



(11) **EP 4 477 785 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
18.12.2024 Bulletin 2024/51

(21) Application number: **23784544.1**

(22) Date of filing: **20.02.2023**

(51) International Patent Classification (IPC):
C25D 5/14 ^(2006.01) **C25D 3/06** ^(2006.01)
C25D 5/26 ^(2006.01) **C25D 5/48** ^(2006.01)

(52) Cooperative Patent Classification (CPC):
C25D 3/06; C25D 5/14; C25D 5/48; C25D 7/0614;
C25D 3/12

(86) International application number:
PCT/JP2023/006069

(87) International publication number:
WO 2023/195251 (12.10.2023 Gazette 2023/41)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **08.04.2022 JP 2022064801**

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(54) **SURFACE-TREATED STEEL SHEET AND METHOD FOR PRODUCING SAME**

(57) Provided is a surface-treated steel sheet that can be produced without the use of hexavalent chromium and that combines excellent film corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability. At least one side of the surface-treated steel sheet includes a Ni-containing

layer, a metallic Cr layer on the Ni-containing layer, and an oxidized Cr layer on the metallic Cr layer. The water contact angle is 50° or less, and the total atomic ratio to Cr of K, Na, Mg, and Ca adsorbed on the surface is 5.0 % or less.

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Description

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to surface-treated steel sheets, and in particular to a surface-treated steel sheet having excellent film corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability. The surface-treated steel sheet according to the present disclosure can be suitably used for containers such as cans. Further, the present disclosure relates to a method of producing the surface-treated steel sheet.

10 BACKGROUND

[0002] Sn-plated steel sheets (tinplate) have excellent corrosion resistance, weldability, and workability, and are easily produced, and have therefore been used for 200 years or more as material for various metal cans such as beverage, food, pail, and 18-liter cans.

15 **[0003]** However, tin is an expensive material, and therefore tin-free steel sheets (TFS), surface-treated steel sheets that do not use Sn, were developed. Tin-free steel sheets are surface-treated steel sheets with a metallic Cr layer and a Cr oxide layer formed on the steel sheet surface, and are typically produced by electrolysis treatment of steel sheets in an electrolyte containing hexavalent Cr (see Patent Literature (PTL) 1 to 3). Tin-free steel sheets have excellent corrosion resistance and coating adhesion properties, and are therefore now very commonly used as steel sheets for containers, replacing tinplate.

20 However, such tin-free steel sheets have a chromium oxide layer, an insulating coating, on the surface layer, and therefore have poor weldability.

[0004] As surface-treated steel sheets that have excellent weldability without Sn, Ni-coated steel sheets using Ni instead of tin are known (see PTL 4 and 5). However, when Ni-coated steel sheets are used as material for welded cans, it is necessary to provide a chromating treatment on Ni-coated steel sheets using an aqueous solution containing hexavalent

25 Cr to secure corrosion resistance and coating adhesion properties.

[0005] In recent years, increasing environmental awareness has led to a worldwide trend toward regulating the use of hexavalent Cr. Accordingly, there is a need to establish a production method that does not use hexavalent chromium in the field of surface-treated steel sheets used for containers and the like.

30 **[0006]** As methods of forming surface-treated steel sheets without using hexavalent chromium, the methods proposed in PTL 6 and 7 are known examples. According to such methods, the surface-treated layer is formed by electrolysis treatment in an electrolyte containing trivalent chromium compounds such as basic chromium sulfate.

CITATION LIST

35 Patent Literature

[0007]

PTL 1: JP S58-110695 A

40 PTL 2: JP S55-134197 A

PTL 3: JP S57-035699 A

PTL 4: JP H11-117085 A

PTL 5: JP 2007-231394 A

PTL 6: JP 2016-505708 A (publication in Japan of WO2014/079910 A1)

45 PTL 7: JP 2015-520794 A (publication in Japan of WO2013/143928 A1)

SUMMARY

(Technical Problem)

50 **[0008]** According to the methods proposed in PTL 6 and 7, a surface-treated layer can be formed without using hexavalent chromium. And according to PTL 6 and 7, the methods can obtain surface-treated steel sheets having excellent adhesion to resin film in a wet environment (hereinafter also referred to as "film wet adhesion") and adhesion to coatings in a wet environment (hereinafter also referred to as "coating secondary adhesion").

55 **[0009]** However, although surface-treated steel sheets obtained by conventional methods such as those proposed in PTL 6 and 7 have excellent film wet adhesion and coating secondary adhesion, weldability is poor, and performance is not sufficient for use as a replacement for surface-treated steel sheets produced by methods using hexavalent chromium.

[0010] Accordingly, there is a need for a surface-treated steel sheet that can be produced without the use of hexavalent

chromium and that combines excellent film corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability.

[0011] It would be helpful to provide a surface-treated steel sheet that can be produced without the use of hexavalent chromium and that has excellent film corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability.

(Solution to Problem)

[0012] As a result of extensive studies, the inventors have made the following discoveries (1) and (2).

(1) In surface-treated steel sheets having a metallic Cr layer and a Cr oxide layer on a Ni-containing layer, the water contact angle and the total atomic ratio of K, Na, Mg, and Ca adsorbed on a surface to Cr are controlled within specific ranges, to obtain surface-treated steel sheets having excellent film corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability.

(2) The surface-treated steel sheets described above can be produced by performing cathodic electrolysis treatment in an electrolyte prepared by a specific method and containing trivalent chromium ions, followed by a final water washing using water whose electrical conductivity is a defined value or less.

[0013] The present disclosure is made based on these discoveries. Primary features of the present disclosure are described below.

1. A surface-treated steel sheet comprising:

a steel sheet;
a Ni-containing layer disposed on at least one surface of the steel sheet;
a metallic Cr layer disposed on the Ni-containing layer; and
a Cr oxide layer disposed on the metallic Cr layer, the surface-treated steel sheet having:

a water contact angle of 50° or less, and
a total atomic ratio of K, Na, Mg, and Ca adsorbed on a surface to Cr of 5.0 % or less.

2. The surface-treated steel sheet according to 1, above, wherein the Ni-containing layer has a Ni coating weight of 200 mg/m² or more and 2000 mg/m² or less per side of the steel sheet.

3. The surface-treated steel sheet according to 1 or 2, above, wherein the metallic Cr layer has a Cr coating weight of 2 mg/m² or more and less than 40 mg/m² per side of the steel sheet.

4. The surface-treated steel sheet according to any one of 1 to 3, above, wherein the Cr oxide layer has a Cr coating weight of 0.1 mg/m² or more and 15.0 mg/m² or less per side of the steel sheet.

5. The surface-treated steel sheet according to any one of 1 to 4, above, having an atomic ratio of Ni on the surface of the surface-treated steel sheet to Cr of 100 % or less.

6. A method of producing a surface-treated steel sheet comprising a steel sheet; a Ni-containing layer disposed on at least one surface of the steel sheet; a metallic Cr layer disposed on the Ni-containing layer; and a Cr oxide layer disposed on the metallic Cr layer, the method comprising:

an electrolyte preparation process of preparing an electrolyte containing trivalent chromium ions;
a cathodic electrolysis treatment process of cathodic electrolysis treatment in the electrolyte of the steel sheet comprising the Ni-containing layer on at least one surface; and
a water washing process of at least one water wash of the steel sheet after the cathodic electrolysis treatment, wherein, in the electrolyte preparation process, the electrolyte is prepared by:

mixing a trivalent chromium ion source, a carboxylic acid compound, and water; and
adjusting the pH to 4.0 to 7.0 and adjusting the temperature to 40 °C to 70 °C, and

in the water washing process,
water having an electrical conductivity of 100 μS/m or less is used in at least the last water wash.

(Advantageous Effect)

[0014] According to the present disclosure, a surface-treated steel sheet can be provided that has excellent film

corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability, without the use of hexavalent chromium. The surface-treated steel sheet according to the present disclosure can be suitably used as a material for containers and the like.

5 DETAILED DESCRIPTION

[0015] A method implementing the techniques of the present disclosure is described in detail below. The following description merely presents examples of preferred embodiments of the present disclosure, and the present disclosure is not limited to these embodiments.

[0016] The surface-treated steel sheet according to an embodiment of the present disclosure is a surface-treated steel sheet including a steel sheet; a Ni-containing layer disposed on at least one surface of the steel sheet; a metallic Cr layer disposed on the Ni-containing layer; and a Cr oxide layer disposed on the metallic Cr layer. According to the present disclosure, it is important that the surface-treated steel sheet have a water contact angle of 50° or less, and a total atomic ratio of K, Na, Mg, and Ca adsorbed on the surface to Cr of 5.0 % or less. The following is a description of each of the components of the surface-treated steel sheet.

[Steel sheet]

[0017] Any steel sheet may be used as the steel sheet without being particularly limited. The steel sheet is preferably a steel sheet for cans. For example, an ultra low carbon steel sheet or a low carbon steel sheet can be used as the steel sheet. The method of producing the steel sheet is not particularly limited, and a steel sheet produced by any method may be used. Typically, a cold-rolled steel sheet is used as the steel sheet. The cold-rolled steel sheet may be produced by a typical production process of, for example, hot rolling, pickling, cold rolling, annealing, and temper rolling.

[0018] The chemical composition of the steel sheet is not particularly limited. The Cr content is preferably 0.10 mass% or less. The Cr content is more preferably 0.08 mass% or less. When the Cr content of the steel sheet is in a range described above, there is no excessive Cr concentration on the steel sheet surface, and as a result, the atomic ratio of Ni on the surface of the final surface-treated steel sheet to Cr can be 100 % or less. Further, the steel sheet may contain C, Mn, P, S, Si, Cu, Ni, Mo, Al, and inevitable impurity to an extent that effects of the scope of the present disclosure are not impaired. For example, a steel sheet chemical composition specified in ASTM A623M-09 can be suitably used as the steel sheet.

[0019] According to an embodiment of the present disclosure, a steel sheet is preferably used that has a chemical composition containing, in mass%,

C: 0.0001 % to 0.13 %,

Si: 0 % to 0.020 %,

Mn: 0.01 % to 0.60 %,

P: 0 % to 0.020 %,

S: 0 % to 0.030 %,

Al: 0 % to 0.20 %,

N: 0 % to 0.040 %,

Cu: 0 % to 0.20 %,

Ni: 0 % to 0.15 %,

Cr: 0 % to 0.10 %,

Mo: 0 % to 0.05 %,

Ti: 0 % to 0.020 %,

Nb: 0 % to 0.020 %,

B: 0 % to 0.020 %,

Ca: 0 % to 0.020 %,

Sn: 0 % to 0.020 %,

Sb: 0 % to 0.020 %,

with the balance being Fe and inevitable impurity. Of the above chemical components, the lower the content of Si, P, S, Al, and N, the better, while Cu, Ni, Cr, Mo, Ti, Nb, B, Ca, Sn, and Sb are optionally added components.

