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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 using hexavalent chromium and has excellent corrosion resistance at BPA-free painted worked part. A surface-treated steel sheet comprises: a steel sheet; and a chromium-containing layer disposed on a surface of the steel sheet on at least one side,

wherein when the chromium-containing layer is observed from a surface direction, linear regions in which an element smaller in atomic number than chromium is concentrated are present, and the number of the linear regions is 5.0 or more per 100 nm.

EP 4 520 857 A1

Description

TECHNICAL FIELD

5 **[0001]** The present disclosure relates to a surface-treated steel sheet, and in particular to a surface-treated steel sheet having excellent corrosion resistance at bisphenol A (BPA)-free painted worked part. The surface-treated steel sheet according to the present disclosure is suitable for use for containers such as cans. The present disclosure also relates to a production method for the surface-treated steel sheet.

10 BACKGROUND

[0002] Sn coated steel sheets (tinplate) and tin-free steel sheets (TFS) have been widely used as materials for various metal cans such as beverage cans, food cans, pails, and 18-liter cans.

15 **[0003]** Tinplate and TFS are used with organic resin coatings such as epoxy-based paint and PET films in order to accommodate various contents. When applying an organic resin coating to tinplate or TFS, a Cr (chromium) oxide layer formed on the outermost surface of the steel sheet by subjecting the steel sheet to electrolysis treatment or immersion treatment in an aqueous solution containing hexavalent Cr exhibits excellent adhesion to the organic resin coating layer. Thus, the deformation of the organic resin coating layer follows the deformation of the steel sheet during can production, as a result of which corrosion resistance to various contents is ensured after can production.

20 **[0004]** Meanwhile, given the indication that BPA contained in epoxy-based paint may be harmful to humans, development of BPA-free paint using polyester-based resin not containing BPA is underway (PTL 1 and PTL 2), and there is a demand to replace epoxy-based paint with BPA-free paint. However, tinplate and TFS that have been used have poor adhesion to BPA-free paint compared to epoxy-based paint. Accordingly, the deformation of the BPA-free paint cannot follow the deformation of the steel sheet during can production, and sufficient corrosion resistance to various contents cannot be ensured after can production. Hence, the application of BPA-free paint to various metal cans has not progressed.

[0005] In recent years, growing environmental awareness has accelerated the worldwide trend toward restricting the use of hexavalent Cr. In the field of surface-treated steel sheets used for various metal cans, too, there is a need to establish a production method that does not use hexavalent chromium.

30 **[0006]** Examples of known methods of forming a surface-treated steel sheet without using hexavalent chromium include the methods proposed in PTL 3 to PTL 6. These methods form a surface-treatment layer by performing electrolysis treatment in an electrolytic solution containing a trivalent chromium compound such as basic chromium sulfate.

CITATION LIST

35 Patent Literature

[0007]

40 PTL 1: JP 2013-144753 A
 PTL 2: JP 2008-50486 A
 PTL 3: JP 2016-501985 A
 PTL 4: JP 2016-505708 A
 PTL 5: JP 2020-172700 A
 45 PTL 6: JP 2020-172701 A

SUMMARY

(Technical Problem)

50 **[0008]** With the methods proposed in PTL 3 to PTL 6, a surface-treatment layer can be formed without using hexavalent chromium. According to PTL 3 to PTL 6, a surface-treated steel sheet with excellent adhesion to epoxy-based paint can be obtained by the methods. Moreover, according to PTL 3 and PTL 4, a surface-treated steel sheet that exhibits excellent corrosion resistance even after being painted (coated) with epoxy-based paint and deformed can be obtained.

55 **[0009]** However, while the surface-treated steel sheet obtained by each of the conventional methods proposed in PTL 3 to PTL 6 has excellent adhesion to epoxy-based paint and has excellent corrosion resistance at epoxy-based painted worked part, its corrosion resistance at BPA-free painted worked part is insufficient. This makes it impossible to replace conventional epoxy-based paint with BPA-free paint while maintaining corrosion resistance to various contents.

[0010] There is thus a demand for a surface-treated steel sheet that can be produced without using hexavalent chromium and has excellent corrosion resistance at BPA-free painted worked part.

[0011] It could therefore be helpful to provide a surface-treated steel sheet that can be produced without using hexavalent chromium and has excellent corrosion resistance at BPA-free painted worked part.

(Solution to Problem)

[0012] Upon careful examination, we discovered the following (1) and (2).

(1) By controlling, in a surface-treated steel sheet having a chromium-containing layer on at least one side, the number of linear regions in which an element smaller in atomic number than chromium is concentrated, which are seen when the chromium-containing layer is observed from the surface direction, within a specific range, a surface-treated steel sheet having excellent corrosion resistance at BPA-free painted worked part can be obtained.

(2) Such a surface-treated steel sheet can be produced by bringing a steel sheet into contact with an aqueous solution containing sulfate ions, holding the steel sheet in a state in which 1.0 g/m² to 30.0 g/m² of the aqueous solution is present on the surface of the steel sheet for 0.1 seconds to 20.0 seconds, and then subjecting the steel sheet to cathodic electrolysis treatment in an electrolytic solution containing 0.05 mol/L or more of trivalent chromium ions.

[0013] The present disclosure is based on these discoveries. We thus provide the following.

1. A surface-treated steel sheet comprising: a steel sheet; and a chromium-containing layer disposed on a surface of the steel sheet on at least one side, wherein when the chromium-containing layer is observed from a surface direction, linear regions in which an element smaller in atomic number than chromium is concentrated are present, and the number of the linear regions is 5.0 or more per 100 nm.

2. The surface-treated steel sheet according to 1., wherein the linear regions have a mesh-like connected structure.

3. The surface-treated steel sheet according to 2., wherein a standard deviation of an equivalent circular diameter of the mesh is 30 nm or less.

4. The surface-treated steel sheet according to 2. or 3., wherein average roundness of the mesh is 0.5 to 1.0.

5. The surface-treated steel sheet according to any one of 1. to 4., wherein a chromium coating weight of the chromium-containing layer is 40.0 mg/m² to 500.0 mg/m² per one side.

6. The surface-treated steel sheet according to any one of 1. to 5., wherein a chromium oxide coating weight of the chromium-containing layer is 40.0 mg/m² or less per one side.

7. The surface-treated steel sheet according to any one of 1. to 6., wherein an area ratio of a crystalline region when the chromium-containing layer is observed from the surface direction is 30 % or less.

8. A production method for a surface-treated steel sheet that includes: a steel sheet; and a chromium-containing layer disposed on a surface of the steel sheet on at least one side, the production method comprising: bringing the steel sheet into contact with an aqueous solution containing sulfate ions, and holding the steel sheet in a state in which 1.0 g/m² to 30.0 g/m² of the aqueous solution is present on the surface of the steel sheet for 0.1 seconds to 20.0 seconds; and subjecting the steel sheet to cathodic electrolysis treatment in an electrolytic solution containing 0.05 mol/L or more of trivalent chromium ions.

