount of the Fe-based coating film per one surface of the base steel sheet is 1.0 g/m² or more.

20 [3] The raw material cold-rolled steel sheet with Fe-based coating film according to [1] or [2], wherein the chemical composition further contains at least one element selected from the group consisting of: N in an amount of 0.0100 mass% or less, B in an amount of 0.0050 mass% or less, Ti in an amount of 0.200 mass% or less, Cr in an amount of 1.000 mass% or less, Mo in an amount of 1.000 mass% or less, Cu in an amount of 1.000 mass% or less, Ni in an amount of 1.000 mass% or less, Nb in an amount of 0.200 mass% or less, V in an amount of 0.500 mass% or less, Sb in an amount of 0.200 mass% or less, Ta in an amount of 0.100 mass% or less, W in an amount of 0.500 mass% or less, Zr in an amount of 0.1000 mass% or less, Sn in an amount of 0.200 mass% or less, Ca in an amount of 0.0050 mass% or less, Mg in an amount of 0.0050 mass% or less, and REM in an amount of 0.0050 mass% or less.

25 [4] The raw material cold-rolled steel sheet with Fe-based coating film according to [1] or [2], wherein the Fe-based coating film has a chemical composition containing at least one element selected from the group consisting of B, C, P, N, O, Ni, Mn, Mo, Zn, W, Pb, Sn, Cr, V, and Co in a total amount of 10 mass% or less, with a remaining part consisting of Fe and inevitable impurities.

30 [5] A method for producing a raw material cold-rolled steel sheet with Fe-based coating film, the method comprising: subjecting a base steel sheet having a chemical composition containing C in an amount of 0.80 mass% or less, Si in an amount of 0.10 mass% or more and 3.00 mass% or less, Mn in an amount of 1.50 mass% or more and 3.50 mass% or less, P in an amount of 0.100 mass% or less, S in an amount of 0.0300 mass% or less, Al in an amount of 0.100 mass% or less, with a remaining part consisting of Fe and inevitable impurities to an Fe-based electroplating treatment to form an Fe-based coating film on at least one surface of the base steel sheet; and bringing a surface of the Fe-based coating film into contact with an alkaline aqueous solution for 0.5 seconds or more followed by rinsing the surface of the Fe-based coating film with water and drying, wherein the alkaline aqueous solution contains P-containing ions, and a content of the P-containing ions in the alkaline aqueous solution is 0.01 g/L or more in terms of P.

[6] The method for producing a raw material cold-rolled steel sheet with Fe-based coating film according to [5], wherein the alkaline aqueous solution contains at least one phosphorus compound selected from the group consisting of a phosphate, a pyrophosphate, and a triphosphate.

45 [7] The method for producing a raw material cold-rolled steel sheet with Fe-based coating film according to [5] or [6], wherein pH of the alkaline aqueous solution is 8 or more.

[8] The method for producing a raw material cold-rolled steel sheet with Fe-based coating film according to [5] or [6], wherein the chemical composition further contains at least one element selected from the group consisting of: N in an amount of 0.0100 mass% or less, B in an amount of 0.0050 mass% or less, Ti in an amount of 0.200 mass% or less, Cr in an amount of 1.000 mass% or less, Mo in an amount of 1.000 mass% or less, Cu in an amount of 1.000 mass% or less, Ni in an amount of 1.000 mass% or less, Nb in an amount of 0.200 mass% or less, V in an amount of 0.500 mass% or less, Sb in an amount of 0.200 mass% or less, Ta in an amount of 0.100 mass% or less, W in an amount of 0.500 mass% or less, Zr in an amount of 0.1000 mass% or less, Sn in an amount of 0.200 mass% or less, Ca in an amount of 0.0050 mass% or less, Mg in an amount of 0.0050 mass% or less, and REM in an amount of 0.0050 mass% or less.

55 [9] A method for producing a cold-rolled steel sheet with Fe-based coating film, the method comprising subjecting the raw material cold-rolled steel sheet with Fe-based coating film according to [1] or [2] to an annealing treatment to obtain the cold-rolled steel sheet with Fe-based coating film.

[10] A method for producing a hot-dip galvanized steel sheet, the method comprising subjecting the cold-rolled steel

sheet with Fe-based coating film obtained by the method according to [9] to a hot-dip galvanizing treatment to obtain the hot-dip galvanized steel sheet.

[11] A method for producing an alloyed hot-dip galvanized steel sheet, the method comprising subjecting the hot-dip galvanized steel sheet obtained by the method according to

[10] to an alloying treatment to obtain the alloyed hot-dip galvanized steel sheet.

ADVANTAGEOUS EFFECTS OF INVENTION

[0015] According to the present invention, it is possible to provide a raw material cold-rolled steel sheet with Fe-based coating film excellent in primary rust prevention property or plating appearance.

DESCRIPTION OF EMBODIMENTS

[0016] In the present description, a numerical range represented using "to" means a range including numerical values described before and after "to" as a lower limit value and an upper limit value.

[Findings Obtained by The Present Inventions]

[0017] The present inventors have intensively studied the cause of insufficient primary rust prevention property after an Fe-based electroplating treatment, and have obtained the following findings.

[0018] The Fe-based electroplating treatment is generally performed using a sulfuric acid bath as a plating bath from the viewpoint of cost and productivity. After a steel sheet is subjected to an Fe-based electroplating treatment to form an Fe-based coating film, the steel sheet with Fe-based coating film is subjected to rinsing with water and subsequent roll drawing. Thus, a plating bath solution on the steel sheet with Fe-based coating film is cleaned and removed. Thereafter, the steel sheet with Fe-based coating film is dried, and then subjected to an annealing treatment and a hot-dip galvanizing treatment.

[0019] At this time, in rinsing with water and roll drawing, the plating bath solution on the steel sheet with Fe-based coating film cannot be sufficiently removed, and therefore a sulfated compound may remain on the surface of the steel sheet with Fe-based coating film.

[0020] This is considered to cause deterioration in the primary rust prevention property of the steel sheet with Fe-based coating film after the Fe-based electroplating treatment.

[0021] Since a high-strength steel sheet is hard, the shape of a coil edge after cold rolling may be poor. When such high-strength steel sheet is passed through rolls for an Fe-based electroplating treatment, rinsing with water, and roll drawing, both ends of the high-strength steel sheet in a width direction tend to have a wavy shape.

[0022] Therefore, when the steel sheet (base steel sheet) on which the Fe-based coating film is formed is the high-strength steel sheet, the removal of the plating bath solution becomes more insufficient, and therefore there is a high possibility that the primary rust prevention property is further deteriorated.

[0023] Therefore, the present inventors have intensively studied. As a result, by immersing the steel sheet with Fe-based coating film after the Fe-based electroplating treatment in an alkaline aqueous solution containing P-containing ions (PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, $\text{P}_3\text{O}_9^{5-}$, etc.), the primary rust prevention property was improved.

[0024] Although the reason for this is not clear, the primary rust prevention property is presumed to be improved by the substitution reaction of the sulfated compound remaining on the surface of the Fe-based coating film with the P-containing ions.

[Raw Material Cold-Rolled Steel Sheet with Fe-Based Coating Film]

[0025] The raw material cold-rolled steel sheet with Fe-based coating film of the present embodiment includes a base steel sheet having a chemical composition containing, C in an amount of 0.80 mass% or less, Si in an amount of 0.10 mass% or more and 3.00 mass% or less, Mn in an amount of 1.50 mass% or more and 3.50 mass% or less, P in an amount of 0.100 mass% or less, S in an amount of 0.0300 mass% or less, Al in an amount of 0.100 mass% or less, with a remaining part consisting of Fe and inevitable impurities, and a P-adhered Fe-based coating film including an Fe-based coating film disposed on at least one surface of the base steel sheet and a P-containing substance adhered to a surface of the Fe-based coating film, wherein an adhesion amount of the P-containing substance in terms of P is 0.2 mg/m² or more.

<Base Steel Sheet>

[0026] The base steel sheet is a cold-rolled steel sheet (raw material cold-rolled steel sheet) before being subjected

to an annealing treatment described later.