[0020] Thickness of the steel sheet is not particularly limited. The steel sheet preferably has a thickness of 0.60 mm or less. The term "steel sheet" is defined here to include a "steel strip". A lower limit of the thickness of the steel sheet is not particularly limited. The lower limit is preferably 0.10 mm or more.

[Ni-containing layer]

[0021] When surface-treated steel sheets are used as steel sheets for cans, the surface-treated steel sheets are typically welded by resistance welding such as wire seam welding. Ni is an element having excellent forge weldability, and therefore weldability can be improved by disposition of a Ni-containing layer. That is, when a Ni-containing layer is present, excellent weld strength is obtainable from lower resistance heat generation, and therefore the range of a lower limit of weldable current is extended.

[0022] The Ni-containing layer need only be provided on at least one side of the steel sheet, and may be provided on both sides. The Ni-containing layer need only cover at least a portion of the steel sheet, and may cover the entire surface on which the Ni-containing layer is provided. Further, the Ni-containing layer may be a continuous layer or a discontinuous layer. As the discontinuous layer, examples include a layer having an island-like structure.

[0023] As the Ni-containing layer, any layer containing nickel may be used, and, for example, one or both of a Ni layer and a Ni alloy layer may be used. For example, a Ni alloy layer due to diffusion annealing treatment after Ni coating or plating is also included in the Ni alloy layer. Further, as the Ni alloy layer, examples include a Ni-Fe alloy layer.

[0024] The Ni-containing layer is preferably a Ni-based coated or plated layer. Here, "Ni-based coated or plated layer" is defined as a coated or plated layer having a Ni content of 50 mass% or more. In other words, the Ni-based coated or plated layer is a Ni coated or plated layer or a coated or plated layer made of Ni-based alloy.

[0025] The Ni-based coated or plated layer may be a dispersion coated or plated layer (composite coated or plated layer) in which solid microparticles are dispersed in Ni or Ni-based alloy as a matrix. As the solid microparticles, microparticles of any material property may be used without any particular limitation. The microparticles may be inorganic microparticles or organic microparticles. As the organic microparticles, examples include microparticles made of resin. Any resin may be used as the resin, but use of fluororesin is preferred, and polytetrafluoroethylene (PTFE) is more preferred. As the inorganic particles, microparticles made of any inorganic material may be used without any particular limitation. The inorganic material may be, for example, a metal (including alloys), a compound, or other single substance. Among these, microparticles are preferably used that consist of at least one selected from the group consisting of oxides, nitrides, and carbides, and use of microparticles of metal oxides is preferred. As the metal oxides, examples include aluminum oxide, chromium oxide, titanium oxide, and zinc oxide.

[0026] The particle size of microparticles used for the dispersion coating or plating is not particularly limited and particles of any size may be used. However, the size of the microparticles preferably does not exceed the thickness of the dispersion coated or plated layer as the Ni-containing layer. Typically, the size of the microparticles is preferably 1 nm to 50 μm . The size of the microparticles is more preferably 10 nm to 1000 nm.

[0027] Ni coating weight of the Ni-containing layer may be any amount without particular limitation. However, from the viewpoint of further improving weldability and corrosion resistance of the surface-treated steel sheet, the Ni coating weight is preferably 200 mg/m^2 or more per coated side of the steel sheet. The Ni coating weight is more preferably 250 mg/m^2 or more per coated side of the steel sheet. On the other hand, when the Ni coating weight exceeds 2000 mg/m^2 , the effect of improving weldability becomes saturated. Accordingly, from the viewpoint of reducing excessive costs, the Ni coating weight is preferably 2000 mg/m^2 or less. The Ni coating weight is more preferably 1800 mg/m^2 or less.

[0028] The Ni coating weight of the Ni-containing layer is measured by an X-ray fluorescence calibration curve method. A plurality of steel sheets having known Ni coating weights are prepared, X-ray fluorescence intensity derived from Ni is measured in advance, and the relationship between the measured X-ray fluorescence intensity and Ni coating weight is linearly approximated to a calibration curve. The Ni coating weight of the Ni-containing layer may be measured by measuring the X-ray fluorescence intensity derived from Ni of the surface-treated steel sheet and using the calibration curve described above.

[0029] Formation of the Ni-containing layer may be achieved by any method, including electroplating, without any particular limitation. When forming the Ni-containing layer by electroplating, any plating bath may be used. As a plating bath that may be used, examples include a Watts bath, a sulfamic acid bath, and a Wood's bath. When forming a Ni-Fe alloy layer as the Ni-containing layer, the Ni-Fe alloy layer may be formed by forming a Ni layer on the surface of the steel sheet by electroplating or the like, and then subjecting the steel sheet to annealing.

[0030] A surface side of the Ni-containing layer may contain Ni oxide or not contain any Ni oxide at all, but from the viewpoint of further improving coating secondary adhesion and sulfide staining resistance, the surface side of the Ni-containing layer preferably does not contain Ni oxide. Although Ni oxide can be formed by dissolved oxygen contained in water washing water after Ni coating or plating, Ni oxide contained in the Ni-containing layer is preferably removed by pretreatment as described below.

[Metallic Cr layer]

[0031] A metallic Cr layer is present on the Ni-containing layer.

[0032] Coating weight of the metallic Cr layer is not particularly limited and may be any value. However, from the

viewpoint of further improving corrosion resistance, the coating weight of the metallic Cr layer is preferably 2 mg/m² or more per coated side of the steel sheet. The coating weight of the metallic Cr layer is more preferably 4 mg/m² or more per coated side of the steel sheet. An upper limit of the coating weight of the metallic Cr layer is also not particularly limited, but excessive coating weight of the metallic Cr layer may increase contact resistance and impair weldability. Therefore, from the viewpoint of securing more stable weldability, the Cr coating weight of the metallic Cr layer is preferably less than 40 mg/m² per coated side of the steel sheet. The Cr coating weight of the metallic Cr layer is more preferably 35 mg/m² or less per coated side of the steel sheet.

[0033] The Cr coating weight of the metallic Cr layer may be measured by an X-ray fluorescence method. Specifically, first, amount of Cr (total Cr) in the surface-treated steel sheet is measured using an X-ray fluorescence device. The surface-treated steel sheet is then subjected to alkali treatment by immersion in 7.5N-NaOH at 90 °C for 10 min, followed by a thorough water washing. Amount of Cr (post-alkali treatment Cr) is then measured again using an X-ray fluorescence device. Further, after the metallic Cr layer and the Cr oxide layer are stripped, amount of Cr (original sheet Cr) in the steel sheet is measured using an X-ray fluorescence device. For stripping of the metallic Cr layer and the Cr oxide layer, a commercially available chromium plating separating agent may be used, such as hydrochloric acid separating agent. The post-alkali treatment Cr minus the original sheet Cr is the Cr coating weight per side of the steel sheet of the metallic Cr layer. The total Cr mentioned above is used to calculate Cr coating weight of the Cr oxide layer as described below.

[0034] The metallic Cr of the metallic Cr layer may be amorphous Cr or crystalline Cr. That is, the metallic Cr layer may contain one or both of amorphous Cr and crystalline Cr. The metallic Cr layer produced by the method described below typically contains amorphous Cr and may also contain crystalline Cr. Although the formation mechanism of the metallic Cr layer is not clear, it is thought that partial crystallization proceeds during the formation of amorphous Cr, resulting in a metallic Cr layer containing both amorphous and crystalline phases.

[0035] The ratio of crystalline Cr to the sum of amorphous Cr and crystalline Cr in the metallic Cr layer is preferably 0 % or more and 80 % or less. The ratio is more preferably 0 % or more and 50 % or less. The ratio of crystalline Cr can be measured by observing the metallic Cr layer with a scanning transmission electron microscope (STEM). Specifically, first, STEM images are acquired at a magnification of 2 million to 10 million at a beam diameter that provides a resolution of 1 nm or less. In the obtained STEM images, a region where lattice fringes can be seen is regarded as crystalline phase, and a region where a maze pattern can be seen is regarded as amorphous phase, and the areas of both are determined. From the results, the ratio of the area of crystalline Cr to the total area of amorphous Cr and crystalline Cr is calculated.

[Cr oxide layer]

[0036] The Cr oxide layer is present on the metallic Cr layer. The coating weight of the Cr oxide layer is not particularly limited and may be any value. However, from the viewpoint of further improving corrosion resistance, the coating weight of the Cr oxide layer is preferably 0.1 mg/m² or more in Cr coating weight per side of the steel sheet. An upper limit of the coating weight of the Cr oxide layer is also not particularly limited, but excessive coating weight of the Cr oxide layer may increase contact resistance and impair weldability. Therefore, from the viewpoint of securing more stable weldability, the coating weight of the Cr oxide layer is preferably 15.0 mg/m² or less in Cr coating weight per side of the steel sheet. The Cr coating weight of the Cr oxide layer can be measured by an X-ray fluorescence method. Specifically, the Cr coating weight of the Cr oxide layer may be obtained by subtracting the post-alkali treatment Cr from the total Cr measured using the X-ray fluorescence device as described above.

[0037] One or both of the metallic Cr layer and the Cr oxide layer may contain C. However, excessive C in the metallic Cr layer and the Cr oxide layer may cause hardening of the heat-affected zone and cracking when welding is performed. Therefore, C content in the metallic Cr layer as an atomic ratio to Cr is preferably 40 % or less. C content in the metallic Cr layer as an atomic ratio to Cr is more preferably 35 % or less. Similarly, the C content in the Cr oxide layer as an atomic ratio to Cr is preferably 40 % or less. C content in the Cr oxide layer as an atomic ratio to Cr is more preferably 35 % or less. The metallic Cr layer and the Cr oxide layer need not contain C. Accordingly, a lower limit of C content in the metallic Cr layer and the Cr oxide layer as an atomic ratio to Cr may be 0 %.

[0038] The C content in the metallic Cr layer and the Cr oxide layer can respectively be measured by X-ray photoelectron spectroscopy (XPS). Specifically, measurement of the C content by XPS can be performed by calculating the C atomic ratio and the Cr atomic ratio from the integrated intensities of the Cr2p and C1s narrow spectra measured by XPS using a relative sensitivity coefficient method, and then calculating C atomic ratio/Cr atomic ratio.