9. The production method for a surface-treated steel sheet according to 8., wherein the electrolytic solution is prepared by mixing a trivalent chromium ion source, a carboxylic acid compound, and water, adjusting pH to 4.0 to 7.0, and adjusting temperature to 40 °C to 70 °C.

(Advantageous Effect)

[0014] It is thus possible to provide a surface-treated steel sheet having excellent corrosion resistance at BPA-free painted worked part without using hexavalent chromium. The surface-treated steel sheet is suitable for use as a material for containers and the like.

DETAILED DESCRIPTION

[0015] A method for carrying out the present disclosure will be described in detail below. The following description shows an example of a preferred embodiment of the present disclosure, and the present disclosure is not limited to such.

[0016] A surface-treated steel sheet in one embodiment of the present disclosure is a surface-treated steel sheet comprising: a steel sheet; and a chromium-containing layer disposed on a surface of the steel sheet on at least one side. In the present disclosure, it is important that, when the chromium-containing layer is observed from the surface direction, linear regions in which an element smaller in atomic number than chromium is concentrated are present and the number of

the linear regions is 5 or more per 100 nm. Each of the components in the surface-treated steel sheet will be described below.

[Steel sheet]

[0017] The steel sheet is not limited and any steel sheet may be used. The steel sheet is preferably a steel sheet for cans. As the steel sheet, for example, an ultra low carbon steel sheet or a low carbon steel sheet may be used. The production method for the steel sheet is not limited, and a steel sheet produced by any method may be used. Typically, a cold-rolled steel sheet may be used as the steel sheet. The cold-rolled steel sheet can be produced, for example, by a typical production process that includes hot rolling, pickling, cold rolling, annealing, and temper rolling.

[0018] The chemical composition of the steel sheet is not limited, and may contain C, Mn, P, S, Si, Cu, Ni, Mo, Al, and inevitable impurities within such ranges that do not undermine the effects according to the present disclosure. In this case, for example, a steel sheet having a chemical composition specified in ASTM A623M-09 can be suitably used as the steel sheet.

[0019] In one embodiment of the present disclosure, it is preferable to use a steel sheet having 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 %, and

Sb: 0 % to 0.020 %, with the balance consisting of Fe and inevitable impurities. In the chemical composition, Si, P, S, Al, and N are components whose contents are preferably as low as possible, and Cu, Ni, Cr, Mo, Ti, Nb, B, Ca, Sn, and Sb are components that may be added optionally.

[0020] The sheet thickness of the steel sheet is not limited, but is preferably 0.60 mm or less. No lower limit is placed on the sheet thickness, but the sheet thickness is preferably 0.10 mm or more. Herein, the term "steel sheet" is defined to include "steel strip".

[Chromium-containing layer]

[0021] The chromium-containing layer is present on at least one side of the steel sheet. The components constituting the chromium-containing layer are not limited, but may include metallic chromium and one or more chromium compounds. The one or more chromium compounds are not limited, and any chromium compound(s) may be contained. As the chromium compound(s), for example, at least one selected from the group consisting of chromium oxide, chromium carbide, chromium sulfide, chromium nitride, chromium chloride, chromium bromide, and chromium boride may be contained. The chromium-containing layer may also contain impurities in addition to metallic chromium and chromium compounds. Examples of the impurities include metallic elements such as Ni, Cu, Sn, and Zn that are mixed in the below-described electrolytic solution as impurities. The metallic elements are considered to typically exist in the chromium-containing layer in a metallic state, but may exist as compounds.

[0022] In the chromium-containing layer in one embodiment of the present disclosure, the total content of metallic chromium and elements constituting chromium compounds is preferably 90 at% (atomic %) or more. Herein, the total content is the ratio of the total atomic number of metallic chromium and elements constituting chromium compounds to the total atomic number of all elements other than Fe, expressed as a percentage.

[0023] The total content can be determined by measuring the content (at%) of each of the metallic chromium and

elements constituting chromium compounds contained in the chromium-containing layer by X-ray photoelectron spectroscopy (XPS) and adding them up. In the measurement of the content of each element by XPS, the content (atomic ratio) of the element can be calculated from the integrated intensity of the peak corresponding to the element by the relative sensibility coefficient method.

[0024] For example, the content of chromium carbide (Cr_2C_3) can be determined from the integrated intensity of the C 1s carbide peak that appears around 281.0 eV. For example, if the C content (atomic ratio to the total of all elements other than Fe) calculated from the integrated intensity of the peak is 6 at%, the Cr_2C_3 content is $6 \times (2 + 3)/3 = 10$ at%.

[0025] For chromium oxide, the Cr_2O_3 content can be determined from the integrated intensity of the Cr 2p oxide peak that appears around 576.7 eV. The CrO_3 content can be determined from the integrated intensity of the Cr 2p oxide peak that appears around 579.2 eV.

[0026] Likewise, the contents of other chromium compounds can be determined using the integrated intensities of the following peaks, for example.

- Chromium sulfide (Cr_2S_3): S 2p sulfide peak that appears around 162.3 eV
- Chromium nitride (CrN): N 1S peak that appears around 397.3 eV
- Chromium chloride (CrCl_3): Cl 2p peak that appears around 199.8 eV
- Chromium bromide (CrBr_3): Br 3d peak that appears around 69.1 eV
- Chromium boride (CrB): Br 1s peak that appears around 188.2 eV

[0027] The content of metallic chromium is determined by calculating the Cr content from the integrated intensity of the Cr 2p peak that appears around 573.8 eV and subtracting, from the chromium content, the content of Cr atoms contained as chromium compounds.

[0028] Adding the content of metallic chromium and the contents of elements constituting chromium compounds obtained by this method can yield the total content of metallic chromium and elements constituting chromium compounds.

[0029] The total content refers to the value at the 1/2 position (i.e. position of 1/2) of the thickness of the chromium-containing layer. The 1/2 position can be determined by the following procedure. First, while sputtering the chromium-containing layer from its outermost surface, the total content of metallic chromium and elements constituting chromium compounds and the Fe content are measured by the foregoing method. The position (depth) at which the measured total content of metallic chromium and elements constituting chromium compounds and Fe content are equal is taken to be the interface between the chromium-containing layer and the steel sheet. The thickness from the outermost surface of the chromium-containing layer to the interface is taken to be the thickness of the chromium-containing layer, and the 1/2 position of the thickness is determined.

[0030] A scanning X-ray photoelectron spectrometer PHI X-tool produced by ULVAC-PHI, Inc. can be used for the measurement by XPS, for example. For example, the X-ray source is a monochromatic $\text{AlK}\alpha$ ray, the voltage is 15 kV, the beam diameter is 100 $\mu\text{m}\phi$, the extraction angle is 45° , and the sputtering conditions are Ar ions with an acceleration voltage of 1 kV and a sputtering rate of 1.50 nm/min in terms of SiO_2 .