[0027] The sheet thickness of the base steel sheet is not particularly limited, and is, for example, 0.5 to 3.0 mm, and preferably 1.0 to 2.5 mm.

5 <<Chemical Composition>>

[0028] The chemical composition of the base steel sheet will be described.

[0029] The unit of the content of each element in the chemical composition of the base steel sheet is "mass%", and the unit "mass%" is simply expressed as "%" unless otherwise specified.

10

(C: 0.80% or less)

[0030] C causes the formation of martensite or the like as a steel structure, and thus improves the workability of the base steel sheet.

15 **[0031]** When C is added, in order to obtain good weldability, the amount of C is 0.80% or less, and preferably 0.30% or less.

[0032] The lower limit of the amount of C is not particularly limited, but in order to obtain good workability of the base steel sheet, the amount of C is preferably 0.03% or more, and more preferably 0.05% or more.

20 (Si: 0.10% or more and 3.00% or less)

[0033] Si improves the work hardening ability of ferrite, and is therefore effective for ensuring good ductility of the base steel sheet. In order to obtain such an effect, the amount of Si is 0.10% or more, and preferably 0.40% or more.

25 **[0034]** However, the excessive amount of Si causes not only embrittlement of steel but also deterioration in surface properties due to the occurrence of a belt-like scale pattern called red scale, and the like. When the amount of Si is excessive, good adhesion of the Fe-based coating film cannot be secured. Therefore, the amount of Si is 3.00% or less, and preferably 2.50% or less.

(Mn: 1.50% or more and 3.50% or less)

30

[0035] Mn subjects steel to solid-solution strengthening to increase the strength of the steel. Furthermore, Mn enhances the hardenability of the steel and promotes the formation of retained austenite, bainite and martensite. In order to obtain such an effect, the amount of Mn is 1.50% or more, and preferably 1.80% or more.

35 **[0036]** Meanwhile, when Mn is excessively added, the plating appearance becomes insufficient, and there is also a concern about an increase in cost. Therefore, the amount of Mn is 3.50% or less, and preferably 3.30% or less.

(P: 0.100% or less)

40 **[0037]** By suppressing the amount of P, deterioration in the weldability of the steel can be prevented. Furthermore, the segregation of P to grain boundaries can be prevented to prevent deterioration in the ductility, bendability, and toughness of the steel. The excessive amount of P promotes ferrite transformation, and therefore the crystal grain size increases. Therefore, the amount of P is 0.100% or less, and preferably 0.050% or less.

[0038] The lower limit of the amount of P is not particularly limited, but the amount of P is, for example, more than 0% under restrictions on production technique, and may be 0.001% or more.

45

(S: 0.0300% or less)

[0039] By suppressing the amount of S, deterioration in the weldability of the steel can be prevented. Furthermore, a decrease in hot ductility can be prevented to suppress hot cracking, and the surface properties can be significantly improved. When the amount of S is excessive, the ductility, bendability, and stretch flangeability and the like of the steel sheet may be deteriorated due to the formation of coarse sulfide as an impurity element. Therefore, it is preferable to reduce the amount of S as much as possible. Specifically, the amount of S is 0.0300% or less, and preferably 0.0200% or less.

50 **[0040]** The lower limit of the amount of S is not particularly limited, but the amount of S is, for example, more than 0% under restrictions on production technique, and may be 0.0001% or more.

55

(Al: 0.100% or less)

[0041] Since Al is most likely to be thermodynamically oxidized, Al is oxidized prior to Si and Mn, so that the oxidation of Si and Mn in the outermost layer of the steel sheet is suppressed, and the oxidation of Si and Mn inside the steel sheet is promoted.

[0042] However, the excessive amount of Al causes an increase in cost. Therefore, when Al is added, the amount of Al is 0.100% or less, and preferably 0.060% or less.

[0043] The lower limit of the amount of Al is not particularly limited, but the amount of Al is, for example, more than 0%, and may be 0.001% or more. From the viewpoint of obtaining the effect of adding Al, the amount of Al is preferably 0.010% or more, and more preferably 0.020% or more.

(Other Elements)

[0044] The chemical composition of the base steel sheet may further contain at least one element selected from the group consisting of elements described below in terms of mass%.

((N: 0.0100% or less))

[0045] When the amount of N is excessive, N forms coarse nitride with Ti, Nb, and V at a high temperature, so that the effect of increasing the strength of the steel sheet due to the addition of Ti, Nb, and V may be impaired, the toughness of the steel sheet may be reduced, or slab cracking or surface defects or the like may occur during hot rolling. Therefore, the amount of N is preferably 0.0100% or less, more preferably 0.0050% or less, still more preferably 0.0030% or less, and particularly preferably 0.0020% or less.

[0046] The lower limit of the amount of N is not particularly limited, but the amount of N is, for example, more than 0% under restrictions on production technique, and may be 0.0005% or more.

((B: 0.0050% or less))

[0047] From the viewpoint of suppressing the oxidation of Si in the outermost layer of the steel sheet to obtain good adhesion of the Fe-based coating film, the amount of B is preferably 0.0050% or less, and more preferably 0.0030% or less.

[0048] Meanwhile, B is an element effective for improving the hardenability of the steel. From the viewpoint of improving the hardenability, the amount of B is preferably 0.0003% or more, and more preferably 0.0005% or more.

((Ti: 0.200% or less))

[0049] When Ti is added, the amount of Ti is preferably 0.200% or less, and more preferably 0.050% or less. With this addition, good adhesion of the Fe-based coating film is obtained.

[0050] The lower limit of the amount of Ti is not particularly limited, but from the viewpoint of obtaining the effect of the strength adjustment of the steel, the amount of Ti is preferably 0.005% or more, and more preferably 0.010% or more.

((Cr: 1.000% or less))

[0051] The addition of Cr can improve the hardenability of the steel sheet to improve the balance between the strength and ductility of the steel sheet.

[0052] However, when Cr is added, the amount of Cr is preferably 1.000% or less, and more preferably 0.700% or less, from the viewpoint of preventing an increase in cost.

[0053] Meanwhile, from the viewpoint of obtaining the effect of adding Cr, the amount of Cr is preferably 0.005% or more, more preferably 0.050% or more, and still more preferably 0.200% or more.

((Mo: 1.000% or less))

[0054] The strength of the steel sheet can be adjusted by adding Mo. The adhesion of the Fe-based coating film can be improved at the time of combined addition with Nb, Ni, and Cu.

[0055] Meanwhile, when Mo is added, the amount of Mo is preferably 1.000% or less, and more preferably 0.700% or less, from the viewpoint of preventing an increase in cost.

[0056] Meanwhile, from the viewpoint of obtaining the effect of adding Mo, the amount of Mo is preferably 0.005% or more, more preferably 0.010% or more, and still more preferably 0.050% or more.

((Cu: 1.000% or less))

[0057] By adding Cu, the formation of a residual γ phase in the steel sheet can be promoted, and the adhesion of the Fe-based coating film can be improved when Cu is added in combination with Ni and Mo.

[0058] However, when Cu is added, the amount of Cu is preferably 1.000% or less, and more preferably 0.700% or less, from the viewpoint of preventing an increase in cost.

[0059] Meanwhile, from the viewpoint of obtaining the effect of adding Cu, the amount of Cu is preferably 0.005% or more, more preferably 0.010% or more, and still more preferably 0.030% or more.

((Ni: 1.000% or less))

[0060] By adding Ni, the formation of a residual γ phase in the steel sheet can be promoted, and the adhesion of the Fe-based coating film can be improved when Ni is added in combination with Cu and Mo.

[0061] However, when Ni is added, the amount of Ni is preferably 1.000% or less, and more preferably 0.700% or less, from the viewpoint of preventing an increase in cost.

[0062] Meanwhile, from the viewpoint of obtaining the effect of adding Ni, the amount of Ni is preferably 0.005% or more, more preferably 0.010% or more, and still more preferably 0.030% or more.

((Nb: 0.200% or less))

[0063] By adding Nb, the effect of improving the strength of the steel sheet can be obtained.

[0064] However, when Nb is added, the amount of Nb is preferably 0.200% or less, and more preferably 0.150% or less, from the viewpoint of preventing an increase in cost.