[0039] Contamination-derived C can be detected from the outermost surface layer of the surface-treated steel sheet, and therefore in order to accurately measure the C content in the Cr oxide layer, measurement may be performed after sputtering from the outermost surface layer to a depth of at least 0.2 nm in SiO₂ equivalent, for example. On the other hand, the C content in the metallic Cr layer may be measured after sputtering from the outermost surface layer to a depth of 1/2 the thickness of the metallic Cr layer after the alkali treatment described above.

[0040] The thickness of the metallic Cr layer for the above measurement can be determined by the following procedure. First, the Cr atomic ratio and Ni atomic ratio are measured by XPS every 1 nm in the depth direction from the outermost

surface layer after alkali treatment. Then, a cubic expression approximating the relationship of Ni atomic ratio/Cr atomic ratio to depth from the outermost surface layer after alkali treatment is obtained by the least squares method. Using the obtained cubic expression, the depth from the outermost surface layer at which the Ni atomic ratio/Cr atomic ratio becomes 1 is calculated, and this is taken as the thickness of the metallic Cr layer.

[0041] For the measurements, a scanning X-ray photoelectron spectroscopy analyzer such as PHI X-tool, produced by Ulvac Phi, Inc., may be used, for example. The X-ray source may be a monochrome AlK α ray, the voltage 15 kV, the beam diameter 100 μ m, and the extraction angle 45°. The sputtering conditions may be Ar ions at an accelerating voltage of 1 kV and a sputtering rate of 1.50 nm/min on a SiO₂ equivalent.

[0042] Although the mechanism by which C is contained in the metallic Cr and Cr oxide layers is not clear, it is thought that carboxylic acid compounds in the electrolyte are decomposed and incorporated into the coating during the process of forming the metallic Cr layer and the Cr oxide layer on the steel sheet.

[0043] The form of C present in the metallic Cr layer and the Cr oxide layer is not particularly limited, but when present as precipitates, corrosion resistance may decrease due to the formation of local batteries. Therefore, the sum of the volume fractions of carbides and clusters having a clear crystal structure is preferably 10 % or less. The sum of the volume fractions of carbides and clusters having a clear crystal structure is more preferably 0 %. The presence or absence of carbides can be confirmed, for example, by composition analysis using energy dispersive X-ray spectroscopy (EDS) or wavelength dispersive X-ray spectroscopy (WDS) attached to a scanning electron microscope (SEM) or transmission electron microscope (TEM). The presence or absence of clusters can be confirmed, for example, by performing a cluster analysis on the data after 3D composition analysis using a 3D atom probe (3DAP).

[0044] The metallic Cr layer may contain O. An upper limit of O content in the metallic Cr layer is not particularly limited, but when the O content is high, Cr oxide may precipitate and corrosion resistance may decrease due to the formation of local batteries. Therefore, the O content, as an atomic ratio to Cr, is preferably 30 % or less. The O content, as an atomic ratio to Cr, is more preferably 25 % or less. The metallic Cr layer need not contain O. Therefore, a lower limit of O as an atomic ratio to Cr in the metallic Cr layer is not particularly limited and may be 0 %.

[0045] The O content in the metallic Cr layer can be measured by compositional analysis using EDS or WDS, attached to a SEM or TEM, or 3DAP.

[0046] One or both of the metallic Cr layer and the Cr oxide layer may contain Ni. An upper limit of Ni content in the metallic Cr layer is not particularly limited. The upper limit of Ni in the metallic Cr layer as an atomic ratio to Cr is preferably less than 100 %. Similarly, the upper limit of the Ni content in the Cr oxide layer is not particularly limited. The upper limit of the Ni in the Cr oxide layer as an atomic ratio to Cr is preferably less than 100 %. The metallic Cr layer and the Cr oxide layer need not contain Ni, and therefore a lower limit of the atomic ratio of Ni to Cr is not particularly limited and may be 0 %.

[0047] The Ni content on the surface of the surface-treated steel sheet, that is, the surface of the Cr oxide layer, is not particularly limited, but the lower the Ni content, the better the film wet adhesion and coating secondary adhesion. Therefore, the surface-treated steel sheet preferably has the atomic ratio to Cr of Ni on the surface of the surface-treated steel sheet of 100 % or less. The atomic ratio to Cr of Ni on the surface of the surface-treated steel sheet is more preferably 80 % or less.

[0048] The Ni content in the metallic Cr layer and the Cr oxide layer can be measured by XPS, similarly to the C content. The atomic ratio of Ni to Cr on the surface of the surface-treated steel sheet, that is, the surface of the Cr oxide layer, can be measured by XPS on the surface of the surface-treated steel sheet. The Cr2p and Ni2p narrow spectra can be used to calculate the atomic ratio.

[0049] Although the mechanism by which Ni is contained in the metallic Cr layer and the Cr oxide layer is not clear, it is thought that Ni in the Ni-containing layer dissolves in the electrolyte in minute amounts during the process of forming the metallic Cr layer and the Cr oxide layer on the steel sheet, and Ni is incorporated into the coating.

[0050] Aside from Cr, O, Ni, C, and K, Na, Mg, and Ca described below, the metallic Cr layer and the Cr oxide layer may contain metallic impurity such as Cu, Zn, Sn, Fe, and the like in aqueous solution, or S, N, Cl, Br, and the like. However, the presence of such elements may decrease film wet adhesion and coating secondary adhesion. Accordingly, the content of Fe in the metallic Cr layer and the Cr oxide layer as an atomic ratio to Cr is preferably 10 % or less. The content of Fe in the metallic Cr layer and the Cr oxide layer as an atomic ratio to Cr is more preferably 0 %. The sum of elements other than Cr, O, Ni, C, K, Na, Mg, Ca, and Fe as an atomic ratio to Cr is preferably 3 % or less. The sum of elements other than Cr, O, Ni, C, K, Na, Mg, Ca, and Fe as an atomic ratio to Cr is more preferably 0 %. Measurement of the content of the above elements is not particularly limited, but may be via XPS, for example, as per measurement of the C content. In particular, when the content of Fe is measured by XPS, the narrow spectrum of Fe2p is used, but the quantified value of Fe content may be calculated higher than actual due to overlap with the NiLLM peak, and therefore, as mentioned above, unlike other elements, Fe content, as an atomic ratio to Cr, is preferably controlled to be 10 % or less.

[0051] The metallic Cr layer and the Cr oxide layer are preferably crack-free. The presence or absence of cracks can be confirmed, for example, by cutting out a cross-section of the coating using a focused ion beam (FIB) or the like and direct observation using a transmission electron microscope (TEM).

[0052] Further, surface roughness of the surface-treated steel sheet is not greatly changed by the formation of the

metallic Cr layer and the Cr oxide layer, and is normally equivalent to surface roughness of the base steel sheet used. The surface roughness of the surface-treated steel sheet is not particularly limited. Arithmetic mean roughness Ra is preferably 0.1 μm or more. Arithmetic mean roughness Ra is preferably 4 μm or less. Further, ten-point mean roughness Rz is preferably 0.2 μm or more. Ten-point mean roughness Rz is preferably 6 μm or less.

[Water contact angle]

[0053] According to the present disclosure, it is important that the surface-treated steel sheet have a water contact angle of 50° or less. By highly hydrophilizing the surface of the surface-treated steel sheet so that the water contact angle is 50° or less, firm hydrogen bonds are formed between resin in a coating and the surface-treated steel sheet, and as a result, high adhesion can be obtained even in wet environments. From the viewpoint of further improving coating secondary adhesion, the water contact angle is preferably 48° or less. The water contact angle is more preferably 45° or less. From the viewpoint of improving adhesion, the lower the water contact angle, the better, and therefore a lower limit of the water contact angle is not particularly limited and may be 0°. However, from the viewpoint of ease of production and the like, the water contact angle is preferably 3° or more. The water contact angle is preferably 6° or more. The water contact angle can be measured by a method described in the EXAMPLES section.

[0054] Although the mechanism by which the surface of surface-treated steel sheets becomes hydrophilic is not clear, it is thought that carboxylic acids or carboxylic acid salts in the electrolyte are decomposed and incorporated into the coating when the metallic Cr layer and the Cr oxide layer are formed by cathodic electrolysis in the electrolyte, thereby providing hydrophilic functional groups such as carboxyl groups to the surface. However, when the electrolyte is not prepared under specific conditions as described below, the surface of the surface-treated steel sheet does not become hydrophilic even when the electrolyte contains carboxylic acid or carboxylic acid salts. The mechanism by which the electrolyte preparation conditions affect the hydrophilicity of the surface of the surface-treated steel sheet is not clear, but it is assumed to be due to the formation of complexes such that hydrophilic functional groups such as carboxyl groups are easily provided to the surface when the electrolyte is appropriately prepared under the conditions described below.

[0055] In surface-treated steel sheets produced using conventional hexavalent chromium baths as proposed in PTL 1 to 5, it has been reported that the composition of the chromium hydrated oxide layer on the surface layer has a significant effect on adhesion to coatings or films in a wet environment. In a wet environment, water that has penetrated through the coating or film hinders adhesion at the interface between the coating or film and the chromium hydrated oxide layer. Therefore, it was thought that when hydrophilic OH groups are present in large numbers in the chromium hydrated oxide layer, extended wetting of water at the interface is promoted, resulting in decreased adhesive strength. Accordingly, in conventional surface-treated steel sheets, the decrease of OH groups due to the oxidation of chromium hydrated oxide, that is, hydrophobization of the surface, was to improve adhesion to coatings and films in a wet environment.

[0056] In contrast, the present disclosure is based on a technical concept that is completely opposite to the conventional technology described above, in which the surface is made hydrophilic to a near superhydrophilic level to form firm hydrogen bonds at an interface between a coating and the surface-treated steel sheet, thereby maintaining high adhesion even under a wet environment.

[Atomic ratio of adsorbed elements]

[0057] As mentioned above, the surface-treated steel sheet has a high hydrophilic property with a water contact angle of 50° or less, and a chemically active surface. Therefore, cations of elements such as K, Na, Mg, and Ca are easily adsorbed on the surface of the surface-treated steel sheet. The inventors have found that simply making the water contact angle be 50° or less does not provide the intended adhesion properties, due to the effect of the adsorbed cations. By decreasing the amount of the cations adsorbed on the surface of the surface-treated steel sheet, adhesion to resin can be improved and excellent film wet adhesion and coating secondary adhesion can be achieved.