[0031] The spatial structure of the components constituting the chromium-containing layer is not limited. For example, the components may be separated as separate layers within the chromium-containing layer, or may be mixed throughout the chromium-containing layer. In other words, the spatial structure of the components constituting the chromium-containing layer may contain one or both of separate layers and a mixed layer.

[0032] The chromium coating weight of the chromium-containing layer is not limited. If the chromium coating weight of the chromium-containing layer is excessively high, however, cohesive fracture may occur in the chromium-containing layer when working the surface-treated steel sheet. Therefore, from the viewpoint of more stably ensuring corrosion resistance at BPA-free painted worked part, the chromium coating weight of the chromium-containing layer per one side is preferably 500.0 mg/m^2 or less and more preferably 450.0 mg/m^2 or less. From the viewpoint of further improving corrosion resistance at BPA-free painted worked part, the chromium coating weight of the chromium-containing layer per one side is preferably 40.0 mg/m^2 or more and more preferably 50.0 mg/m^2 or more. Herein, the term "chromium coating weight" refers to the total coating weight of chromium present in various forms.

[0033] The chromium coating weight can be measured by X-ray fluorescence analysis. More specifically, the chromium coating weight is measured by the following procedure. First, the Cr amount (total Cr amount) in the surface-treated steel sheet is measured using an X-ray fluorescence instrument. Next, the Cr amount (blank sheet Cr amount) in the steel sheet on which the chromium-containing layer has not been formed yet or the steel sheet from which the chromium-containing layer has been peeled off is measured using the X-ray fluorescence instrument. The value obtained by subtracting the blank sheet Cr amount from the total Cr amount is taken to be the chromium coating weight of the chromium-containing layer. For example, a commercially available chromium coating separating agent such as a hydrochloric acid-based agent may be used to peel off the chromium-containing layer.

[Cr oxide coating weight]

[0034] Chromium oxide may be present in the chromium-containing layer. The location of chromium oxide is not limited, and chromium oxide may be present in the form of O concentrated in the below-described linear regions. The location of O can be determined, 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), or by three-dimensional composition analysis using a three-dimensional atom probe (3DAP).

[0035] The chromium oxide coating weight of the chromium-containing layer is not limited. If the chromium oxide coating weight of the chromium-containing layer is excessively high, however, cohesive fracture may occur starting from Cr oxide in the chromium-containing layer when working the surface-treated steel sheet, causing degradation in corrosion resistance at BPA-free painted worked part. Therefore, from the viewpoint of more stably ensuring corrosion resistance at BPA-free painted worked part, the chromium oxide coating weight of the chromium-containing layer per one side is preferably 40.0 mg/m² or less and more preferably 35.0 mg/m² or less. The chromium-containing layer may contain no chromium oxide. Thus, no lower limit is placed on the chromium oxide coating weight of the chromium-containing layer, and the chromium oxide coating weight of the chromium-containing layer per one side may be 0.0 mg/m².

[0036] The chromium oxide coating weight can be measured by X-ray fluorescence analysis. More specifically, the chromium oxide coating weight is measured by the following procedure. First, the Cr amount (total Cr amount) in the surface-treated steel sheet is measured. Next, the surface-treated steel sheet is subjected to alkali treatment of immersing in 7.5N-NaOH at 90 °C for 10 minutes to remove chromium oxide. The surface-treated steel sheet after the alkali treatment is thoroughly washed with water, and then the Cr amount (the Cr amount after alkali treatment) is measured again using an X-ray fluorescence instrument. The value obtained by subtracting the Cr amount after alkali treatment from the total Cr amount is taken to be the chromium oxide coating weight of the chromium-containing layer.

[0037] The chromium-containing layer may be amorphous or crystalline. In other words, the chromium-containing layer may contain one or both of amorphous and crystalline phases. The chromium-containing layer produced by the below-described method usually contains amorphous phase, and may also contain crystalline phase. The mechanism by which the chromium-containing layer is formed is not clear, but it is presumed that, during formation of amorphous phase, the amorphous phase is partially crystallized and as a result a chromium-containing layer containing both amorphous and crystalline phases is formed. The area ratio of the crystalline region is not limited, but is preferably 30 % or less when the chromium-containing layer is observed from the surface direction. Since the crystalline region may not be present, the lower limit of the area ratio of the crystalline region may be 0 %.

[0038] The crystalline region in the chromium-containing layer can be determined by removing the base steel sheet from the surface-treated steel sheet to prepare a single-layer sample of the chromium-containing layer and observing the single-layer sample of the chromium-containing layer from the surface side using a TEM or STEM. The method of preparing the single-layer sample of the chromium-containing layer is not limited. For example, the single-layer sample of the chromium-containing layer can be prepared by applying an ion beam of Ar or the like from the base steel sheet side and ion milling the steel sheet. In the case of preparing the single-layer region of the chromium-containing layer with an ion beam, the ion beam is applied with an acceleration voltage of 5 kV or less and an incidence angle of 1 degree to 5 degrees relative to the base steel sheet, thereby ensuring an observation field of a single chromium layer region of several μm² or more. Here, the bottom of the chromium-containing layer is also milled to some extent and as a result the film thickness of the chromium-containing layer decreases in some cases. This, however, does not affect the measurement result of the crystalline region.

[0039] The area ratio of the crystalline region in the chromium-containing layer can be measured using a TEM. Specifically, first, a diffraction pattern of the chromium-containing layer is obtained by selected area diffraction of the TEM. Next, a dark field image is obtained for all diffraction spots in the diffraction pattern, and a region that appears with high brightness in the dark field image is taken to be the crystalline region. The area of the obtained crystalline region is calculated by image processing, and the calculated area is divided by the area of the chromium-containing layer in the selected area aperture to calculate the area ratio of the crystalline region. For example, image analysis software such as Image-J may be used to calculate the area ratio.

[0040] The chromium-containing layer may contain C. No upper limit is placed on the C content in the chromium-containing layer, but the atomic ratio of C to Cr is preferably 50 % or less and more preferably 45 % or less. The chromium-containing layer may not contain C. Thus, no lower limit is placed on the atomic ratio of C to Cr in the chromium-containing layer, and the lower limit may be 0 %.

[0041] The C content in the chromium-containing layer can be measured by XPS. In detail, for the C content in the chromium-containing layer, sputtering is performed from the outermost layer to a depth of 0.2 nm or more in terms of SiO₂, the respective atomic ratios are quantified by the relative sensitivity coefficient method from the integrated intensities of the narrow spectra of Cr2p and C1s, and (the C atomic ratio)/(the Cr atomic ratio) is calculated. A scanning X-ray photoelectron spectrometer PHI X-tool produced by ULVAC-PHI, Inc. can be used for the measurement by XPS, for example. For example, the X-ray source is a monochromatic AlKα ray, the voltage is 15 kV, the beam diameter is 100 μmφ, the extraction

angle is 45°, and the sputtering conditions are Ar ions with an acceleration voltage of 1 kV and a sputtering rate of 1.50 nm/min in terms of SiO₂.