[0065] Meanwhile, from the viewpoint of obtaining the effect of adding Nb, the amount of Nb is preferably 0.005% or more, and more preferably 0.010% or more.

((V: 0.500% or less))

[0066] By adding V, the effect of improving the strength of the steel sheet can be obtained.

[0067] However, when V is contained, the amount of V is preferably 0.500% or less, and more preferably 0.300% or less, from the viewpoint of preventing an increase in cost.

[0068] Meanwhile, from the viewpoint of obtaining the effect of adding V, the amount of V is preferably 0.005% or more, and more preferably 0.010% or more.

((Sb: 0.200% or less))

[0069] In order to obtain good toughness, the amount of Sb is preferably 0.200% or less, and more preferably 0.100% or less.

[0070] Meanwhile, by adding Sb, the nitridization and oxidation of the surface of the steel sheet can be suppressed, and decarburization in a region of several tens of microns of the surface of the steel sheet caused by oxidation can be suppressed. Sb suppresses the nitridization and oxidation of the surface of the steel sheet, thereby preventing a decrease in the amount of martensite generated on the surface of the steel sheet and improving the fatigue characteristics and surface quality of the steel sheet. In order to obtain such an effect, the amount of Sb is preferably 0.001% or more, and more preferably 0.010% or more.

((Ta: 0.100% or less))

[0071] By adding Ta, the effect of improving the strength of the steel sheet can be obtained.

[0072] However, when Ta is added, the amount of Ta is preferably 0.100% or less, and more preferably 0.050% or less, from the viewpoint of preventing an increase in cost.

[0073] Meanwhile, from the viewpoint of obtaining the effect of adding Ta, the amount of Ta is preferably 0.001% or more, and more preferably 0.010% or more.

((W: 0.500% or less))

[0074] By adding W, the effect of improving the strength of the steel sheet can be obtained.

[0075] However, when W is added, the amount of W is preferably 0.500% or less, and more preferably 0.300% or less, from the viewpoint of preventing an increase in cost.

[0076] Meanwhile, from the viewpoint of obtaining the effect of adding W, the amount of W is preferably 0.005% or more, and more preferably 0.010% or more.

((Zr: 0.1000% or less))

[0077] By adding Zr, the effect of improving the strength of the steel sheet can be obtained.

[0078] However, when Zr is added, the amount of Zr is preferably 0.1000% or less, and more preferably 0.0500% or less, from the viewpoint of preventing an increase in cost.

[0079] Meanwhile, from the viewpoint of obtaining the effect of adding Zr, the amount of Zr is preferably 0.0005% or more, more preferably 0.0010% or more, and still more preferably 0.0050% or more.

((Sn: 0.200% or less))

[0080] In order to obtain good impact resistance, the amount of Sn is preferably 0.200% or less, and more preferably 0.100% or less.

[0081] Meanwhile, Sn is an element effective in suppressing denitrification and deboronization and the like to suppress a decrease in the strength of the steel. In order to obtain such an effect, the amount of Sn is preferably 0.002% or more, and more preferably 0.010% or more.

((Ca: 0.0050% or less))

[0082] From the viewpoint of improving the ductility of the steel sheet, the amount of Ca is preferably 0.0050% or less, and more preferably 0.0030% or less.

[0083] Meanwhile, the amount of Ca is preferably 0.0005% or more, and more preferably 0.0010% or more, for the reason that the morphology of sulfide can be controlled to improve the ductility and toughness of the steel sheet.

((Mg: 0.0050% or less))

[0084] By adding Mg, the morphology of sulfide can be controlled to improve the ductility and toughness of the steel sheet.

[0085] However, when Mg is added, the amount of Mg is preferably 0.0050% or less, and more preferably 0.0030% or less, from the viewpoint of preventing an increase in cost.

[0086] Meanwhile, from the viewpoint of obtaining the effect of adding Mg, the amount of Mg is preferably 0.0005% or more, and more preferably 0.0010% or more.

((REM: 0.0050% or less))

[0087] When a rare earth metal (REM) is added, the amount of REM is preferably 0.0050% or less, and more preferably 0.0030% or less, from the viewpoint of obtaining good toughness of the steel sheet.

[0088] Meanwhile, the amount of REM is preferably 0.0005% or more, and more preferably 0.0010% or more, for the reason that the morphology of sulfide can be controlled to improve the ductility and toughness of the steel sheet.

(Remaining Part)

[0089] The remaining part other than the above-described components (elements) in the chemical composition of the base steel sheet consists of Fe and inevitable impurities.

<P-Adhered Fe-Based Coating Film>

[0090] Next, the P-adhered Fe-based coating film will be described.

[0091] The P-adhered Fe-based coating film includes an Fe-based coating film disposed on at least one surface of the above-described base steel sheet and a P-containing substance adhered to the surface of the Fe-based coating film.

<<Fe-Based Coating Film>>

[0092] The Fe-based coating film is preferably disposed not only on one surface of the base steel sheet but also on both front and back surfaces of the base steel sheet.

[0093] Examples of the Fe-based coating film include a pure Fe plating layer; and an alloy plating layer made of an

Fe-B alloy, an Fe-C alloy, an Fe-P alloy, an Fe-N alloy, an Fe-O alloy, an Fe-Ni alloy, an Fe-Mn alloy, an Fe-Mo alloy, or an Fe-W alloy or the like.

[0094] The chemical composition of the Fe-based coating film is not particularly limited, but the Fe-based coating film preferably has a chemical composition containing at least one element selected from the group consisting of B, C, P, N, O, Ni, Mn, Mo, Zn, W, Pb, Sn, Cr, V, and Co in a total amount of 10 mass% or less, with a remaining part consisting of Fe and inevitable impurities. The Fe-based coating film having such a chemical composition can be formed at low cost while a decrease in electrolysis efficiency is prevented.

(Coating Amount)

[0095] Next, the coating amount of the Fe-based coating film per one surface of the base steel sheet (hereinafter, also simply referred to as "coating amount of Fe-based coating film") will be described.

[0096] When the coating amount of the Fe-based coating film is too small, Si and Mn may be diffused in the surface of the Fe-based coating film in the annealing treatment described later, resulting in insufficient plating appearance. Therefore, the coating amount of the Fe-based coating film is preferably 1.0 g/m² or more, more preferably 3.0 g/m² or more, and still more preferably 5.0 g/m² or more, for the reason that the plating appearance is more excellent.

[0097] Meanwhile, from the viewpoint of suppressing an increase in cost, the coating amount of the Fe-based coating film is preferably 60.0 g/m² or less, more preferably 50.0 g/m² or less, still more preferably 40.0 g/m² or less, and particularly preferably 30.0 g/m² or less.

[0098] The coating amount of the Fe-based coating film is measured as follows.

[0099] A sample having a size of 10 × 15 mm is collected from the raw material cold-rolled steel sheet with Fe-based coating film and embedded in a resin to obtain an embedded sample having an exposed cross section. Three optional points in this cross section are observed using a scanning electron microscope (SEM) under the conditions of an acceleration voltage of 15 kV and a magnification of 2000 to 10000 times depending on the thickness of the Fe-based coating film. The average value of the thicknesses of the three fields of view is multiplied by the specific gravity of iron to be converted into the coating amount of the Fe-based coating film.

<<P-Containing Substance>>

[0100] Suitable examples of the P-containing substance contained in the P-adhered Fe-based coating film (the P-containing substance adhered to the surface of the Fe-based coating film) include at least one selected from the group consisting of PO₄³⁻, P₂O₇⁴⁻, and P₃O₉⁵⁻, inorganic acids thereof (inorganic acid salts of PO₄³⁻, P₂O₇⁴⁻, and P₃O₉⁵⁻), and metal compounds thereof (metal compounds of PO₄³⁻, P₂O₇⁴⁻, and P₃O₉⁵⁻).

[0101] Here, suitable examples of the metal compound include a metal compound containing at least one selected from the group consisting of PO₄³⁻, P₂O₇⁴⁻, and P₃O₉⁵⁻ and at least one selected from the group consisting of hydrogen, sodium, and iron.