[0058] Specifically, the surface-treated steel sheet have the sum of the atomic ratio of K, Na, Mg, and Ca adsorbed on the surface to Cr of 5.0 % or less. The sum of the atomic ratio of K, Na, Mg, and Ca adsorbed on the surface of the surface-treated steel sheet to Cr is preferably 3.0 % or less. The sum of the atomic ratio of K, Na, Mg, and Ca adsorbed on the surface of the surface-treated steel sheet to Cr is more preferably 1.0 % or less. The lower the sum of the above atomic ratio, the better, and therefore a lower limit is not particularly limited and may be 0 %. The sum of the above atomic ratio can be measured by a method described in the EXAMPLES section.

[Production method]

[0059] In the method of producing a surface-treated steel sheet according to an embodiment of the present disclosure, a surface-treated steel sheet having the properties described above can be produced by the method described below.

[0060] The method of producing a surface-treated steel sheet according to an embodiment of the present disclosure is a

method of producing a surface-treated steel sheet including a Ni-containing layer disposed on at least one surface of a steel sheet, a metallic Cr layer disposed on the Ni-containing layer, and a Cr oxide layer disposed on the metallic Cr layer, and includes the following processes (1) to (3). The following describes each of the processes.

- (1) An electrolyte preparation process of preparing an electrolyte containing trivalent chromium ions
- (2) A cathodic electrolysis treatment process of cathodic electrolysis treatment in the electrolyte of the steel sheet including the Ni-containing layer
- (3) A water washing process of at least one water wash of the steel sheet after the cathodic electrolysis treatment

[Electrolyte preparation process]

(i) Mixing

[0061] In the electrolyte preparation process, a trivalent chromium ion source, a carboxylic acid compound, and water are first mixed to form an aqueous solution.

[0062] Any compound that can supply trivalent chromium ions can be used as the trivalent chromium ion source. For example, at least one selected from the group consisting of chromium chloride, chromium sulfate, and chromium nitrate can be used as the trivalent chromium ion source.

[0063] The amount of the trivalent chromium ion source in the aqueous solution is not particularly limited. In terms of trivalent chromium ions, the amount of the trivalent chromium ion source is preferably 3 g/L or more. The amount is particularly 50 g/L or less. The amount is more preferably 5 g/L or more. The amount is more preferably 40 g/L or less. BluCr® (BluCr is a registered trademark in Japan, other countries, or both) TFS A, produced by Atotech, can be used as the trivalent chromium ion source.

[0064] Any carboxylic acid compound can be used as the carboxylic acid compound, without particular limitation. The carboxylic acid compound may be at least one of a carboxylic acid or a carboxylic acid salt, and is preferably at least one of an aliphatic carboxylic acid or an aliphatic carboxylic acid salt. The carbon number of the aliphatic carboxylic acid is preferably 1 to 10. The carbon number of the aliphatic carboxylic acid is more preferably 1 to 5. The carbon number of the aliphatic carboxylic acid salt is preferably 1 to 10. The carbon number of the aliphatic carboxylic acid salt is more preferably 1 to 5. The content of the carboxylic acid compound is not particularly limited. The content of the carboxylic acid compound is preferably 0.1 mol/L or more. The content is preferably 5.5 mol/L or less. The content is more preferably 0.15 mol/L or more. The content is more preferably 5.3 mol/L or less. BluCr® TFS B, produced by Atotech, can be used as the carboxylic acid compound.

[0065] According to the present disclosure, water is used as the solvent for preparing the electrolyte. As the water, it is preferable to use highly pure water such as deionized water from which cations have been removed in advance using an ion-exchange resin or the like, or distilled water. As discussed below, from the perspective of decreasing the amount of K, Na, Mg, and Ca in the electrolyte, it is preferable to use water having an electrical conductivity of 30 μ S/m or less.

[0066] In order to decrease the amount of K, Na, Mg, and Ca adsorbed on the surface of the surface-treated steel sheet, it is preferable to not intentionally include K, Na, Mg, and Ca in the aqueous solution described above. Accordingly, it is preferable that the components added to the aqueous solution, such as the trivalent chromium ion source and the carboxylic acid compound mentioned above, and pH adjusters detailed below, be free of K, Na, Mg, and Ca. As pH adjusters, hydrochloric acid, sulfuric acid, nitric acid, and the like are preferably used to lower pH, while ammonia water and the like are preferably used to raise pH. Although K, Na, Mg, and Ca being inevitably mixed into the aqueous solution or electrolyte is permitted, the total concentration of K, Na, Mg, and Ca is preferably 2.0 mol/L or less. The total concentration is more preferably 1.5 mol/L or less. The total concentration is even more preferably 1.0 mol/L or less.

[0067] To effectively suppress the formation of hexavalent chromium at the anode in the cathodic electrolysis treatment process and to improve the stability of the electrolyte described above, at least one type of halide ion is preferably included in the aqueous solution. The content of halide ions is not particularly limited. The content of halide ions is preferably 0.05 mol/L or more. The content is preferably 3.0 mol/L or less. The content is more preferably 0.10 mol/L or more. The content is more preferably 2.5 mol/L or less. BluCr® TFS C1 and BluCr® TFS C2, produced by Atotech, can be used to include the halide ions.

[0068] Hexavalent chromium is preferably not added to the aqueous solution described above. Except for a very small amount of hexavalent chromium formed at the anode in the cathodic electrolysis treatment process, there is no hexavalent chromium in the electrolyte described above. The concentration of hexavalent chromium in the electrolyte does not increase because the very small amount of hexavalent chromium formed at the anode in the cathodic electrolysis treatment process is reduced to trivalent chromium.

[0069] The aqueous solution described above preferably has no metal ions other than trivalent chromium ions intentionally added. The metal ions are not particularly limited, but examples include Cu ions, Zn ions, Ni ions, Fe ions, Sn ions, and the like. Concentration of such metal ions is preferably 0 mg/L or more and 40 mg/L or less. Concentration is

more preferably 0 mg/L or more and 20 mg/L or less. Concentration is most preferably 0 mg/L or more and 10 mg/L or less. Of the above metal ions, Ni ions may dissolve in the electrolyte and co-precipitate in the coating when the steel sheet is immersed in the electrolyte described above during the cathodic electrolysis treatment process, but this does not affect film wet adhesion, coating secondary adhesion, or weldability. Ni ion concentration is preferably 0 mg/L or more and 40 mg/L or less. Ni ion concentration is more preferably 0 mg/L or more and 20 mg/L or less. Ni ion concentration is most preferably 0 mg/L or more and 10 mg/L or less. Although the Ni ion concentration is preferably in a range described above during the bath, the Ni ion concentration in the electrolyte is preferably also maintained in a range described above during the cathodic electrolysis treatment process. When the Ni ions are controlled within a range described above, the Ni ions do not inhibit the formation of the metallic Cr layer or the Cr oxide layer, and the metallic Cr layer and the Cr oxide layer can be formed to have the required thickness.

(ii) Adjustment of pH and temperature

[0070] The electrolyte is then prepared by adjusting the pH of the aqueous solution to 4.0 to 7.0 and the temperature of the aqueous solution to 40 °C to 70 °C. To produce the surface-treated steel sheet described above, simply dissolving the trivalent chromium ion source and the carboxylic acid compound in water is insufficient; it is important to appropriately control the pH and temperature as described above.

pH: 4.0 to 7.0

[0071] In the electrolyte solution preparation process, the pH of the aqueous solution after mixing is adjusted to 4.0 to 7.0. When the pH is less than 4.0 or greater than 7.0, the water contact angle of a surface-treated steel sheet produced using the resulting electrolyte is more than 50°. The pH is preferably 4.5 to 6.5.

Temperature: 40 °C to 70 °C

[0072] In the electrolyte preparation process, the temperature of the aqueous solution after mixing is adjusted to 40 °C to 70 °C. When the temperature is less than 40 °C or greater than 70 °C, the water contact angle of a surface-treated steel sheet produced using the resulting electrolyte is more than 50°. Holding time in the temperature range from 40 °C to 70 °C is not particularly limited.

[0073] The above procedure can be used to obtain the electrolyte to be used in the following cathodic electrolysis treatment process. The electrolyte produced by the above procedure can be stored at room temperature.

[Cathodic electrolysis treatment process]

[0074] Next, the steel sheet including the Ni-containing layer on at least one surface is subjected to cathodic electrolysis treatment in the electrolyte obtained by the electrolyte preparation process. The cathodic electrolysis treatment can form the metallic Cr layer and the Cr oxide layer on the Ni-containing layer.

[0075] The temperature of the electrolyte during the cathodic electrolysis treatment is not particularly limited. To efficiently form the metallic Cr layer and the Cr oxide layer, the temperature is preferably in a temperature range from 40 °C or more to 70 °C or less. From the viewpoint of stable production of the surface-treated steel sheet described above, temperature of the electrolyte during the cathodic electrolysis treatment process is preferably monitored and maintained in the temperature range described above.

[0076] The pH of the electrolyte during the cathodic electrolysis treatment is not particularly limited. The pH is preferably 4.0 or more. The pH is more preferably 4.5 or more. Further, the pH is preferably 7.0 or less. The pH is more preferably 6.5 or less. From the viewpoint of stable production of the surface-treated steel sheet described above, the pH of the electrolyte in the cathodic electrolysis treatment process is preferably monitored and maintained within a pH range described above.

[0077] The current density in the cathodic electrolysis treatment is not particularly limited and may be adjusted as appropriate to form the desired surface-treated layer. However, excessively high current density may increase the C content in the metallic Cr layer and degrade weldability. Therefore, the current density is preferably less than 5.0 A/dm². The current density is preferably 3.0 A/dm² or less. A lower limit of current density is not particularly limited, but when the current density is excessively low, hexavalent Cr may be formed in the electrolyte and stability of the bath may be disrupted. The current density is therefore preferably 0.01 A/dm² or more. The current density is more preferably 0.03 A/dm² or more.

[0078] The number of times cathodic electrolysis treatment is applied to a steel sheet is not particularly limited and may be any number of times. In other words, cathodic electrolysis treatment may be performed using an electrolytic processing apparatus with any number of passes, one or two or more. For example, conducting cathodic electrolysis treatment continuously by passing a steel sheet (steel strip) through multiple times during transport is preferable. As the number of cathodic electrolytic treatments (that is, number of passes) increases, a commensurate number of electrolyzers is

required, and therefore the number of cathodic electrolysis treatments (number of passes) is preferably 20 or less.