[0042] The mechanism by which C is contained in the chromium-containing layer is not clear, but it is presumed that, in the process of forming the chromium-containing layer on the steel sheet, if the electrolytic solution contains a carboxylic acid compound, the carboxylic acid compound decomposes and is incorporated into the layer.

[0043] The location of C in the chromium-containing layer is not limited, and C may be present in the form of being concentrated in the below-described linear regions. The location of C can be determined, 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), or by three-dimensional composition analysis using a three-dimensional atom probe (3DAP).

[0044] The chromium-containing layer may contain Fe. No upper limit is placed on the Fe content in the chromium-containing layer, but the atomic ratio of Fe to Cr is preferably 100 % or less. The chromium-containing layer may not contain Fe. Thus, no lower limit is placed on the atomic ratio of Fe to Cr, and the lower limit may be 0 %. The Fe content in the chromium-containing layer can be measured by XPS, as with the C content. The atomic ratio can be calculated using the narrow spectra of Cr2p and Fe2p.

[0045] The mechanism by which Fe is contained in the chromium-containing layer is not clear, but it is presumed that, in the process of forming the chromium-containing layer on the steel sheet, Fe contained in the steel sheet dissolves in a small amount into the electrolytic solution and is incorporated into the layer.

[0046] The chromium-containing layer may contain metal impurities such as K, Na, Mg, and Ca contained in water and Sn, Ni, Cu, and Zn contained in the aqueous solution, and S, N, Cl, Br, etc., besides Cr, O, Fe, and C. However, the presence of these elements may cause a decrease in corrosion resistance at BPA-free painted worked part. Therefore, the total content of elements other than Cr, O, Fe, and C is preferably 3 % or less and more preferably 0 % (i.e. the other elements are not contained at all) in terms of atomic ratio to Cr. For example, the content of these elements can be measured by XPS as with the C content, without being limited thereto.

[Linear region]

[0047] When the chromium-containing layer in the surface-treated steel sheet according to the present disclosure is observed from the surface direction, linear regions in which an element smaller in atomic number than chromium is concentrated are present, and the number of the linear regions is 5.0 or more per 100 nm. As a result of the number of the linear regions being 5.0 or more per 100 nm, excellent corrosion resistance at BPA-free painted worked part can be achieved. From the viewpoint of further improving corrosion resistance at BPA-free painted worked part, the number of the linear regions is preferably 7.0 or more per 100 nm and more preferably 10.0 or more per 100 nm. No upper limit is placed on the number of the linear regions, and the number of the linear regions may be, for example, 50.0 or less per 100 nm, 45.0 or less per 100 nm, or 40.0 or less per 100 nm.

[0048] The reason why the provision of the linear regions as described above improves corrosion resistance at BPA-free painted worked part is as follows.

[0049] A typical chromium-containing layer formed from a hexavalent Cr bath or trivalent Cr bath is composed of metallic chromium and chromium oxide. A surface-treated steel sheet including such a chromium-containing layer is usually worked into cans or the like after an organic resin coating is formed on its surface. However, since metallic chromium has poor workability, the chromium-containing layer cannot fully follow the deformation of the steel sheet during working, and consequently the organic resin coating on the chromium-containing layer is damaged. This causes a decrease in post-working corrosion resistance.

[0050] In view of this, in conventional surface-treated steel sheets, chromium oxide is provided in the top layer to ensure post-working corrosion resistance. Since chromium oxide has excellent adhesion to epoxy-based paint, even though metallic chromium cannot follow the deformation of the base steel sheet, the chromium-containing layer and the epoxy-based paint firmly adhere to each other and the coating properties of the epoxy-based paint can be maintained even after can production.

[0051] However, such conventional surface-treated steel sheets have poor adhesion to BPA-free paint, and therefore have poor worked part corrosion resistance in the case where BPA-free paint is applied.

[0052] The surface-treated steel sheet according to the present disclosure, on the other hand, achieves excellent corrosion resistance at BPA-free painted worked part by including 5.0 or more linear regions per 100 nm in its chromium-containing layer as described above. The present disclosure is thus based on a technical idea completely different from the conventional ones, i.e. improving the deformability of the chromium-containing layer itself rather than the adhesion to paint.

[0053] In the present disclosure, a region in which an element smaller in atomic number than chromium is detected in a larger amount than the average composition of the chromium-containing layer by 20 at% or more in an EDS quantitative map obtained by STEM/EDS analysis of the chromium-containing layer is defined as a "linear region in which an element

smaller in atomic number than chromium is concentrated". The STEM/EDS analysis is performed using a single-layer sample of the chromium-containing layer. The single-layer sample of the chromium-containing layer can be prepared by the foregoing method.

[0054] The number of linear regions can be measured, for example, from an EDS quantitative map of the chromium-containing layer. Any ten 100 nm lines are drawn on the map image, the intersections of each line with linear regions are counted, and the arithmetic mean value is taken to be the number of linear regions.

[0055] The element concentrated in the linear region is not limited, and may be any element smaller in atomic number than chromium. In one embodiment of the present disclosure, the element may include at least one selected from the group consisting of O, C, N, and S.

[0056] The linear regions may be isolated from each other, may intersect with each other, or may be connected in a mesh-like manner. The linear regions preferably have a mesh-like connected structure.

[0057] In the case where the linear regions have a mesh-like connected structure, the size, number, and shape of the mesh are not limited, but the standard deviation of the equivalent circular diameter of the mesh is preferably 30 nm or less and more preferably 20 nm or less from the viewpoint of further improving corrosion resistance at BPA-free painted worked part. No lower limit is placed on the standard deviation, and the standard deviation may be, for example, 0.5 nm or more or 1.0 nm or more.

[0058] The equivalent circular diameter of the mesh can be calculated by image analysis of an STEM/EDS map. Specifically, from an STEM/EDS map observed at a magnification of 450,000 times, the number of pixels in the region surrounded by the mesh is calculated using image analysis software such as Image-J, and the calculated number is multiplied by the area per pixel to obtain the area of the mesh. Then, the equivalent circular diameter is calculated from the obtained area. The standard deviation of the equivalent circular diameter is calculated from a total of 100 pieces of equivalent circular diameter data.

[0059] The shape of the mesh is not limited, but is desirably close to a perfect circle. Specifically, the average roundness of the mesh is preferably 0.5 or more. In the case where the shape of the mesh is a perfect circle, the roundness is 1. Hence, the average roundness may be 1.0 or less.