[0102] As described later, the P-containing substance can be adhered to the surface of the Fe-based coating film by bringing the surface of the Fe-based coating film into contact with an alkaline aqueous solution containing P-containing ions (PO₄³⁻, P₂O₇⁴⁻, and P₃O₉⁵⁻ and the like).

(Adhesion Amount of P)

[0103] Next, the adhesion amount of the P-containing substance in terms of P (also simply referred to as "adhesion amount of P") will be described.

[0104] The adhesion amount of P is 0.2 mg/m² or more. This provides excellent primary rust prevention property and plating appearance. The adhesion amount of P is preferably 0.4 mg/m² or more, more preferably 0.6 mg/m² or more, and still more preferably 0.8 mg/m² or more, for the reason that the primary rust prevention property and the plating appearance are more excellent.

[0105] Meanwhile, the upper limit of the adhesion amount of P is not particularly limited, but when the adhesion amount of P is excessive, there are concerns about a decrease in spot weldability and an increase in cost, and the like. Therefore, the adhesion amount of P is preferably 30.0 mg/m² or less, more preferably 20.0 mg/m² or less, and still more preferably 10.0 mg/m² or less.

[0106] The adhesion amount of P is measured by fluorescent X-ray analysis under the following conditions. P intensity obtained from the fluorescent X-ray analysis is converted into the adhesion amount of P based on the value of the cold-rolled steel sheet including a P-containing oxide layer in which the adhesion amount of P is known.

Tube voltage: 45 kV

Tube current: 45 mA

Tube type: Rh
Measurement diameter: 25 mm
Measurement line: P-K α ray
Integration time: 20 seconds

[Method for Producing Raw Material Cold-Rolled Steel Sheet with Fe-Based Coating Film]

[0107] Next, a method for producing the above-described raw material cold-rolled steel sheet with Fe-based coating film will be described.

[0108] In the present method, generally, the base steel sheet having the chemical composition described above is subjected to an Fe-based electroplating treatment to form an Fe-based coating film on at least one surface of the base steel sheet, and the surface of the Fe-based coating film is then brought into contact with an alkaline aqueous solution described later.

<Production of Base Steel Sheet>

[0109] The base steel sheet can be produced by a known method. For example, a slab having the above-described chemical composition is subjected to hot rolling to obtain a hot-rolled steel sheet. Then, the obtained hot-rolled steel sheet is optionally subjected to pickling, and then subjected to cold rolling to obtain the base steel sheet. The slab may be heated prior to hot rolling.

[0110] The base steel sheet thus produced is optionally subjected to degreasing and pickling. Thus, an oxide coating film on the surface of the base steel sheet is removed.

[0111] The degreasing is not particularly limited, and examples thereof include electrolytic degreasing in an alkaline solution.

[0112] The pickling method is also not particularly limited. Examples of acids used for pickling include sulfuric acid, hydrochloric acid, nitric acid, and a mixture thereof, and among them, sulfuric acid, hydrochloric acid, or a mixture thereof is preferable. The concentration of the acid is not particularly limited, but is preferably about 1 to 20 mass% in consideration of the ability to remove the oxide coating film, and prevention of skin roughness (surface defect) due to excessive pickling, and the like. An antifoaming agent, a pickling accelerator, or a pickling inhibitor or the like may be added to the acid used for pickling.

<Fe-Based Electroplating Treatment>

[0113] Then, the base steel sheet optionally subjected to degreasing and pickling is subjected to an Fe-based electroplating treatment to form an Fe-based coating film.

[0114] The method of the Fe-based electroplating treatment is not particularly limited.

[0115] Examples of a plating bath (Fe-based electroplating bath) used for the Fe-based electroplating treatment include a sulfuric acid bath, a hydrochloric acid bath, and a mixture of both, and specific examples thereof include an iron sulfate plating bath.

[0116] The Fe-based electroplating bath contains, for example, Fe ions and alloying elements such as B, C, P, N, O, Ni, Mn, Mo, Zn, W, Pb, Sn, Cr, V, and Co. Among the alloying elements, a metal element can be contained as a metal ion, and a nonmetal element can be contained as a part of boric acid, phosphoric acid, nitric acid, or organic acid or the like.

[0117] The Fe-based electroplating bath may further contain a conductivity auxiliary agent such as sodium sulfate or potassium sulfate; a chelating agent; and a pH buffering agent and the like.

[0118] The other conditions are not particularly limited, but the bath temperature of the Fe-based electroplating bath is preferably 30°C or higher in consideration of constant temperature retention property.

[0119] The pH of the Fe-based electroplating bath is preferably 3.0 or less in consideration of the electrical conductivity of the Fe-based electroplating bath.

[0120] The current density of the Fe-based electroplating treatment is normally 10 to 150 A/dm².

[0121] The sheet passing speed in the Fe-based electroplating treatment is preferably 5 mpm or more because of excellent productivity. Meanwhile, from the viewpoint of stably controlling the coating amount of the Fe-based coating film, the sheet passing speed is preferably 150 mpm or less.

<Contact with Alkaline Aqueous Solution>

[0122] Then, the surface of the Fe-based coating film formed by the Fe-based electroplating treatment is brought into contact with an alkaline aqueous solution, and then rinsed with water and dried.

[0123] The alkaline aqueous solution contains P-containing ions.

[0124] Examples of the P-containing ions include PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, and $\text{P}_3\text{O}_9^{5-}$.

[0125] From the viewpoint of sufficiently adhesion of the above-described P-containing substance to the surface of the Fe-based coating film, the content of the P-containing ions in the alkaline aqueous solution is 0.01 g/L or more, preferably 0.05 g/L or more, more preferably 0.10 g/L or more, and still more preferably 0.50 g/L or more in terms of P.

[0126] Meanwhile, the upper limit of the content is not particularly limited. However, from the viewpoint of preventing an increase in cost, the content of the P-containing ions in the alkaline aqueous solution is preferably 30.00 g/L or less, more preferably 20.00 g/L or less, and still more preferably 10.00 g/L or less in terms of P.

[0127] The alkaline aqueous solution may contain the P-containing ions in the form of a phosphorus compound that supplies the P-containing ions into the alkaline aqueous solution.

[0128] Such a phosphorus compound is not particularly limited as long as the above-described P-containing ions can be supplied into the alkaline aqueous solution, but from the viewpoint of cost and ease of procurement, at least one selected from the group consisting of a phosphate, a pyrophosphate, and a triphosphate is preferable.

[0129] The alkaline aqueous solution is not particularly limited as long as the solution is alkaline, but the pH of the solution is preferably 8 or more, and more preferably 9 or more, for the reason that the primary rust prevention property can be further improved.

[0130] A contact time between the surface of the Fe-based coating film and the alkaline aqueous solution is 0.5 seconds or more, preferably 3.0 seconds or more, and more preferably 5.0 seconds or more, from the viewpoint of sufficient adhesion of the above-described P-containing substance to the surface of the Fe-based coating film.

[0131] Meanwhile, the upper limit of the contact time is not particularly limited, but the contact time between the surface of the Fe-based coating film and the alkaline aqueous solution is preferably 30.0 seconds or less, and more preferably 20.0 seconds or less, from the viewpoint of preventing an increase in production cost due to an increase in a treatment time.

[0132] A method for bringing the surface of the Fe-based coating film into contact with the alkaline aqueous solution is not particularly limited, and examples thereof include a method by immersing the base steel sheet on which the Fe-based coating film is formed in the alkaline aqueous solution.

[0133] Rinsing with water and drying may be performed by normal methods, and conditions thereof are not particularly limited.

[Method for Producing Cold-Rolled Steel Sheet with Fe-Based Coating Film]

[0134] The raw material cold-rolled steel sheet with Fe-based coating film obtained by the above method is subjected to an annealing treatment to obtain a cold-rolled steel sheet with Fe-based coating film.

[0135] The annealing treatment removes the distortion of the base steel sheet generated by rolling and recrystallizes crystals, and therefore predetermined tensile strength can be imparted to the obtained cold-rolled steel sheet with Fe-based coating film.

[0136] The conditions for the annealing treatment may be general conditions, and are not particularly limited, but it is preferable to heat the raw material cold-rolled steel sheet with Fe-based coating film at the following annealing temperature for the following annealing time in the following annealing atmosphere.