[0079] The electrolysis time per pass is not particularly limited. However, when the electrolysis time per pass is too long, the steel sheet transport speed (line speed) is reduced and productivity decreases. The electrolysis time per pass is therefore preferably 5 s or less. The electrolysis time per pass is more preferably 3 s or less. A lower limit of electrolysis time per pass is also not particularly limited, but when the electrolysis time is excessively short, the line speed needs to be increased accordingly, making control difficult. The electrolysis time per pass is therefore preferably 0.005 s or more. The electrolysis time per pass is more preferably 0.01 s or more.

[0080] The amount of metallic Cr formed by the cathodic electrolysis treatment can be controlled by total electric quantity density, expressed as the product of current density, electrolysis time, and number of passes. As mentioned above, an excessively high amount of metallic Cr may increase contact resistance and impair weldability, and an excessively low amount of metallic Cr may impair corrosion resistance, and therefore the total electric quantity density is preferably controlled so that the Cr coating weight per side of the steel sheet of the metallic Cr layer is 2 mg/m² or more and less than 40 mg/m². However, the relationship between the amount of metallic Cr and the total electric quantity density varies with the configuration of the equipment used in the cathodic electrolysis treatment process, and therefore actual electrolysis treatment conditions may be adjusted to suit the equipment.

[0081] The type of anode used when conducting the cathodic electrolysis treatment is not particularly limited, and any anode may be used. As the anode, an insoluble anode is preferably used. As the insoluble anode, it is preferable to use at least one selected from the group consisting of a graphite anode and an anode in which Ti is coated with one or both of a platinum group metal or an oxide of a platinum group metal. More specifically, an example of the insoluble anode is an anode coated with platinum, iridium oxide, or ruthenium oxide on the surface of Ti as a substrate.

[0082] In the cathodic electrolysis treatment process, the concentration of the electrolyte is constantly changing due to the formation of the metallic Cr layer and the Cr oxide layer on the steel sheet, being brought in and out of the solution, evaporation of water, and the like. Changes in the concentration of the electrolyte in the cathodic electrolysis treatment process vary with the configuration of equipment and production conditions, and therefore from the viewpoint of more stable production of surface-treated steel sheets, the concentration of the components in the electrolyte in the cathodic electrolysis treatment process are preferably monitored and maintained within the concentration ranges described above.

[0083] Prior to the cathodic electrolysis treatment, the steel sheet including a Ni-containing layer can optionally be pretreated. The pretreatment removes a natural oxide coating on the surface of the Ni-containing layer and activates the surface. The pretreatment method is not particularly limited and any method may be used. For example, pickling by immersion in dilute sulfuric acid may be used.

[0084] After the pretreatment, the steel sheet is preferably water washed from the viewpoint of removing pretreatment coating solution adhering to the surface.

[0085] Further, when forming the Ni-containing layer on the surface of the base steel sheet, pretreatment is preferably performed on the base steel sheet. As the pretreatment, any pretreatment can be performed, but preferably at least one of the following is performed: degreasing, pickling, or water washing.

[0086] Degreasing removes rolling oil, anti-rust oil, and the like adhered to steel sheets. The degreasing may be performed by any method without particular limitation. After degreasing, water washing is preferably performed to remove degreasing treatment solution from the steel sheet surface.

[0087] Further, pickling removes a natural oxide coating on the surface of the steel sheet and activates the surface. The pickling may be performed by any method without particular limitation. After pickling, water washing is preferably performed to remove pickling treatment solution from the steel sheet surface.

[Water washing]

[0088] Next, the steel sheet is water washed at least once after the cathodic electrolysis treatment. Water washing removes residual electrolyte from the surface of the steel sheet. The water washing may be performed by any method without particular limitation. For example, a water washing tank may be installed downstream of an electrolyzer for the cathodic electrolysis treatment, and steel sheets may be continuously immersed in water after the cathodic electrolysis treatment. Further, water washing may be performed by spraying water on the steel sheet after the cathodic electrolysis treatment.

[0089] The number of times water washing is performed is not particularly limited and may be performed once, twice or more. However, to avoid an excessively large number of water washing tanks, the number of times water washing is performed is preferably limited to five or less. Further, when water washing is performed two or more times, each water wash may be performed in the same or a different manner.

[0090] According to the present disclosure, it is important to use water having an electrical conductivity of 100 μ S/m or less in at least the last water wash of the water washing process. This reduces the amount of K, Na, Mg, and Ca adsorbed on the surface of the surface-treated steel sheet and thus improves adhesion. Water having an electrical conductivity of 100 μ S/m or less may be produced by any method. The water having an electrical conductivity of 100 μ S/m or less may be,

for example, deionized water or distilled water. A lower limit of the electrical conductivity is not particularly limited, but an excessive reduction leads to an increase in production costs. From the viewpoint of production cost, the electrical conductivity is therefore preferably 1 $\mu\text{S/m}$ or more. The electrical conductivity is more preferably 5 $\mu\text{S/m}$ or more. The electrical conductivity is even more preferably 10 $\mu\text{S/m}$ or more.

[0091] When water washing is performed twice or more in the water washing process, the above-mentioned effect can be obtained by using water having an electrical conductivity of 100 $\mu\text{S/m}$ or less for the last water wash, and therefore any water may be used for each water wash other than the last water wash. Water having an electrical conductivity of 100 $\mu\text{S/m}$ or less may be used for any water wash other than the last water wash, but from the viewpoint of cost reduction, water having an electrical conductivity of 100 $\mu\text{S/m}$ or less is preferably used only for the last water wash and normal water, such as tap water or industrial water, is preferably used for all water washes except the last water wash.

[0092] From the viewpoint of further decreasing the amount of K, Na, Mg, and Ca adsorbed on the surface of the surface-treated steel sheet, the electrical conductivity of the water used for the final water wash is preferably 50 $\mu\text{S/m}$ or less. The electrical conductivity is more preferably 30 $\mu\text{S/m}$ or less.

[0093] The temperature of water used for water washing treatment is not particularly limited and may be any temperature. However, excessively high temperature places an excessive burden on water washing equipment, and therefore the temperature of the water used for water washing is preferably 95 °C or less. A lower limit of the temperature of water used for water washing is also not particularly limited. The temperature is preferably 0 °C or more. The temperature of the water used in the water washing may be room temperature.

[0094] Water washing time per water washing treatment is not particularly limited. From the viewpoint of increasing the effectiveness of water washing treatment, water washing time per water washing treatment is preferably 0.1 s or more. Water washing time is more preferably 0.2 s or more. An upper limit of water washing time per water washing treatment is also not particularly limited. When producing on a continuous line, line speed is decreased and productivity decreased, and therefore water washing time is preferably 10 s or less. Water washing time is preferably 8 s or less.

[0095] After the water washing process, drying may optionally be performed. Drying methods are not particularly limited. For example, ordinary dryers or electric furnace drying methods may be applied. A temperature of 100 °C or less is preferred for drying treatment. Within the above range, transformation of the surface-coating layer can be suppressed. A lower limit is not particularly limited, but is normally around room temperature.

[0096] Applications of the surface-treated steel sheet are not particularly limited. The surface-treated steel sheet is particularly suitable as a surface-treated steel sheet for containers, to be used in the production of various types of container, such as food cans, beverage cans, pails, and 18-liter cans, for example.

EXAMPLES

[0097] To determine the effect of the present disclosure, surface-treated electrical steel sheets were produced by the following procedures and their properties were evaluated.

(Electrolyte preparation process)

[0098] First, electrolytes having compositions A to G listed in Table 1 were prepared under conditions listed in Table 1. That is, each of the components listed in Table 1 was mixed with water to form an aqueous solution, and then the aqueous solution was adjusted to the pH and temperature listed in Table 1. The electrolyte G corresponds to the electrolyte used in the example in PTL 6. Ammonia water was used for each pH increase, while for pH decreases, sulfuric acid was used for electrolytes A, B, and G, hydrochloric acid was used for electrolytes C and D, and nitric acid was used for electrolytes E and F.

(Formation of Ni-containing layer)

[0099] Ni electroplating was applied to both sides of each steel sheet to obtain a Ni plated steel sheet with a Ni plated layer as the Ni-containing layer on both sides of the steel sheet. A Watts bath was used for the Ni electroplating described above. Prior to Ni electroplating, the steel sheets were subjected to electrolyte degreasing, water washing, pickling by immersion in dilute sulfuric acid, and water washing in this sequence. In the Ni electroplating, the Ni coating weight of the Ni plated layer was set to the values listed in Tables 2 and 3 by changing the electric quantity density. The Ni coating weight of the Ni-containing layer was measured by the X-ray fluorescence calibration curve method described above. After the Ni plated layer was formed and water washed, the Ni plated layer was kept wet for the following cathodic electrolysis treatment process. In some cases, a Ni-Fe alloy layer was formed as the Ni-containing layer. That is, after forming the Ni plated layer by the method described above, the Ni-Fe alloy layer was formed by annealing.

[0100] As the steel sheets, steel sheets for cans (T4 base sheet) having Cr content values listed in Tables 2 and 3 and a thickness of 0.17 mm were used.

(Cathodic electrolysis treatment process)

[0101] Next, the Ni plated steel sheets were subjected to cathodic electrolysis treatment under the conditions listed in Tables 2 and 3. The electrolyte during the cathodic electrolysis treatment process was maintained at the pH and temperature listed in Table 1. The electric quantity densities during the cathodic electrolysis treatment process were as listed in Tables 2 and 3, and the electrolysis time and number of passes were varied accordingly. An insoluble anode of Ti as a substrate coated with iridium oxide was used as the anode during the cathodic electrolysis treatment process. After the cathodic electrolysis treatment, water washing and drying at room temperature using a blower were carried out.

[Water washing process]

[0102] Next, water washing treatment was applied to the steel sheets after the cathodic electrolysis treatment. The water washing treatment was performed 1 to 5 times under the conditions listed in Tables 2 and 3. The method of each water wash and the electrical conductivity of the water used are listed in Tables 2 and 3.

[0103] For each of the surface-treated steel sheets obtained, the Cr coating weight per side of the steel sheet of the metallic Cr layer and Cr coating weight per side of the steel sheet of the Cr oxide layer were measured by the method described above. Similarly, the C atomic ratio of the metallic Cr layer was measured by the method described above. The "C atomic ratio" of the metallic Cr layer listed in Tables 4 and 5 is the value of C content in the metallic Cr layer expressed as an atomic ratio to Cr. The water contact angle, amount of adsorbed elements, and atomic ratio of Ni on the outermost surface of each of the surface-treated steel sheets obtained were measured by the following methods. The measurement results are listed in Tables 4 and 5.