[0060] The roundness of the mesh can be calculated by image analysis of an STEM/EDS map, as with the equivalent circular diameter. Specifically, an STEM/EDS map observed at a magnification of 450,000 times is analyzed using image analysis software such as Image-J, and a circle inscribed in the mesh and a circle circumscribed around the mesh are drawn. The diameter of the inscribed circle is divided by the diameter of the circumscribed circle to find the roundness. The roundness is calculated for a total of 100 inscribed circles, and the average value is taken to be the roundness of the mesh.

[Production method]

[0061] In a production method for a surface-treated steel sheet in one embodiment of the present disclosure, a surface-treated steel sheet having the above-described properties can be produced by the method described below.

[0062] The production method for a surface-treated steel sheet in one embodiment of the present disclosure is a production method for a surface-treated steel sheet that includes: a steel sheet; and a chromium-containing layer disposed on a surface of the steel sheet on at least one side, and comprises a steel sheet surface adjustment process and a cathodic electrolysis process. Each of the processes will be described below.

[Steel sheet surface adjustment process]

[0063] In the present disclosure, it is important to perform the steel sheet surface adjustment process of bringing the steel sheet into contact with an aqueous solution containing sulfate ions and holding the steel sheet in a state in which a predetermined amount of the aqueous solution is present on the surface of the steel sheet for a predetermined time, prior to the below-described cathodic electrolysis treatment.

Amount of aqueous solution: 1.0 g/m² to 30.0 g/m²

Holding time: 0.1 seconds to 20.0 seconds

[0064] In order to cause the number of linear regions in the finally obtained surface-treated steel sheet to be 5.0 or more per 100 nm, in the steel sheet surface adjustment process, it is necessary to bring the steel sheet into contact with an aqueous solution containing sulfate ions and hold the steel sheet in a state in which 1.0 g/m² to 30.0 g/m² of the aqueous solution is present on the surface of the steel sheet for 0.1 seconds or more and 20.0 seconds or less.

[0065] The mechanism by which the linear regions in which an element smaller in atomic number than chromium is concentrated are formed as a result of the steel sheet surface adjustment process is not clear, but it is presumed as follows. When the steel sheet is brought into contact with an aqueous solution containing sulfate ions, a dissolution reaction of Fe

and a decomposition reaction of dissolved oxygen occur on the surface of the steel sheet, and the pH of the surface of the steel sheet increases. Here, if the amount of the aqueous solution is within the foregoing range, the thickness of the aqueous solution on the steel sheet is very thin, so that dissolved oxygen in the aqueous solution increases. This further promotes the foregoing reactions. The state in which the aqueous solution is present on the steel sheet is not limited, but the aqueous solution is preferably in the form of a liquid film from the viewpoint of making the reactions uniform.

[0066] If dissolved Fe ions are present on the surface of the steel sheet where the pH has increased, the Fe ions are oxidized to Fe oxide, which accumulates on the surface of the steel sheet in a very small amount. In the subsequent cathodic electrolysis process, the accumulated small amount of Fe oxide is reduced and a chromium-containing layer is formed. Moreover, the surface potential is microscopically different between the parts where the accumulated small amount of Fe oxide exists and the parts where the accumulated small amount of Fe oxide does not exist. As a result, linear regions in which an element smaller in atomic number than chromium is concentrated are formed.

[0067] From the viewpoint of forming more linear regions and further improving corrosion resistance at BPA-free painted worked part, the amount of the aqueous solution is preferably 2.0 g/m² or more and more preferably 3.0 g/m² or more. From the same viewpoint, the amount of the aqueous solution is preferably 28.0 g/m² or less and more preferably 25.0 g/m² or less.

[0068] From the viewpoint of forming more linear regions and further improving corrosion resistance at BPA-free painted worked part, the holding time is preferably 0.2 seconds or more and more preferably 0.3 seconds or more. From the same viewpoint, the holding time is preferably 18.0 seconds or less and more preferably 15.0 seconds or less.

[0069] The amount of the aqueous solution present on the surface of the steel sheet can be measured with a moisture meter using a filter type infrared absorption method. Specifically, the absorbance on the surface of the steel sheet is measured with the moisture meter using the filter type infrared absorption method, and the amount of the aqueous solution is calculated from the absorbance using a calibration curve obtained in advance. The calibration curve can be created by the following procedure. First, the steel sheet is placed on an electronic balance. The aqueous solution is dropped onto the steel sheet with a pipette to form a liquid film over the entire surface of the steel sheet. The weight of the aqueous solution present on the steel sheet is calculated from the weight of the steel sheet before the aqueous solution is dropped and the weight of the steel sheet after the aqueous solution is dropped. The calculated weight of the aqueous solution is divided by the area of the steel sheet to determine the amount of the aqueous solution per unit area. Simultaneously, the absorbance on the surface of the steel sheet is measured with the moisture meter using the filter type infrared absorption method. The above measurements are carried out a plurality of times while changing the amount of the aqueous solution to create a calibration curve that represents the correlation between the amount of the aqueous solution and the absorbance. As the calibration curve, a linear approximation of the correlation between the amount of the aqueous solution and the absorbance can be used.

[0070] The method of adjusting the amount of the aqueous solution present on the surface of the steel sheet is not limited, and any method may be used. For example, squeezing the solution with a wringer roll, wiping, or the like may be used.

[0071] The composition of the aqueous solution is not limited, but a sulfuric acid aqueous solution such as dilute sulfuric acid is preferable. Herein, the term "sulfuric acid aqueous solution" means an aqueous solution of sulfuric acid, and includes cases where components other than sulfuric acid are contained.

[0072] In the case where a sulfuric acid aqueous solution is used as a pickling liquid in the below-described pretreatment process, the pickling liquid may also be used as the aqueous solution in the steel sheet surface adjustment process. Although pickling liquids typically contain pickling inhibitors, pickling accelerators, etc., these components do not particularly hinder the formation of linear regions. Thus, even when the pickling liquid contains pickling inhibitors, pickling accelerators, etc., the pickling liquid can be used as the aqueous solution in the steel sheet surface adjustment process.

[0073] No lower limit is placed on the concentration of sulfate ions contained in the aqueous solution, but the concentration of sulfate ions contained in the aqueous solution is preferably 3 g/L or more and more preferably 5 g/L or more. No upper limit is placed on the concentration of sulfate ions contained in the aqueous solution, but the concentration of sulfate ions contained in the aqueous solution is preferably 200 g/L or less and more preferably 150 g/L or less.

[0074] No lower limit is placed on the temperature of the aqueous solution, but the temperature of the aqueous solution is preferably 10 °C or more and more preferably 15 °C or more. No upper limit is placed on the temperature of the aqueous solution, but the temperature of the aqueous solution is preferably 70 °C or less and more preferably 60 °C or less.

[0075] After the steel sheet surface adjustment process, it is preferable to wash the steel sheet with water in order to remove the aqueous solution adhering to the steel sheet.