<Hydrogen Concentration in Annealing Atmosphere: 1.0 Vol% or More and 30.0 Vol% or Less>

[0137] The annealing atmosphere (the atmosphere when the annealing treatment is performed) is preferably a reducing atmosphere containing hydrogen. Hydrogen in the annealing atmosphere suppresses the oxidation of the surface of the Fe-based coating film, and activates the surface.

[0138] The hydrogen concentration in the annealing atmosphere is preferably 1.0 vol% or more, and more preferably 2.0 vol% or more. With this concentration, the oxidation of the surface of the Fe-based coating film is suitably prevented, to provide more excellent plating appearance.

[0139] The upper limit of the hydrogen concentration in the annealing atmosphere is not particularly limited, but is preferably 30.0 vol% or less, and more preferably 20.0 vol% or less, from the viewpoint of cost.

<Dew Point of Annealing Atmosphere: -80°C or Higher and +30°C or Lower>

[0140] The dew point of the annealing atmosphere is preferably +30°C or lower, and more preferably +10°C or lower, for the reason that the oxidation of the surface of the Fe-based coating film is suitably prevented and the plating appearance is more excellent.

[0141] Meanwhile, since it is industrially difficult to achieve an excessively low dew point, the dew point of the annealing atmosphere is preferably -80°C or higher, and more preferably -50°C or higher.

<Annealing Temperature: 650°C or Higher and 900°C or Lower>

[0142] The annealing temperature is preferably 650°C or higher, and more preferably 700°C or higher. At this temperature, the recrystallization of the structure of the base steel sheet suitably proceeds, and therefore a higher-strength cold-rolled steel sheet with Fe-based coating film can be produced. A natural oxide film on the Fe-based coating film is suitably reduced, and therefore the plating appearance is more excellent.

[0143] The annealing temperature is preferably 900°C or lower, and more preferably 850°C or lower. This makes it possible to suitably prevent an increase in the diffusion rate of Si and Mn, and the diffusion of Si and Mn into the surface of the Fe-based coating film, and therefore the plating appearance is more excellent. Furthermore, it is possible to prevent the diffusion of Si into the Fe-based coating film, to prevent an alloying temperature from increasing, and to prevent the furnace body damage of an annealing furnace.

[0144] The annealing temperature is the highest achieving temperature of the raw material cold-rolled steel sheet with Fe-based coating film during the annealing treatment, and is the temperature measured at the surface of the raw material cold-rolled steel sheet with Fe-based coating film.

<Annealing Time: 30 Seconds or More and 600 Seconds or Less>

[0145] The annealing time is preferably 30 seconds or more, and more preferably 50 seconds or more. With this annealing time, the natural oxide film on the Fe-based coating film is suitably removed, and therefore the plating appearance is more excellent.

[0146] The upper limit of the annealing time is not particularly limited, but when the annealing time is prolonged, the furnace length of the annealing furnace becomes long, and therefore the productivity of the steel sheet decreases. Therefore, from the viewpoint of improving the productivity, the annealing time is preferably 600 seconds or less, and more preferably 300 seconds or less.

[Method for Producing Hot-Dip Galvanized Steel Sheet]

[0147] The cold-rolled steel sheet with Fe-based coating film obtained by the annealing treatment may be subjected to a hot-dip galvanizing treatment to obtain a hot-dip galvanized steel sheet.

[0148] The hot-dip galvanizing treatment is a treatment in which a cold rolled steel sheet with Fe-based coating film is immersed in a hot-dip galvanizing bath to form a hot-dip galvanized layer.

[0149] The bath temperature of the hot-dip galvanizing bath is preferably 440°C or higher, and more preferably 450°C or higher, for the reason that temperature fluctuation in the bath can be reduced to suitably prevent the solidification of Zn.

[0150] Meanwhile, the bath temperature of the hot-dip galvanizing bath is preferably 550°C or lower, and more preferably 520°C or lower, for the reason that the evaporation of the hot-dip galvanizing bath can be suitably prevented to suitably prevent vaporized Zn from being adhered to an interior of the furnace.

[0151] The in-bath Al concentration in the hot-dip galvanizing bath is preferably 0.10 mass% or more, and more preferably 0.15 mass% or more, for the reason that the formation of a Γ phase is prevented and the plating appearance is more excellent.

[0152] Meanwhile, the in-bath Al concentration in the hot-dip galvanizing bath is preferably 0.30 mass% or less, and more preferably 0.25 mass% or less, for the reason that Al in the hot-dip galvanizing bath suitably prevents the formation of an oxide film on the surface of the bath, thereby providing more excellent plating appearance.

[Method for Producing Alloyed High-Strength Hot-Dip Galvanized Steel Sheet]

[0153] The hot-dip galvanized steel sheet obtained by the hot-dip galvanizing treatment may be subjected to an alloying treatment to obtain an alloyed hot-dip galvanized steel sheet.

[0154] The conditions for the alloying treatment are not particularly limited, but the alloying temperature is preferably 460°C or higher, and more preferably 470°C or higher, for the reason that the productivity can be improved by increasing an alloying rate.

[0155] Meanwhile, the alloying temperature is preferably 560°C or lower, and more preferably 530°C or lower, for the reason that the formation of the Γ phase is prevented and the plating appearance is more excellent.

EXAMPLES

[0156] Hereinafter, the present invention will be specifically described with reference to Examples. However, the present invention is not limited to Examples described below.

<Production of Raw Material Cold-Rolled Steel Sheet with Fe-Based Coating Film>

[0157] Steels each having a chemical composition containing elements shown in the following Table 1, with a remaining part consisting of Fe and inevitable impurities were smelted in a converter, and made into slabs by continuous casting. In the following Table 1, "-" indicates a content at an inevitable impurity level. Underlines in the following Table 1 indicate that they are outside the scope of the present invention (the same applies to Tables 2 to 4 described later).

[0158] Each of the obtained slabs was hot-rolled to obtain a hot-rolled steel sheet. Then, the hot-rolled steel sheet was subjected to pickling to remove black scale, and then subjected to cold rolling to obtain a base steel sheet having a sheet thickness of 1.4 mm.

<<Fe-Based Electroplating Treatment>>

[0159] The obtained base steel sheet was subjected to electrolytic degreasing in an alkaline solution and pickling in sulfuric acid, and then subjected to an Fe-based electroplating treatment using an Fe-based electroplating bath (iron sulfate plating bath) under the following conditions. As a result, an Fe-based coating film was formed on each of both surfaces of the base steel sheet. The coating amount (unit: g/m²) of the formed Fe-based coating film is shown in the following Tables 2 to 4. The coating amount of the Fe-based coating film was controlled by adjusting an energization time.

(Conditions of Fe-Based Electroplating Treatment)

[0160]

Bath temperature of Fe-based electroplating bath: 50°C

pH of Fe-based electroplating bath: 2.0

Content of Fe²⁺ ions of Fe-based electroplating bath: 1.5 mol/L

Current density: 45 A/dm²

Electrode (anode): iridium oxide electrode

[0161] In some examples (Inventive Examples and Comparative Examples), a situation where a plating bath solution on the Fe-based coating film could not be sufficiently removed in rinsing with water after the Fe-based electroplating treatment (a situation where a sulfated compound remained on the surface of the Fe-based coating film) was reproduced. Specifically, rinsing was performed using a solution obtained by diluting the Fe-based electroplating bath solution used for the Fe-based electroplating treatment 100 times, followed by drying. In this case, "diluted solution" was described in each of the columns of "rinsing" in the following Tables 2 to 4.

[0162] In the remaining examples, normal cleaning was performed. That is, the base steel sheet was rinsed with water, and then dried. In this case, "normal" was described in each of the columns of "rinsing" in the following Tables 2 to 4.

<<Contact with Alkaline Aqueous Solution>>

[0163] Then, the base steel sheet on which the Fe-based coating film was formed was brought into contact with an alkaline aqueous solution by immersion. The "type" and the "content" of "P-containing ions" in the alkaline aqueous solution used and the "contact time" with the alkaline aqueous solution are shown in the following Table 2. As the "type" of the "P-containing ions", "phosphoric acid" in the case of PO₄³⁻, "pyrophosphoric acid" in the case of P₂O₇⁴⁻, and "triposphoric acid" in the case of P₃O₉⁵⁻ were described. All of the alkaline aqueous solutions used had pH of 8 or more.