(Water contact angle)

[0104] The water contact angle was measured using an automatic contact angle meter model CA-VP, produced by Kyowa Interface Science Co., Ltd. The surface temperature of the surface-treated steel sheet was $20\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$, and distilled water was used at $20\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. Distilled water was dropped onto the surface of the surface-treated steel sheet in 2 μl droplet volume, the contact angle was measured after 1 s by the 0/2 method, and the arithmetic mean of contact angles for five droplets was taken as the water contact angle.

(Amount of adsorbed elements)

[0105] The total atomic ratio of K, Na, Mg, and Ca adsorbed on the surface of each surface-treated steel sheet to Cr was measured by XPS. No sputtering was performed in the measurements. The atomic ratios were quantified from the integrated intensities of the narrow spectra of K2p, Nals, Ca2p, Mg1s, and Cr2p at the outermost surface of each sample by the relative sensitivity coefficient method, and $(\text{K atomic ratio} + \text{Na atomic ratio} + \text{Ca atomic ratio} + \text{Mg atomic ratio}) / \text{Cr atomic ratio}$ was calculated. For the XPS measurements, a scanning X-ray photoelectron spectroscopy analyzer PHI X-tool, produced by Ulvac Phi, Inc. was used. The X-ray source was a monochrome $\text{AlK}\alpha$ beam, the voltage was 15 kV, the beam diameter was 100 μm , and the extraction angle was 45° .

(Atomic ratio of Ni at outermost surface)

[0106] The atomic ratio of Ni content to Cr at the outermost surface of each surface-treated steel sheet was measured by XPS. No sputtering was performed in the measurements. The atomic ratios were quantified from the integrated intensities of the narrow spectra of Ni2p and Cr2p at the outermost surface of each sample by the relative sensitivity coefficient method, and the Ni atomic ratio / Cr atomic ratio was calculated. For the XPS measurements, a scanning X-ray photoelectron spectroscopy analyzer PHI X-tool, produced by Ulvac Phi, Inc. was used. The X-ray source was a monochrome $\text{AlK}\alpha$ beam, the voltage was 15 kV, the beam diameter was 100 μm , and the extraction angle was 45° .

[0107] Further, the surface-treated steel sheets were evaluated for film wet adhesion, coating secondary adhesion, and weldability by the following methods. The evaluation results are listed in Tables 4 and 5.

(Sample preparation)

[0108] Laminated steel sheets as samples used to evaluate film corrosion resistance and film wet adhesion were prepared according to the following procedure.

[0109] The surface-treated steel sheets were laminated on both sides with isophthalic acid copolymerized polyethylene terephthalate film having a stretch ratio of 3.1×3.1 , a thickness of 25 μm , a copolymerization ratio of 12 mol%, and a melting point of $224\text{ }^{\circ}\text{C}$ to produce laminated steel sheets. The lamination was performed under conditions where the

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crystallinity of the resin film was 10 % or less, and specifically, a steel sheet feed rate of 40 m/min, a rubber roll nip length of 17 mm, and a time from pressing to water cooling of 1 s. The crystallinity of the resin film was determined by a density gradient tube method in accordance with Japanese Industrial Standard JIS K7112. Further, nip length is the length in the transport direction of a portion where the rubber rolls and the steel sheet come in contact.

[0110] Further, prepainted steel sheets as samples used to evaluate coating corrosion resistance and coating secondary adhesion were prepared by the following procedure.

[0111] The surface of the surface-treated steel sheets was coated with epoxy phenolic paint and baked at 210 °C for 10 min to produce prepainted steel sheets. The coating weight of the coating was 50 mg/dm².

(Film corrosion resistance, coating corrosion resistance)

[0112] Cross cuts were made on the film side of the produced laminated steel sheet and on the coated side of the prepainted steel sheet using a cutter to a depth that reaches the steel substrate (steel sheet). The laminated steel sheets and the prepainted steel sheets with crosscuts were immersed in test solutions at 55 °C each consisting of a mixed aqueous solution containing 1.5 mass% citric acid and 1.5 mass% salt for 96 h. After immersion, washing and drying, cellophane adhesive tape was applied to the film side of the laminated steel sheet and the coated side of the prepainted steel sheet, and peeled off to carry out tape separation. For film corrosion resistance, film separation width (total width on both sides extending from the cut) was measured at four arbitrary locations at the crosscut of the laminated steel sheet, and the average value of the four locations was obtained and considered as corrosion width. For coating corrosion resistance, the coating separation width (total width on both sides extending from the cut) was measured at four arbitrary locations at the crosscut of the prepainted steel sheet, and the average of the four locations was obtained and considered as corrosion width. Film corrosion resistance and coating corrosion resistance were evaluated at the following four levels. For practical use, an evaluation of 1 to 3 indicates excellent corrosion resistance.

- 1: corrosion width less than 0.3 mm
- 2: corrosion width 0.3 mm or more and less than 0.5 mm
- 3: corrosion width 0.5 mm or more and less than 1.0 mm
- 4: corrosion width 1.0 mm or more

(Film wet adhesion)

[0113] Film wet adhesion was evaluated by a 180° peel test in a retort atmosphere at a temperature of 130 °C and 100 % relative humidity using the laminated steel sheets. The specific procedures were as follows.

[0114] First, a total of six test pieces were cut from each of the laminated steel sheets, three test pieces with a front surface as the target surface and three test pieces with a back surface as the target surface. The size of each test piece was 30 mm wide and 100 mm long. Next, at 15 mm from an upper portion of each test piece in the longitudinal direction, the film on the target side was left and the film and steel sheet on the side opposite the target side were cut. After cutting, the test piece was fixed so that the steel sheet was perpendicular to the ground, a portion from a lower portion to 15 mm in the longitudinal direction of the test piece being fixed, and a 30 mm wide and 15 mm long portion past the cut position hanging down, connected by the film on the target surface. Then, a 100 g weight was attached to the 30 mm wide and 15 mm long portion that was hanging down.

[0115] The test pieces in this condition were each left in a retort atmosphere at a temperature of 130 °C and 100 % relative humidity for 30 min and then opened to the air. The length at which the film on the target surface peeled away from the surface-treated steel sheet was defined as the film separation length, and the average film separation length for the six test pieces was determined for each laminated steel sheet. The average film separation length obtained was used to evaluate film wet adhesion at the following four levels. For practical use, an evaluation of 1 to 3 indicates excellent film wet adhesion.

- 1: separation length less than 20 mm
- 2: separation length 20 mm or more and less than 40 mm
- 3: separation length 40 mm or more and less than 60 mm
- 4: separation length 60 mm or more

(Coating secondary adhesion)

[0116] Two prepainted steel sheets made under the same conditions were stacked so that coated surfaces faced each other with a nylon adhesive film in between, and then bonded together under pressure of 2.94×10^5 Pa, a temperature of 190 °C, and compression time of 30 s. The stack was then portioned into 5 mm wide test pieces. The portioned test pieces

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were immersed in a test solution at 55 °C consisting of a mixed aqueous solution containing 1.5 mass% citric acid and 1.5 mass% salt for 168 h. After immersion, washing and drying, the two steel sheets of each of the portioned test pieces were pulled apart in a tensile testing machine, and the tensile strength when pulled apart was measured. The average of three test pieces was evaluated at the following four levels. For practical use, an evaluation of 1 to 3 indicates excellent coating secondary adhesion.

- 1: 2.5 kgf or more
- 2: 2.0 kgf or more and less than 2.5 kgf
- 3: 1.5 kgf or more and less than 2.0 kgf
- 4: Less than 1.5 kgf

(Weldability)

[0117] After the surface-treated steel sheets were subjected to heat treatment at 210 °C × 10 min, assuming a coating baking process, two samples were sandwiched between DR-type 1 mass% Cr-Cu electrodes (electrodes machined to have 2.3 mm tip diameter and R 40 mm curvature) and welded under the following conditions.

- Transistorized power source produced by Amada Co., Ltd.: MDA-8000A
- Welding head: AH-200
- Pressurization: 40 kgf
- Current passage time: 1.6 ms (slope 0.2 ms)
- Waveform: square wave

[0118] An appropriate current range (= upper limit current - lower limit current) was determined from the lower limit current at which sufficient intensity can be obtained and the upper limit current at which no spattering occurs, and evaluated at the following four levels. For practical use, an evaluation of 1 to 3 indicates excellent weldability.

- 1: 2.5 kA or more
- 2: 2.0 kA or more and less than 2.5 kA
- 3: 1.5 kA or more and less than 2.0 kA
- 4: less than 1.5 kA

[0119] As is clear from Tables 4 and 5, the surface-treated steel sheets meeting the conditions of the present disclosure all had excellent film corrosion resistance, coating corrosion resistance, film wet adhesion, coating secondary adhesion, and weldability, even though produced without the use of hexavalent chromium.

[Table 1]

[0120]

Table 1

Electrolyte		A	B	C	D	E	F	G
Composition (mol/L)	Cr(OH) SO ₄ ·Na ₂ SO ₄	-	-	-	-	-	-	0.39
	Cr ₂ (SO ₄) ₃	0.1	0.2	-	-	-	-	-
	CrCl ₃	-	-	0.2	0.5	-	-	-
	Cr(NO ₃) ₃	-	-	-	-	0.2	0.5	-
	HCO ₂ H	4.2	-	0.4	-	4.8	-	-
	NH ₄ CHO ₂	-	0.5	-	3.5	-	0.5	-
	HCO ₂ K	-	-	-	-	-	-	0.61
	NH ₄ Cl	1.1	1.4	0.7	-	1.5	-	-
	NH ₄ Br	-	0.3	0.6	0.4	0.2	1.3	-

(continued)

Electrolyte		A	B	C	D	E	F	<u>G</u>
5	KCl	-	-	-	-	-	-	3.35
	KBr	-	-	-	-	-	-	0.13
pH		5.0	5.7	5.1	4.3	6.8	5.8	<u>2.3</u>
Temperature (°C)		42	50	65	55	55	53	50
10	Remarks	Example	Example	Example	Example	Example	Example	Comparative Example

[Table 2]

[0121]