[Cathodic electrolysis process]

[0076] Next, the steel sheet is subjected to cathodic electrolysis treatment in an electrolytic solution containing 0.05 mol/L or more of trivalent chromium ions. As a result of the cathodic electrolysis treatment, a chromium-containing layer

can be formed on the steel sheet. As the trivalent chromium ion source, any compound that can supply trivalent chromium ions may 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 may be used.

[0077] The temperature of the electrolytic solution during the cathodic electrolysis treatment is not limited, but is preferably 40 °C or more in order to efficiently form the chromium-containing layer. For the same reason, the temperature of the electrolytic solution is preferably 70 °C or less. From the viewpoint of stably producing the above-described surface-treated steel sheet, it is preferable to monitor the temperature of the electrolytic solution and maintain the temperature within a temperature range of 40 °C to 70 °C in the cathodic electrolysis process.

[0078] The pH of the electrolytic solution during the cathodic electrolysis treatment is not limited, but is preferably 4.0 or more and more preferably 4.5 or more. The pH is preferably 7.0 or less and more preferably 6.5 or less. From the viewpoint of stably producing the above-described surface-treated steel sheet, it is preferable to monitor the pH of the electrolytic solution and maintain the pH within the foregoing pH range in the cathodic electrolysis process.

[0079] The current density in the cathodic electrolysis treatment is not limited and may be adjusted appropriately so that the desired surface-treatment layer will be formed. If the current density is excessively high, an excessive load is put on the cathodic electrolytic device. The current density is therefore preferably 200.0 A/dm² or less and more preferably 100 A/dm² or less. Although no lower limit is placed on the current density, if the current density is excessively low, hexavalent Cr may form in the electrolytic solution, causing the stability of the bath to be lost. The current density is therefore preferably 5.0 A/dm² or more and more preferably 10.0 A/dm² or more.

[0080] The number of times the steel sheet is subjected to cathodic electrolysis treatment is not limited and may be any number. In other words, cathodic electrolysis treatment can be performed using an electrolytic device having any number of passes where the number is one or more. For example, it is preferable to perform cathodic electrolysis treatment continuously by passing the steel sheet (steel strip) through a plurality of passes while conveying it. If the number of times cathodic electrolysis treatment is performed (i.e. the number of passes) is increased, the corresponding number of electrolysis tanks are required. Accordingly, the number of times cathodic electrolysis treatment is performed (i.e. the number of passes) is preferably 20 or less.

[0081] The electrolysis time per pass is not limited. If the electrolysis time per pass is excessively long, however, the conveyance speed (line speed) of the steel sheet decreases and productivity decreases. The electrolysis time per pass is therefore preferably 5 seconds or less and more preferably 3 seconds or less. Although no lower limit is placed on the electrolysis time per pass, if the electrolysis time is excessively short, the line speed needs to be increased accordingly, which makes control difficult. The electrolysis time per pass is therefore preferably 0.005 seconds or more and more preferably 0.01 seconds or more.

[0082] The Cr coating weight of the chromium-containing layer formed by cathodic electrolysis treatment can be controlled by the total electric charge density, which is expressed as the product of the current density, the electrolysis time, and the number of passes. An excessively small Cr coating weight may impair corrosion resistance at BPA-free painted worked part, and an excessively large Cr coating weight may cause cohesive fracture in the chromium-containing layer during working, as mentioned above. From the viewpoint of more stably ensuring corrosion resistance at BPA-free painted worked part, it is preferable to control the total electric charge density so that the Cr coating weight of the chromium-containing layer per one side of the steel sheet will be within an appropriate range. Here, since the relationship between the Cr coating weight of the chromium-containing layer per one side of the steel sheet and the total electric charge density varies depending on the structure of the device used in the cathodic electrolysis process, the actual electrolysis treatment conditions are adjusted depending on the device.

[0083] The type of the anode used when performing cathodic electrolysis treatment is not limited and any anode may be used. As the anode, an insoluble anode is preferably used. As the insoluble anode, at least one selected from the group consisting of an anode in which Ti is coated with one or both of a platinum group metal and an oxide of a platinum group metal and a graphite anode is preferably used. A more specific example of the insoluble anode is an anode in which the surface of Ti as a substrate is coated with platinum, iridium oxide, or ruthenium oxide.

[0084] In the cathodic electrolysis process, the concentration of the electrolytic solution changes constantly due to the formation of the chromium-containing layer on the steel sheet, the introduction and removal of liquid, the evaporation of water, etc. Since the change in the concentration of the electrolytic solution in the cathodic electrolysis process varies depending on the structure of the device and the production conditions, it is preferable to monitor the concentration of each component in the electrolytic solution and maintain it within the below-described concentration range in the cathodic electrolysis process from the viewpoint of more stably producing the surface-treated steel sheet.

[0085] The steel sheet after the cathodic electrolysis process is preferably washed with water at least once. As a result of water washing, the electrolytic solution remaining on the surface of the steel sheet can be removed.

[0086] The water washing is not limited and may be performed by any method. For example, a water washing tank may be provided downstream of the immersion tank for performing the immersion process so that the steel sheet after immersion can be continuously immersed in water. Water washing may be performed by spraying water on the steel sheet after immersion.

[0087] The water used for the water washing is not limited, but it is preferable to use at least one of reverse osmosis water (RO water), ion-exchanged water, and distilled water. The electrical conductivity of the water used for the water washing is not limited, but is preferably 100 $\mu\text{S}/\text{m}$ or less, more preferably 50 $\mu\text{S}/\text{m}$ or less, and further preferably 30 $\mu\text{S}/\text{m}$ or less.

[0088] The temperature of the water used for the water washing is not limited and may be any temperature. Since an excessively high temperature puts an excessive load on the water washing equipment, the temperature of the water used in the water washing is preferably 95 °C or less. No lower limit is placed on the temperature of the water used in the water washing, but the temperature is preferably 0 °C or more. The temperature of the water used in the water washing may be room temperature.

[0089] After the water washing, drying may be optionally performed. The drying method is not limited, and a typical dryer or electric furnace drying method may be used. The temperature during the drying treatment is preferably 100 °C or less, from the viewpoint of suppressing the deterioration of the surface-coating layer. Although no lower limit is placed on the temperature during the drying treatment, the temperature is typically about room temperature.

[0090] The steel sheet may be optionally subjected to pretreatment before the steel sheet surface adjustment process. It is preferable to perform at least one of degreasing, pickling, and water washing as the pretreatment.

[0091] Degreasing can remove rolling oil, rust preventive oil, etc. adhering to the steel sheet. The degreasing is not limited and may be performed by any method. After the degreasing, it is preferable to perform water washing to remove the degreasing liquid adhering to the surface of the steel sheet.