[0164] Thereafter, rinsing with water and drying were performed. Thus, a raw material cold-rolled steel sheet with Fe-based coating film was obtained.

[0165] The "adhesion amount of P" of the obtained raw material cold-rolled steel sheet with Fe-based coating film is shown in the following Tables 2 to 4.

[0166] When the contact with the alkaline aqueous solution was not performed, "-" was described in each of the corresponding columns of the following Tables 2 to 4.

<Evaluation>

[0167] The obtained raw material cold-rolled steel sheet with Fe-based coating film was subjected to the following test to evaluate the primary rust prevention property. The evaluation results are shown in the following Tables 2 to 4.

<<Primary Rust Prevention Property>>

[0168] The raw material cold-rolled steel sheet with Fe-based coating film was sheared to a size of 50 mm × 50 mm, and left standing in a room for 10 days with no oil applied. After being left, the proportion of an area where red rust occurred (hereinafter, referred to as "red rust occurrence area ratio") was determined.

[0169] "Excellent" when the red rust occurrence area ratio was less than 5%, "Good" when the red rust occurrence area ratio was 5% or more and less than 20%, "Fair" when the red rust occurrence area ratio was 20% or more and less than 50%, and "Poor" when the red rust occurrence area ratio was 50% or more were described in the following Tables 2 to 4. Practically, "Excellent" or "Good" is preferable.

[0170] In some examples (Inventive Examples and Comparative Examples), an annealing treatment was performed after the above test.

[0171] More specifically, the raw material cold-rolled steel sheet with Fe-based coating film after the test was heated at 800°C for 100 seconds in a reducing atmosphere having a dew point of -35°C and a hydrogen concentration of 15 vol% (remaining part: nitrogen).

[0172] Thus, a cold-rolled steel sheet with Fe-based coating film was obtained.

[0173] After the annealing treatment, in some of the examples, both surfaces of the obtained cold-rolled steel sheet with Fe-based coating film were further subjected to a hot-dip galvanizing treatment to obtain a hot-dip galvanized steel sheet.

[0174] After the annealing treatment, in the remaining examples, both surfaces of the obtained cold-rolled steel sheet with Fe-based coating film were further subjected to a hot-dip galvanizing treatment to obtain a hot-dip galvanized steel sheet, and then subjected to an alloying treatment at an alloying temperature of 480°C to obtain an alloyed hot-dip galvanized steel sheet.

[0175] In the production of the hot-dip galvanized steel sheet, a hot-dip galvanizing bath having a bath temperature of 460°C and an in-bath Al concentration of 0.20 mass% was used. In the production of the alloyed hot-dip galvanized steel sheet, a hot-dip galvanizing bath having a bath temperature of 460°C and an in-bath Al concentration of 0.14 mass% was used.

[0176] The coating amount of a hot-dip galvanizing layer per one surface of the base steel sheet was 45 to 55 g/m².

[0177] In the case where each of the hot-dip galvanizing treatment and the alloying treatment was performed after the annealing treatment, "DONE" was described in each of the corresponding columns in the following Tables 2 to 4, and in the case where the treatment was not performed, "-" was described.

<<Plating Appearance>>

[0178] For the obtained hot-dip galvanized steel sheet (or the alloyed hot-dip galvanized steel sheet), the appearance of the hot-dip galvanized layer (or the alloyed hot-dip galvanized layer) was visually observed. "Excellent" when the appearance had no plating defects, "Good" when the appearance had slight plating defects but was generally good, "Fair" when the appearance had much plating defects, and "Poor" when the appearance had much plating defects were described in the following Tables 2 to 4.

[Table 1]

Table 1

Steel type	C	Si	Mn	P	S	Al	N	B	Ti	Cr	Mo	Cu	Ni	
A	0.13	1.39	1.94	0.010	0.0010	0.033	0.0070	0.0010	0.010	-	-	-	-	Inventive Example
B	0.09	0.61	2.69	0.030	0.0020	0.037	0.0050	0.0010	0.010	-	-	-	-	Inventive Example
C	0.15	0.91	2.16	0.020	0.0020	0.036	0.0040	0.0010	0.010	-	-	-	-	Inventive Example
D	0.18	1.02	3.08	0.020	0.0020	0.038	0.0060	0.0010	0.010	-	-	-	-	Inventive Example
E	0.12	1.20	1.85	0.010	0.0010	0.032	0.0040	0.0010	0.010	-	-	-	-	Inventive Example
F	0.24	1.41	1.33	0.010	0.0010	0.034	0.0030	0.0010	0.010	-	-	-	-	Inventive Example
G	0.11	0.52	2.56	0.010	0.0010	0.033	0.0030	0.0010	0.010	0.590	-	-	-	Inventive Example
H	0.12	1.49	1.52	0.010	0.0010	0.035	0.0030	0.0010	0.010	-	-	-	-	Inventive Example
I	0.17	1.53	2.31	0.010	0.0010	0.037	0.0040	0.0010	0.010	-	0.110	-	-	Inventive Example
J	0.19	1.51	2.72	0.010	0.0010	0.034	0.0040	0.0010	0.010	-	-	0.120	-	Inventive Example
K	0.15	1.65	1.33	0.020	0.0020	0.036	0.0050	0.0010	0.010	-	-	-	0.140	Inventive Example
L	0.17	1.68	2.51	0.030	0.0020	0.036	0.0040	0.0010	0.010	-	-	-	-	Inventive Example
M	0.15	3.52	2.88	0.006	0.0016	0.040	0.0028	-	-	-	-	-	-	Comparative Example
N	0.15	0.64	7.88	0.008	0.0014	0.045	0.0040	-	-	-	-	-	-	Comparative Example

[0179]

Table 2

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
				P-containing ions		Contact time	Adhesion amount of P							
		Coating amount of Fe-based coating film	Rinsing	Type	Content									
						g/m ²								
1	A	5.3	Normal	-	-	-	-	-	Fair	-	-	-	-	Comparative Example
2	A	5.3	Normal	-	-	-	-	-	Fair	DONE	DONE	-	Fair	Comparative Example
3	A	5.3	Normal	-	-	-	-	-	Fair	DONE	DONE	DONE	Fair	Comparative Example
4	A	5.3	Normal	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	-	Inventive Example
5	A	5.3	Normal	Pyrophosphate	1.00	5.0	1.2	Excellent	DONE	DONE	DONE	-	Excellent	Inventive Example
6	A	5.3	Normal	Pyrophosphate	1.00	5.0	1.1	Excellent	DONE	DONE	DONE	DONE	Excellent	Inventive Example
7	A	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	-	Comparative Example
8	A	5.3	Diluted solution	-	-	-	-	Poor	DONE	DONE	DONE	-	Poor	Comparative Example
9	A	5.3	Diluted solution	-	-	-	-	Poor	DONE	DONE	DONE	DONE	Poor	Comparative Example
10	A	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.3	Excellent	-	-	-	-	-	Inventive Example
11	A	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	DONE	DONE	DONE	-	Excellent	Inventive Example

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
				P-containing ions		Contact time	Adhesion amount of P							
		Coating amount of Fe-based coating film	Rinsing	Type	Content		Second	mg/m ²						
					g/m ²			g/L						
12	A	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	DONE	DONE	DONE	Excellent	Inventive Examole	
13	A	5.3	Diluted solution	Pyrophosphate	0.01	5.0	0.5	Good	-	-	-	-	Inventive Examole	
14	A	5.3	Diluted solution	Pyrophosphate	0.10	5.0	0.8	Excellent	-	-	-	-	Inventive Examole	
15	A	5.3	Diluted solution	Pyrophosphate	5.00	5.0	3.5	Excellent	-	-	-	-	Inventive Examole	
16	A	5.3	Diluted solution	Pyrophosphate	10.00	5.0	7.6	Excellent	-	-	-	-	Inventive Example	
17	A	0.2	Normal	-	-	-	-	-	DONE	DONE	DONE	Poor	Comparative Examole	
18	A	0.2	Normal	Pyrophosphate	1.00	5.0	1.4	-	DONE	DONE	DONE	Good	Inventive Examole	
19	A	10.2	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	Inventive Examole	
20	A	10.2	Diluted solution	Pyrophosphate	1.00	5.0	1.2	-	DONE	DONE	DONE	Excellent	Inventive Examole	
21	A	15.8	Diluted solution	Pyrophosphate	1.00	5.0	1.1	Excellent	-	-	-	-	Inventive Example	
22	A	15.8	Diluted solution	Pyrophosphate	1.00	5.0	0.9	-	DONE	DONE	DONE	Excellent	Inventive Examole	