Table 2

No.	Production conditions															Remarks
	Steel sheet	Ni-containing layer	Cathodic electrolysis treatment				Water washing									
Cr content [%]	Type	Ni coating weight [mg/m ²]	Electrolyte	Current density [A/dm ²]	Electric quantity density [C/dm ²]	1st		2nd		3rd		4th		5th		
						Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	
1	0.04	Ni	A	0.15	210	Immer-sion	23	-	-	-	-	-	-	-	-	Example
2	0.04	Ni	B	1.30	1.30	Spray	11	-	-	-	-	-	-	-	-	Example
3	0.04	Ni	C	0.50	1.25	Spray	16	Immer-sion	26	-	-	-	-	-	-	Example
4	0.04	Ni	D	0.90	1.80	Spray	8	Spray	29	-	-	-	-	-	-	Example
5	0.04	Ni	E	2.90	4.35	Spray	9	Immer-sion	15	Immer-sion	12	-	-	-	-	Example
6	0.04	Ni	F	0.35	4.90	Immer-sion	29	Immer-sion	8	Spray	19	-	-	-	-	Example
7	0.04	Ni	A	2.85	6.27	Spray	11	Immer-sion	4	Immer-sion	27	Immer-sion	21	-	-	Example
8	0.04	Ni	B	0.05	3.25	Immer-sion	3	Immer-sion	25	Spray	21	Spray	14	-	-	Example
9	0.04	Ni	C	0.35	3.15	Immer-sion	6	Immer-sion	18	Immer-sion	10	Immer-sion	21	Immer-sion	13	Example
10	0.04	Ni	D	0.65	5.20	Immer-sion	11	Spray	22	Spray	14	Immer-sion	17	Spray	26	Example

(continued)

No.	Production conditions																Remarks
	Steel sheet	Ni-containing layer	Cathodic electrolysis treatment			Water washing											
Cr content [%]	Type	Ni coating weight [mg/m ²]	Electrolyte	Current density [A/dm ²]	Electric quantity density [C/dm ²]	1st		2nd		3rd		4th		5th			
						Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]		
11	0.04	Ni-Fe	287	E	0.75	3.75	Immersion	62	Immersion	23	Spray	28	-	-	-	-	
12	0.04	Ni-Fe	1796	F	0.10	1.55	Immersion	109	Spray	18	Spray	30	-	-	-	-	
13	0.04	Ni-Fe	1983	A	0.60	123	Immersion	19	Immersion	268	Spray	12	-	-	-	-	
14	0.04	Ni-Fe	1230	B	0.50	1.45	Immersion	22	Spray	56	Spray	17	-	-	-	-	
15	0.04	Ni-Fe	929	C	0.20	1.70	Immersion	51	Immersion	112	Spray	26	-	-	-	-	
16	0.04	Ni-Fe	789	D	210	315	Immersion	45	Spray	38	Spray	27	-	-	-	-	
17	0.04	Ni	306	E	1.90	2.66	Immersion	38	-	-	-	-	-	-	-	-	
18	0.04	Ni	465	F	1.20	5.76	Spray	42	-	-	-	-	-	-	-	-	
19	0.04	Ni	328	A	1.30	7.80	Immersion	58	-	-	-	-	-	-	-	-	
20	0.04	Ni	402	B	2.60	5.46	Spray	83	-	-	-	-	-	-	-	-	
21	0.04	Ni	267	C	0.06	4.32	Immersion	<u>211</u>	-	-	-	-	-	-	-	Comparative Example	

(continued)

Production conditions																	Remarks
Steel sheet	Ni-containing layer	Cathodic electrolysis treatment			Water washing												
					1st		2nd		3rd		4th		5th				
					Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]			
No.	Cr content [%]	Type	Ni coating weight [mg/m ²]	Electrolyte	Current density [A/dm ²]	Electric quantity density [C/dm ²]	Spray	<u>152</u>	-	-	-	-	-	-	-	-	
							Immersion	21	Immersion	49	-	-	-	-	-	-	
							Immersion	25	Spray	32	-	-	-	-	-	-	
							Immersion	10	Immersion	66	-	-	-	-	-	-	
							Immersion	5	Spray	78	-	-	-	-	-	-	
							Immersion	7	Immersion	<u>113</u>	-	-	-	-	-	-	
No.	Cr content [%]	Type	Ni coating weight [mg/m ²]	Electrolyte	Current density [A/dm ²]	Electric quantity density [C/dm ²]	Immersion	21	Spray	<u>109</u>	-	-	-	-	-	-	
							Immersion	29	Immersion	17	Immersion	36	-	-	-	-	
							Immersion	9	Immersion	22	Spray	41	-	-	-	-	
							Immersion	255	Immersion	5.61	Immersion	5.61	Immersion	5.61	Immersion	5.61	
							Immersion	1.30	Immersion	1.30	Immersion	1.30	Immersion	1.30	Immersion	1.30	
							Immersion	1.30	Immersion	1.30	Immersion	1.30	Immersion	1.30	Immersion	1.30	

[Table 3]

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[0122]

Table 3

No.	Production conditions															Remarks
	Steel sheet	Ni-containing layer	Cathodic electrolysis treatment			Water washing										
Cr content [%]	Type	Ni coating weight [mg/m ²]	Electric quantity density [A/d-m ²]	Current density [A/d-m ²]	Electrolyte	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]	Method	Conduc-tivity [μS/m]		
31	0.04	Ni	A	2.20	2.20	Immer-sion	12	Spray	29	Immer-sion	52	-	-	-	-	Example
32	0.04	Ni	B	0.07	3.64	Immer-sion	14	Immer-sion	21	Spray	98	-	-	-	-	Example
33	0.04	Ni	C	0.50	4.00	Immer-sion	10	Spray	4	Immer-sion	<u>135</u>	-	-	-	-	Compara-tive Ex-ample
34	0.04	Ni	D	0.70	4.27	Immer-sion	12	Immer-sion	7	Spray	<u>189</u>	-	-	-	-	Compara-tive Ex-ample
35	0.04	Ni	E	0.25	5.55	Immer-sion	19	Immer-sion	24	Spray	15	Immer-sion	48	-	-	Example
36	0.04	Ni	F	0.60	3.00	Immer-sion	27	Spray	15	Immer-sion	12	Spray	43	-	-	Example
37	0.04	Ni	A	1.00	7.00	Immer-sion	10	Immer-sion	19	Spray	11	Immer-sion	77	-	-	Example
38	0.04	Ni	B	1.90	5.89	Spray	17	Immer-sion	24	Spray	28	Spray	63	-	-	Example

(continued)

Production conditions																	
No.	Steel sheet	Ni-containing layer		Cathodic electrolysis treatment			Water washing								Remarks		
	Cr content [%]	Type	Ni coating weight [mg/m ²]	Electrolyte	Current density [A/dm ²]	Electric quantity density [C/dm ²]	1st		2nd		3rd		4th			5th	
							Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]		Method	Conductivity [μS/m]
39	0.04	Ni	1826	C	0.28	3.08	Immersion	21	Immersion	29	Spray	13	Immersion	106	-	-	Comparative Example
40	0.04	Ni	293	D	1.10	4.40	Spray	25	Immersion	24	Spray	22	Spray	103	-	-	Comparative Example
41	0.04	Ni	689	E	1.50	4.50	Immersion	8	Spray	18	Spray	16	Immersion	21	Immersion	31	Example
42	0.04	Ni	302	F	1.80	2.70	Immersion	26	Spray	24	Immersion	17	Immersion	14	Spray	45	Example
43	0.04	Ni	405	A	2.20	2.53	Immersion	19	Immersion	7	Spray	22	Immersion	9	Immersion	59	Example
44	0.04	Ni	379	B	2.90	1.16	Immersion	10	Immersion	9	Spray	28	Immersion	10	Spray	84	Example
45	0.04	Ni	338	C	3.00	1.95	Immersion	20	Immersion	15	Spray	21	Immersion	16	Immersion	255	Comparative Example
46	0.04	Ni	368	D	2.20	2.20	Immersion	16	Immersion	20	Spray	25	Immersion	14	Spray	108	Comparative Example

(continued)

Production conditions															Remarks
No.	Steel sheet	Ni-containing layer	Cathodic electrolysis treatment			Water washing									
						1st		2nd		3rd		4th		5th	
			Type	Ni coating weight [mg/m ²]	Electrolyte	Current density [A/dm ²]	Electric quantity density [C/dm ²]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	Conductivity [μS/m]	Method	
47	0.04	Ni	1481	E	1.60	7.28	<u>None</u>	-	-	-	-	-	-	-	Comparative Example
48	0.04	Ni	809	<u>G</u>	1.20	3.60	Immersion	11	Immersion	16	Spray	21	-	-	Comparative Example
49	0.04	Ni	723	<u>G</u>	5.60	4.20	Immersion	12	Spray	24	Immersion	8	-	-	Comparative Example
50	0.04	Ni	234	A	1.40	5.74	Spray	16	Spray	15	-	-	-	-	Example
51	0.04	Ni	189	B	1.50	6.60	Spray	17	Spray	12	-	-	-	-	Example
52	0.04	Ni	503	D	3.60	1.32	Spray	8	Spray	24	-	-	-	-	Example
53	0.04	Ni	226	E	5.40	1.15	Spray	10	Spray	22	-	-	-	-	Example
54	0.04	Ni	436	A	2.40	0.96	Spray	8	Spray	24	-	-	-	-	Example
55	0.04	Ni	609	B	1.50	0.75	Spray	10	Spray	22	-	-	-	-	Example
56	0.04	Ni	668	A	0.60	8.40	Spray	24	Spray	16	-	-	-	-	Example
57	0.04	Ni	1630	B	1.50	9.60	Spray	16	Spray	14	-	-	-	-	Example
58	0.09	Ni	810	D	0.70	4.90	Spray	15	Spray	12	-	-	-	-	Example
59	0.12	Ni	653	F	0.85	4.25	Spray	26	Spray	11	-	-	-	-	Example

[Table 4]

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[0123]