[0092] Pickling can remove a natural oxide layer present at the surface of the steel sheet, with it being possible to effectively adjust the surface in the subsequent steel sheet surface adjustment process. The pickling is not limited and may be performed by any method. After the pickling, it is preferable to perform water washing to remove the pickling liquid adhering to the surface of the steel sheet. If an aqueous solution containing sulfate ions is used as the pickling liquid, it is preferable to use the aqueous solution containing sulfate ions in the steel sheet surface adjustment process.

[0093] The method of preparing the electrolytic solution used in the cathodic electrolysis process is not limited, but the below-described electrolytic solution preparation process enables the electrolytic solution to be provided in the cathodic electrolysis process stably for a long period of time.

[Electrolytic solution preparation process]

(i) Mixing

[0094] In the electrolytic solution preparation process, first, a trivalent chromium ion source, a carboxylic acid compound, and water are mixed to prepare an aqueous solution.

[0095] As the trivalent chromium ion source, any compound that can supply trivalent chromium ions may 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 may be used.

[0096] The content of the trivalent chromium ion source in the aqueous solution needs to be 0.05 mol/L or more and is preferably 0.08 mol/L or more and more preferably 0.10 mol/L or more in terms of trivalent chromium ions. No upper limit is placed on the content of the trivalent chromium ion source, but the content of the trivalent chromium ion source is preferably 1.50 mol/L or less and more preferably 1.30 mol/L or less in terms of trivalent chromium ions. As the trivalent chromium ion source, BluCr® (BluCr is a registered trademark in Japan, other countries, or both) TFS A produced by Atotech can be used.

[0097] The carboxylic acid compound is not limited and any carboxylic acid compound may be used. The carboxylic acid compound may be at least one of a carboxylic acid and a carboxylate, and is preferably at least one of an aliphatic carboxylic acid and an aliphatic carboxylate. The carbon number of the aliphatic carboxylic acid is preferably 1 to 10 and more preferably 1 to 5. The carbon number of the aliphatic carboxylate is preferably 1 to 10 and more preferably 1 to 5. The content of the carboxylic acid compound is not limited. The content of the carboxylic acid compound is preferably 0.1 mol/L or more. The content of the carboxylic acid compound is preferably 5.5 mol/L or less. The content of the carboxylic acid compound is more preferably 0.15 mol/L or more. The content of the carboxylic acid compound is more preferably 5.3 mol/L or less. As the carboxylic acid compound, BluCr® TFS B produced by Atotech can be used.

[0098] Water may be used as a solvent for preparing the aqueous solution. As the water, it is preferable to use at least one of ion-exchanged water and distilled water.

[0099] In order to effectively suppress the formation of hexavalent chromium at the anode in the cathodic electrolysis process and improve the stability of the electrolytic solution, it is preferable that the aqueous solution further contains at least one type of halide ion. The content of the halide ion is not limited. The content of the halide ion is preferably 0.05 mol/L or more. The content of the halide ion is preferably 3.0 mol/L or less. The content of the halide ion is more preferably 0.10 mol/L or more. The content of the halide ion is more preferably 2.5 mol/L or less. BluCr® TFS C1 and BluCr® TFS C2 produced by Atotech can be used to contain the halide ion.

[0100] It is preferable not to add hexavalent chromium to the aqueous solution. It has been confirmed that in principle

hexavalent chromium is not formed in the cathodic electrolysis process. Even if a small amount of hexavalent chromium is formed at the anode or the like, it is immediately reduced to trivalent chromium, so that the concentration of hexavalent chromium in the electrolytic solution does not increase.

[0101] It is preferable not to intentionally add metal ions other than trivalent chromium ions to the aqueous solution. The metal ions are not limited, and examples thereof include Cu ions, Zn ions, Fe ions, Sn ions, and Ni ions. The content of each of these ions is preferably 0 mg/L or more and 40 mg/L or less, more preferably 0 mg/L or more and 20 mg/L or less, and most preferably 0 mg/L or more and 10 mg/L or less. Of these metal ions, Fe ions may dissolve in the electrolytic solution in the cathodic electrolysis process and the immersion process and co-deposit in the layer (coating), but does not affect corrosion resistance at BPA-free painted worked part. The concentration of Fe ions is preferably within the foregoing range at initial make-up of electrolytic bath. It is also preferable to maintain the concentration of Fe ions in the electrolytic solution within the foregoing range in the cathodic electrolysis process and the immersion process. If Fe ions are controlled within the foregoing range, the formation of the chromium-containing layer is not hindered and the necessary amount of the chromium-containing layer can be formed.

(ii) Adjustment of pH and temperature

[0102] Next, the pH of the aqueous solution is adjusted to 4.0 to 7.0 and the temperature of the aqueous solution is adjusted to 40 °C to 70 °C to prepare the electrolytic solution. As mentioned above, in order to provide the electrolytic solution in the cathodic electrolysis process stably for a long period of time, it is preferable to not only dissolve the trivalent chromium ion source and the carboxylic acid compound in water but also appropriately control the pH and the temperature as described above.

pH: 4.0 to 7.0

[0103] In the electrolytic solution preparation process, the pH of the aqueous solution after mixing is adjusted to 4.0 to 7.0. The pH is preferably 4.5 or more. The pH is preferably 6.5 or less.

[0104] Any reagent may be used to adjust the pH. For example, it is preferable to use hydrochloric acid, sulfuric acid, nitric acid, etc. to decrease the pH, and use ammonia water, etc. to increase the pH.

Temperature: 40 °C to 70 °C

[0105] In the electrolytic solution preparation process, the temperature of the aqueous solution after mixing is adjusted to 40 °C to 70 °C. The holding time in the temperature range of 40 °C to 70 °C is not limited.

[0106] The electrolytic solution obtained by this procedure can be provided in the cathodic electrolysis process stably for a long period of time. The electrolytic solution produced by this procedure can be stored at room temperature.

[0107] The use of the surface-treated steel sheet according to the present disclosure is not limited. For example, the surface-treated steel sheet is suitable as a surface-treated steel sheet for containers used in the production of various containers such as food cans, beverage cans, pails, and 18-liter cans.

EXAMPLES

[0108] In order to determine the effects according to the present disclosure, surface-treated steel sheets were produced by the procedure described below and their properties were evaluated.

(Electrolytic solution preparation process)

[0109] First, electrolytic solutions having compositions A to G shown in Table 1 were prepared under the conditions shown in Table 1. In detail, the components shown in Table 1 were mixed with water to prepare an aqueous solution, and the aqueous solution was then adjusted to the pH and temperature shown in Table 1. Electrolytic solution G corresponds to the electrolytic solution used in the examples in PTL 6. Ammonia water was used to increase the pH for each electrolytic solution. Sulfuric acid was used to decrease the pH for electrolytic solutions A, B, and G. Hydrochloric acid was used to decrease the pH for electrolytic solutions C and D. Nitric acid was used to decrease the pH for electrolytic solutions E and F.