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
				P-containing ions		Contact time	Adhesion amount of P							
		Coating amount of Fe-based coating film	Rinsing solution	Type	Content		mg/m ²							
					g/m ²	g/L		Second						
23	A	29.6	Diluted solution	Pyrophosphate	1.00	5.0	1.3	Excellent	-	-	-	-	Inventive Examole	
24	A	29.6	Diluted solution	Pyrophosphate	1.00	5.0	1.2	-	DONE	DONE	-	Excellent	Inventive Examole	
25	A	5.3	Diluted solution	Phosphate	1.00	5.0	0.9	Excellent	-	-	-	-	Inventive Examole	
26	A	5.3	Diluted solution	Phosphate	1.00	5.0	0.8	-	DONE	DONE	-	Excellent	Inventive Examole	
27	A	5.3	Diluted solution	Phosphate	1.00	5.0	0.8	Excellent	-	-	-	-	Inventive Examole	
28	A	5.3	Diluted solution	Triphosphate	1.00	5.0	1.2	-	DONE	DONE	-	Excellent	Inventive Examole	
29	A	5.3	Diluted solution	Triphosphate	1.00	5.0	1.3	Excellent	-	-	-	-	Inventive Examole	
30	A	5.3	Diluted solution	Triphosphate	1.00	5.0	1.4	-	DONE	DONE	-	Excellent	Inventive Examole	

[Table 3]

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[0180]

Table 3

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution				Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
		Coating amount of Fe-based coating film	Rinsing	P-containing ions		Contact time	Adhesion amount of P						
				Type	Content								
31	B	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Example
32	B	5.3	Normal	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	Inventive Example
33	B	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Example
34	B	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Example
35	B	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.2	Excellent	-	-	-	-	Inventive Example
36	B	5.3	Diluted solution	Pyrophosphate	1.00	5.0	0.9	-	DONE	DONE	-	Excellent	Inventive Example
37	C	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Example
38	C	5.3	Normal	Pyrophosphate	1.00	5.0	1.4	Excellent	-	-	-	-	Inventive Example
39	C	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Example
40	C	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Example
41	C	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	Inventive Example

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks	
		Coating amount of Fe-based coating film	Rinsing	P-containing ions		Contact time	Adhesion amount of P								
				Type	Content		mg/L	Second							mg/m ²
42	C	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	-	DONE	DONE	-	Excellent	Inventive Examole		
43	D	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole		
44	D	5.3	Normal	Pyrophosphate	1.00	5.0	1.1	Excellent	-	-	-	-	Inventive Examole		
45	D	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole		
46	D	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole		
47	D	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.2	Excellent	-	-	-	-	Inventive Examole		
48	D	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.1	-	DONE	DONE	-	Excellent	Inventive Examole		
49	E	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole		
50	E	5.3	Normal	Pyrophosphate	1.00	5.0	1.3	Excellent	-	-	-	-	Inventive Examole		
51	E	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole		
52	E	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole		

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
				P-containing ions		Contact time	Adhesion amount of P							
		Coating amount of Fe-based coating film	Rinsing	Type	Content									
							g/m ²	g/L						
53	E	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.1	Excellent	-	-	-	-	Inventive Examole	
54	E	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.3	-	DONE	DONE	-	Excellent	Inventive Examole	
55	F	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole	
56	F	5.3	Normal	Pyrophosphate	1.00	5.0	1.2	Excellent	-	-	-	-	Inventive Examole	
57	F	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole	
58	F	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole	
59	F	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.2	Excellent	-	-	-	-	Inventive Examole	
60	F	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.1	-	DONE	DONE	-	Excellent	Inventive Examole	

[Table 4]

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[0181]

Table 4

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution				Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
		Coating amount of Fe-based coating film	Rinsing	P-containing ions		Contact time	Adhesion amount of P						
				Type	Content								
61	G	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole
62	G	5.3	Normal	Pyrophosphate	1.00	5.0	0.9	Excellent	-	-	-	-	Inventive Examole
63	G	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole
64	G	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole
65	G	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.1	Excellent	-	-	-	-	Inventive Examole
66	G	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.4	-	DONE	DONE	-	Excellent	Inventive Examole
67	H	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole
68	H	5.3	Normal	Pyrophosphate	1.00	5.0	1.4	Excellent	-	-	-	-	Inventive Example
69	H	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole
70	H	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Example
71	H	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	Inventive Examole

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
		Coating amount of Fe-based coating film	Rinsing	P-containing ions		Contact time	Adhesion amount of P							
				Type	Content									
								g/m ²						
72	H	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	-	DONE	DONE	-	Excellent	Inventive Examole	
73	I	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole	
74	I	5.3	Normal	Pyrophosphate	1.00	5.0	1.3	Excellent	-	-	-	-	Inventive Examole	
75	I	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole	
76	I	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole	
77	I	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.3	Excellent	-	-	-	-	Inventive Examole	
78	I	5.3	Diluted solution	Pyrophosphate	1.00	5.0	0.9	-	DONE	DONE	-	Excellent	Inventive Examole	
79	J	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole	
80	J	5.3	Normal	Pyrophosphate	1.00	5.0	0.9	Excellent	-	-	-	-	Inventive Examole	
81	J	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole	
82	J	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole	

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
		Coating amount of Fe-based coating film	Rinsing	P-containing ions		Contact time	Adhesion amount of P							
				Type	Content									
								g/m ²						
83	J	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.4	Excellent	-	-	-	-	Inventive Examole	
84	J	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.2	-	DONE	DONE	-	Excellent	Inventive Example	
85	K	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole	
86	K	5.3	Normal	Pyrophosphate	1.00	5.0	1.1	Excellent	-	-	-	-	Inventive Examole	
87	K	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole	
88	K	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Examole	
89	K	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	Inventive Examole	
90	K	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.1	-	DONE	DONE	-	Excellent	Inventive Examole	
91	L	5.3	Normal	-	-	-	-	Fair	-	-	-	-	Comparative Examole	
92	L	5.3	Normal	Pyrophosphate	1.00	5.0	1.2	Excellent	-	-	-	-	Inventive Examole	
93	L	5.3	Diluted solution	-	-	-	-	Poor	-	-	-	-	Comparative Examole	

(continued)

No.	Steel type	Fe-based electro-plating treatment		Contact with alkaline aqueous solution					Primary rust prevention property	Annealing treatment	Hot-dip galvanizing treatment	Alloying treatment	Plating appearance	Remarks
		Coating amount of Fe-based coating film	Rinsing	P-containing ions		Contact time	Adhesion amount of P							
				Type	Content		mg/m ²	P						
94	L	5.3	Diluted solution	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Example	
95	L	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.0	Excellent	-	-	-	-	Inventive Example	
96	L	5.3	Diluted solution	Pyrophosphate	1.00	5.0	1.1	-	DONE	DONE	-	Excellent	Inventive Example	
97	M _—	5.3	Normal	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Example	
98	M _—	5.3	Normal	Pyrophosphate	1.00	5.0	1.4	-	DONE	DONE	-	Poor	Comparative Example	
99	N _—	5.3	Normal	-	-	-	-	-	DONE	DONE	-	Poor	Comparative Example	
100	N _—	5.3	Normal	Pyrophosphate	1.00	5.0	0.9	-	DONE	DONE	-	Poor	Comparative Example	

<Summary of Evaluation Results>

[0182] As is apparent from the results shown in Tables 2 to 4, the Inventive Examples using any of base steel sheets of steel types A to L and having an adhesion amount of P of 0.2 mg/m² or more were excellent in primary rust prevention property or plating appearance.