Table 4

No.	Measurement results						Evaluation					Remarks
	Metallic Cr layer		Cr oxide layer	Water contact angle [°]	Atomic ratio of adsorbed elements* 1 [%]	Ni atomic ratio *2 [%]	Film corrosion resistance	Coating corrosion resistance	Film wet adhesion	Coating secondary adhesion	Weldability	
	Cr coating weight [mg/m ²]	C atomic ratio [%]	Cr coating weight [mg/m ²]									
1	10.3	13.5	2.2	43.5	0.0	24.5	1	1	1	1	1	Example
2	4.6	23.4	3.5	34.5	0.0	56.3	1	1	1	1	1	Example
3	5.7	9.8	5.6	12.3	0.0	4.6	1	1	1	1	1	Example
4	8.7	12.3	7.2	41.1	0.0	12.3	1	1	1	1	1	Example
5	17.6	16.9	1.3	23.1	0.7	22.4	1	1	1	1	1	Example
6	22.0	13.8	1.2	35.2	0.0	12.9	1	1	1	1	1	Example
7	34.5	14.7	0.5	15.8	0.0	7.8	1	1	1	1	1	Example
8	25.4	29.8	0.1	28.7	0.0	5.6	1	1	1	1	1	Example
9	13.4	8.9	4.6	24.1	0.0	12.8	1	1	1	1	1	Example
10	22.9	4.8	5.8	10.8	0.0	34.0	1	1	1	1	1	Example
11	15.0	13.0	9.2	17.8	0.0	13.5	1	1	1	1	1	Example
12	6.9	32.4	4.4	14.5	0.3	22.4	1	1	1	1	1	Example
13	4.8	20.9	3.0	26.4	0.0	18.8	1	1	1	1	1	Example
14	5.9	18.3	3.2	27.8	0.6	45.4	1	1	1	1	1	Example
15	7.9	11.0	5.6	32.2	0.0	67.8	1	1	1	1	1	Example
16	14.3	10.6	6.3	12.3	0.2	66.5	1	1	1	1	1	Example
17	12.3	32.3	2.1	7.8	1.5	54.3	2	2	2	2	1	Example
18	23.8	3.9	1.5	13.0	2.3	22.3	2	2	2	2	1	Example
19	34.0	6.5	1.2	8.9	3.7	25.6	3	3	3	3	1	Example
20	23.4	8.3	0.6	11.4	3.2	73.4	3	3	3	3	1	Example

(continued)

No.	Measurement results						Evaluation					Remarks
	Metallic Cr layer		Cr oxide layer	Water contact angle [°]	Atomic ratio of adsorbed elements* 1 [%]	Ni atomic ratio *2 [%]	Film corrosion resistance	Coating corrosion resistance	Film wet adhesion	Coating secondary adhesion	Weldability	
	Cr coating weight [mg/m ²]	C atomic ratio [%]	Cr coating weight [mg/m ²]									
21	17.9	16.3	5.6	5.3	15.8	12.5	4	4	4	4	1	Comparative Example
22	30.9	25.0	8.6	6.7	21.0	54.3	4	4	4	4	1	Comparative Example
23	5.6	11.2	5.4	1.9	44.8	13.4	2	2	2	2	1	Example
24	16.2	16.3	3.4	2.8	39.8	22.5	2	2	2	2	1	Example
25	32.5	17.4	12.3	4.6	32.1	2.8	3	3	3	3	1	Example
26	11.3	18.9	1.2	3.2	14.2	4.3	3	3	3	3	1	Example
27	8.0	7.4	3.4	5.7	26.4	16.9	4	4	4	4	1	Comparative Example
28	32.2	15.3	12.6	8.7	21.2	35.8	4	4	4	4	1	Comparative Example
29	23.3	10.4	13.4	2.3	47.5	65.4	2	2	2	2	1	Example
30	5.3	9.6	2.5	1.1	32.1	32.4	2	2	2	2	1	Example
* 1 Total atomic ratio of K., Na, Mg, and Ca adsorbed on the surface to Cr												
*2 Atomic ratio ofNi on the surface to Cr												

[Table 5]

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[0124]

Table 5

No.	Measurement results						Evaluation					Remarks
	Metallic Cr layer		Cr oxide layer	Water contact angle [°]	Atomic ratio of adsorbed elements * 1 [%]	Ni atomic ratio *2 [%]	Film corrosion resistance	Coating corrosion resistance	Film wet adhesion	Coating secondary adhesion	Weldability	
	Cr coating weight [mg/m ²]	C atomic ratio [%]										
31	8.9	12.4	4.5	27.6	3.6	24.6	3	3	3	3	1	Example
32	15.4	16.9	6.7	28.4	4.8	43.5	3	3	3	3	1	Example
33	16.7	32.6	4.3	23.6	5.3	12.4	4	4	4	4	1	Comparative Example
34	16.9	15.9	3.7	16.4	5.9	22.3	4	4	4	4	1	Comparative Example
35	22.3	17.9	2.8	6.0	2.2	15.6	2	2	2	2	1	Example
36	12.3	12.8	9.6	21.8	1.2	27.5	2	2	2	2	1	Example
37	28.9	15.0	7.4	24.1	3.4	34.2	3	3	3	3	1	Example
38	24.3	9.1	3.2	19.0	3.5	17.8	3	3	3	3	1	Example
39	13.9	5.4	1.2	16.4	5.6	34.2	4	4	4	4	1	Comparative Example
40	17.8	13.7	3.4	36.5	5.9	54.5	4	4	4	4	1	Comparative Example
41	19.5	4.9	6.5	25.0	2.1	32.5	2	2	2	2	1	Example
42	12.2	12.8	7.4	38.8	1.8	14.3	2	2	2	2	1	Example
43	10.6	6.7	3.0	13.2	4.6	77.4	3	3	3	3	1	Example
44	4.5	3.9	3.4	37.4	4.3	44.3	3	3	3	3	1	Example
45	7.9	13.9	4.2	16.3	6.7	32.6	4	4	4	4	1	Comparative Example
46	8.6	17.4	1.8	18.3	5.4	54.3	4	4	4	4	1	Comparative Example

(continued)

No.	Measurement results						Evaluation					Remarks
	Metallic Cr layer		Cr oxide layer	Water contact angle [°]	Atomic ratio of adsorbed elements * 1 [%]	Ni atomic ratio *2 [%]	Film corrosion resistance	Coating corrosion resistance	Film wet adhesion	Coating secondary adhesion	Weldability	
	Cr coating weight [mg/m ²]	C atomic ratio [%]	Cr coating weight [mg/m ²]									
47	28.7	22.9	2.7	<u>67.9</u>	<u>8.9</u>	27.3	4	4	4	4	1	Comparative Example
48	14.7	26.5	6.7	<u>73.4</u>	0.0	43.7	4	4	4	4	4	Comparative Example
49	16.4	43.4	8.6	<u>68.9</u>	0.0	15.4	4	4	4	4	4	Comparative Example
50	24.3	14.8	5.0	16.3	0.0	21.4	2	2	1	1	2	Example
51	27.1	10.8	4.3	8.9	0.0	53.7	3	3	1	1	3	Example
52	5.8	38.9	1.2	14.6	0.0	25.3	1	1	1	1	2	Example
53	4.8	42.5	8.9	17.6	0.4	12.4	1	1	1	1	3	Example
54	3.9	21.8	1.2	12.3	0.0	43.7	2	2	1	1	1	Example
55	1.8	16.7	0.6	6.7	0.3	38.6	3	3	1	1	1	Example
56	36.3	12.2	7.8	10.8	0.0	15.4	1	1	1	1	2	Example
57	42.4	16.9	2.3	15.4	0.0	7.8	1	1	1	1	3	Example
58	18.9	12.6	2.9	21.8	0.0	86.5	2	2	1	1	1	Example
59	16.5	11.2	3.1	32.3	0.0	110.3	3	3	1	1	1	Example
* 1 Total atomic ratio of K, Na, Mg, and Ca adsorbed on the surface to Cr												
* 2 Atomic ratio of Ni on the surface to Cr												

Claims

1. A surface-treated steel sheet comprising:

a steel sheet;
a Ni-containing layer disposed on at least one surface of the steel sheet;
a metallic Cr layer disposed on the Ni-containing layer; and
a Cr oxide layer disposed on the metallic Cr layer, the surface-treated steel sheet having:

a water contact angle of 50° or less, and
a total atomic ratio of K, Na, Mg, and Ca adsorbed on a surface to Cr of 5.0 % or less.

2. The surface-treated steel sheet according to claim 1, wherein the Ni-containing layer has a Ni coating weight of 200 mg/m² or more and 2000 mg/m² or less per side of the steel sheet.

3. The surface-treated steel sheet according to claim 1 or 2, wherein the metallic Cr layer has a Cr coating weight of 2 mg/m² or more and less than 40 mg/m² per side of the steel sheet.

4. The surface-treated steel sheet according to any one of claims 1 to 3, wherein the Cr oxide layer has a Cr coating weight of 0.1 mg/m² or more and 15.0 mg/m² or less per side of the steel sheet.

5. The surface-treated steel sheet according to any one of claims 1 to 4, having an atomic ratio of Ni on the surface of the surface-treated steel sheet to Cr of 100 % or less.

6. A method of producing a surface-treated steel sheet comprising a steel sheet; a Ni-containing layer disposed on at least one surface of the steel sheet; a metallic Cr layer disposed on the Ni-containing layer; and a Cr oxide layer disposed on the metallic Cr layer, the method comprising:

an electrolyte preparation process of preparing an electrolyte containing trivalent chromium ions;
a cathodic electrolysis treatment process of cathodic electrolysis treatment in the electrolyte of the steel sheet comprising the Ni-containing layer on at least one surface; and
a water washing process of at least one water wash of the steel sheet after the cathodic electrolysis treatment, wherein, in the electrolyte preparation process, the electrolyte is prepared by:

mixing a trivalent chromium ion source, a carboxylic acid compound, and water; and
adjusting the pH to 4.0 to 7.0 and adjusting the temperature to 40 °C to 70 °C, and

in the water washing process,
water having an electrical conductivity of 100 μS/m or less is used in at least the last water wash.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/006069

A. CLASSIFICATION OF SUBJECT MATTER

C25D 5/14(2006.01)i; *C25D 3/06*(2006.01)i; *C25D 5/26*(2006.01)i; *C25D 5/48*(2006.01)i
 FI: C25D5/14; C25D5/26 J; C25D5/48; C25D3/06

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)

C25D5/14; C25D3/06; C25D5/26; C25D5/48

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 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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 2020-200533 A (JFE STEEL CORP) 17 December 2020 (2020-12-17) claims, paragraph [0042]	1-6
A	JP 2009-035806 A (OKUNO CHEM IND CO LTD) 19 February 2009 (2009-02-19) claims, paragraphs [0009]-[0013], [0020]-[0036]	1-6
A	JP 2020-109205 A (THYSSENKRUPP RASSELSTEIN GMBH) 16 July 2020 (2020-07-16) paragraphs [0033], [0036], [0042]-[0043], [0048]	1-6
A	JP 2014-513214 A (ATOTECH DEUTSCHLAND GMBH) 29 May 2014 (2014-05-29) paragraphs [0076]-[0077], [0084]-[0088], [0095]	1-6
A	WO 2007/129979 A1 (SANDVIK INTELLECTUAL PROPERTY AB) 15 November 2007 (2007-11-15) p. 15, lines 5-10, table 3	1-6

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

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Date of the actual completion of the international search

13 April 2023

Date of mailing of the international search report

25 April 2023

Name and mailing address of the ISA/JP

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Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/006069

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JP 2020-200533 A	17 December 2020	(Family: none)	
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