[0183] In contrast, in the Comparative Examples in which the steel types A to L were not used or the adhesion amount of P was not 0.2 mg/m² or more, both the primary rust prevention property and the plating appearance were insufficient.

Claims

1. A raw material cold-rolled steel sheet with Fe-based coating film comprising:

a base steel sheet having a chemical composition containing,
 C in an amount of 0.80 mass% or less,
 Si in an amount of 0.10 mass% or more and 3.00 mass% or less,
 Mn in an amount of 1.50 mass% or more and 3.50 mass% or less,
 P in an amount of 0.100 mass% or less;
 S in an amount of 0.0300 mass% or less,
 Al in an amount of 0.100 mass% or less,
 with a remaining part consisting of Fe and inevitable impurities; and
 a P-adhered Fe-based coating film comprising an Fe-based coating film disposed on at least one surface of the base steel sheet and a P-containing substance adhered to a surface of the Fe-based coating film,
 wherein an adhesion amount of the P-containing substance in terms of P is 0.2 mg/m² or more.

2. The raw material cold-rolled steel sheet with Fe-based coating film according to claim 1, wherein a coating amount of the Fe-based coating film per one surface of the base steel sheet is 1.0 g/m² or more.

3. The raw material cold-rolled steel sheet with Fe-based coating film according to claim 1 or 2, wherein the chemical composition further contains at least one element selected from the group consisting of:

N in an amount of 0.0100 mass% or less,
 B in an amount of 0.0050 mass% or less,
 Ti in an amount of 0.200 mass% or less,
 Cr in an amount of 1.000 mass% or less,
 Mo in an amount of 1.000 mass% or less,
 Cu in an amount of 1.000 mass% or less,
 Ni in an amount of 1.000 mass% or less,
 Nb in an amount of 0.200 mass% or less,
 V in an amount of 0.500 mass% or less,
 Sb in an amount of 0.200 mass% or less,
 Ta in an amount of 0.100 mass% or less,
 W in an amount of 0.500 mass% or less,
 Zr in an amount of 0.1000 mass% or less,
 Sn in an amount of 0.200 mass% or less,
 Ca in an amount of 0.0050 mass% or less,
 Mg in an amount of 0.0050 mass% or less, and
 REM in an amount of 0.0050 mass% or less.

4. The raw material cold-rolled steel sheet with Fe-based coating film according to claim 1 or 2, wherein the Fe-based coating film has a chemical composition containing at least one element selected from the group consisting of B, C, P, N, O, Ni, Mn, Mo, Zn, W, Pb, Sn, Cr, V, and Co in a total amount of 10 mass% or less, with a remaining part consisting of Fe and inevitable impurities.

5. A method for producing a raw material cold-rolled steel sheet with Fe-based coating film, the method comprising:

subjecting a base steel sheet having a chemical composition containing C in an amount of 0.80 mass% or less, Si in an amount of 0.10 mass% or more and 3.00 mass% or less, Mn in an amount of 1.50 mass% or more and

3.50 mass% or less, P in an amount of 0.100 mass% or less, S in an amount of 0.0300 mass% or less, Al in an amount of 0.100 mass% or less, with a remaining part consisting of Fe and inevitable impurities to an Fe-based electroplating treatment to form an Fe-based coating film on at least one surface of the base steel sheet; and

bringing a surface of the Fe-based coating film into contact with an alkaline aqueous solution for 0.5 seconds or more followed by rinsing the surface of the Fe-based coating film with water and drying, wherein the alkaline aqueous solution contains P-containing ions, and a content of the P-containing ions in the alkaline aqueous solution is 0.01 g/L or more in terms of P.

6. The method for producing a raw material cold-rolled steel sheet with Fe-based coating film according to claim 5, wherein the alkaline aqueous solution contains at least one phosphorus compound selected from the group consisting of a phosphate, a pyrophosphate, and a triphosphate.

7. The method for producing a raw material cold-rolled steel sheet with Fe-based coating film according to claim 5 or 6, wherein pH of the alkaline aqueous solution is 8 or more.

8. The method for producing a raw material cold-rolled steel sheet with Fe-based coating film according to claim 5 or 6, wherein the chemical composition further contains at least one element selected from the group consisting of:

N in an amount of 0.0100 mass% or less,
B in an amount of 0.0050 mass% or less,
Ti in an amount of 0.200 mass% or less,
Cr in an amount of 1.000 mass% or less,
Mo in an amount of 1.000 mass% or less,
Cu in an amount of 1.000 mass% or less,
Ni in an amount of 1.000 mass% or less,
Nb in an amount of 0.200 mass% or less,
V in an amount of 0.500 mass% or less,
Sb in an amount of 0.200 mass% or less,
Ta in an amount of 0.100 mass% or less,
W in an amount of 0.500 mass% or less,
Zr in an amount of 0.1000 mass% or less,
Sn in an amount of 0.200 mass% or less,
Ca in an amount of 0.0050 mass% or less,
Mg in an amount of 0.0050 mass% or less, and
REM in an amount of 0.0050 mass% or less.

9. A method for producing a cold-rolled steel sheet with Fe-based coating film, the method comprising subjecting the raw material cold-rolled steel sheet with Fe-based coating film according to claim 1 or 2 to an annealing treatment to obtain the cold-rolled steel sheet with Fe-based coating film.

10. A method for producing a hot-dip galvanized steel sheet, the method comprising subjecting the cold-rolled steel sheet with Fe-based coating film obtained by the method according to claim 9 to a hot-dip galvanizing treatment to obtain the hot-dip galvanized steel sheet.

11. A method for producing an alloyed hot-dip galvanized steel sheet, the method comprising subjecting the hot-dip galvanized steel sheet obtained by the method according to claim 10 to an alloying treatment to obtain the alloyed hot-dip galvanized steel sheet.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/020560

A. CLASSIFICATION OF SUBJECT MATTER

C23C 2/02(2006.01)i; **C21D 9/46**(2006.01)i; **C22C 38/00**(2006.01)i; **C22C 38/06**(2006.01)i; **C22C 38/60**(2006.01)i;
C23C 2/06(2006.01)i; **C23C 2/28**(2006.01)i; **C23C 2/40**(2006.01)i; **C23C 28/00**(2006.01)i
 FI: C23C2/02; C21D9/46 J; C22C38/00 301T; C22C38/06; C22C38/60; C23C2/06; C23C2/28; C23C2/40; C23C28/00 A

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)

C21D9/46, C22C38/06, C22C38/60, C23C2/00-2/40, C23C28/00, C25D3/20

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2022
 Registered utility model specifications of Japan 1996-2022
 Published registered utility model applications of Japan 1994-2022

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 63-312960 A (NIPPON STEEL CORP) 21 December 1988 (1988-12-21)	1-11
A	JP 62-139860 A (NIPPON STEEL CORP) 23 June 1987 (1987-06-23)	1-11
A	JP 2-038549 A (SUMITOMO METAL IND LTD) 07 February 1990 (1990-02-07)	1-11
A	JP 4-099853 A (NIPPON STEEL CORP) 31 March 1992 (1992-03-31)	1-11
A	JP 4-224686 A (KAWASAKI STEEL CORP) 13 August 1992 (1992-08-13)	1-11
A	JP 6-287735 A (KAWASAKI STEEL CORP) 11 October 1994 (1994-10-11)	1-11
A	JP 8-269780 A (KAWASAKI STEEL CORP) 15 October 1996 (1996-10-15)	1-11
A	JP 2012-172216 A (NIPPON STEEL CORP) 10 September 2012 (2012-09-10)	1-11

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Date of the actual completion of the international search

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Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2022/020560

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JP 2-038549 A	07 February 1990	(Family: none)	
JP 4-099853 A	31 March 1992	(Family: none)	
JP 4-224686 A	13 August 1992	(Family: none)	
JP 6-287735 A	11 October 1994	(Family: none)	
JP 8-269780 A	15 October 1996	(Family: none)	
JP 2012-172216 A	10 September 2012	(Family: none)	

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2011214102 A [0007]