(Pretreatment of steel sheet)

[0110] As steel sheets, cold-rolled steel sheets were used. More specifically, steel sheets for cans (T4 blank sheets) with a sheet thickness of 0.17 mm were used. As pretreatment, each steel sheet was subjected to electrolytic degreasing, water washing, and pickling in sequence. For the pickling, a sulfuric acid aqueous solution with the sulfate ion concentration

shown in Table 2 was used, and the steel sheet was immersed in the aqueous solution to perform pickling. The steel sheet after the pickling was subjected to the next steel sheet surface adjustment process without water washing.

(Steel sheet surface adjustment process)

[0111] Next, the steel sheet after the pickling was subjected to surface adjustment. Specifically, the pickling liquid remaining on the surface of the steel sheet was squeezed with a wringer roll to adjust the amount of the pickling liquid attached to the surface to the amount shown in Table 2 as "amount of aqueous solution". After this, the steel sheet was held for the holding time shown in Table 2 while maintaining the amount of the pickling liquid attached. The steel sheet was then washed with water to remove the pickling liquid.

(Cathodic electrolysis process)

[0112] The steel sheet was then subjected to cathodic electrolysis treatment under the conditions shown in Table 2. The electrolytic solution during the cathodic electrolysis treatment was maintained at the pH and temperature shown in Table 1. During the cathodic electrolysis treatment, the current density was 40 A/dm², and the electrolysis time and the number of passes were varied as appropriate. As the anode in the cathodic electrolysis treatment, an insoluble anode composed of a Ti substrate coated with iridium oxide was used. After the cathodic electrolysis treatment, the steel sheet was washed with water with an electrical conductivity of 100 μ S/m or less, and dried at room temperature using a blower.

[0113] For each of the obtained surface-treated steel sheets, the chromium coating weight of the chromium-containing layer per one side of the steel sheet and the chromium oxide coating weight of the chromium-containing layer per one side of the steel sheet were measured by the above-described methods. Moreover, for each of the obtained surface-treated steel sheets, the number of linear regions in which an element smaller in atomic number than chromium is concentrated, whether a mesh structure was present, the standard deviation of the mesh, and the roundness of the mesh were measured by the above-described methods. The measurement results are shown in Table 3.

[0114] In all examples, the chromium-containing layer obtained by cathodic electrolysis treatment contained chromium compounds such as chromium oxide and chromium carbide in addition to metallic chromium. The total content of metallic chromium and elements constituting chromium compounds in the chromium-containing layer was 90 mass% or more. In the linear regions, at least one selected from the group consisting of O, C, N, and S was concentrated. In particular, O was observed to be concentrated in the linear regions in all examples.

(Corrosion resistance at BPA-free painted worked part)

[0115] Next, for each of the obtained surface-treated steel sheets, corrosion resistance at BPA-free painted worked part was evaluated by the below-described procedure.

[0116] First, BPA-free paint was applied to the surface of the surface-treated steel sheet to prepare a BPA-free painted steel sheet. As the BPA-free paint, polyester-based paint for the inner surface of a can (BPA-free paint) was used. In the painting, the BPA-free paint was applied to the surface of the surface-treated steel sheet, and then baked at 80 °C for 10 minutes. The coating weight of the paint was 60 mg/dm².

[0117] The obtained BPA-free painted steel sheet was cross-cut through to the base steel sheet, and then a 4 mm-high overhang was formed around the intersection of the cross-cut using an Erichsen tester to prepare a test piece.

[0118] Next, a corrosion resistance test was performed using the test piece by the following procedure. First, the test piece was immersed in a Teflon® (Teflon is a registered trademark in Japan, other countries, or both) container containing a test liquid and covered with a lid. In this state, retort treatment was performed at a temperature of 121 °C for 1 hour. Subsequently, the test piece was removed from the container, washed with water to remove the test liquid, and then dried with a blower.

[0119] The dried test piece was subjected to tape peeling twice. After this, the surface of the test piece was observed with a microscope or the like, and the area of paint peeling and the area of discoloration such as rust were visually evaluated and scored on a 5-point scale. 1 is the poorest performance and 5 is the most excellent performance. The same evaluation was performed on two samples for each example, and the arithmetic mean value of the scores was calculated and taken to be an index of corrosion resistance at BPA-free painted worked part. Practically, if the score is higher than or equal to that of conventional TFS, the corrosion resistance at BPA-free painted worked part can be evaluated as excellent. It is more preferable if the score is higher than or equal to that of conventional TFS and is 3.0 or more.

[0120] In order to simulate the differences in corrosion environment depending on the contents in the case where surface-treated steel sheets are used for cans, the corrosion resistance test was performed using four test liquids having the following compositions (1) to (4). The evaluation results are shown in Table 4.

(1) Cysteine

EP 4 520 857 A1

- Sodium dihydrogen phosphate: 3.56 g/L
- Disodium hydrogen phosphate dodecahydrate: 14.52 g/L
- L-cysteine hydrochloride monohydrate: 0.5 g/L

(2) Lactic acid

- Lactic acid: 22.5 g/L

(3) Citric acid

- Citric acid: 19.2 g/L
- L(+)-ascorbic acid: 3.92 g/L

(4) Salt + Acetic acid

- Salt: 18.7 g/L
- Acetic acid: 30 g/L

[0121] As is clear from the results shown in Table 4, all of the surface-treated steel sheets satisfying the conditions according to the present disclosure were able to be produced without using hexavalent chromium and had excellent BPA-free painting corrosion resistance higher than or equal to that of conventional TFS. Since retort treatment with the test liquid of salt + acetic acid (4) was an extremely severe corrosion environment, the score of each surface-treated steel sheet satisfying the conditions according to the present disclosure was less than 3.0, as with conventional TFS. Therefore, particularly when using the surface-treated steel sheet according to the present disclosure for contents that contain acetic acid, it is necessary to take the same precautions as when using conventional TFS, such as double coating of BPA-free paint and optimization of retort treatment conditions.

[Table 1]

[0122]

Table 1

Electrolytic solution		A	B	C	D	E	F	G
Component (mol/L)	$\text{Cr(OH)SO}_4 \cdot \text{Na}_2\text{SO}_4$	-	-	-	-	-	-	0.39
	$\text{Cr}_2(\text{SO}_4)_3$	0.1	0.2	-	-	-	-	-
	CrCl_3	-	-	0.2	0.5	-	-	-
	$\text{Cr(NO}_3)_3$	-	-	-	-	0.2	0.5	-
	HCO_2H	4.2	-	0.4	-	4.8	-	-
	NH_4CHO_2	-	0.5	-	3.5	-	0.5	-
	HCO_2K	-	-	-	-	-	-	0.61
	NH_4Cl	1.1	1.4	0.7	-	1.5	-	-
	NH_4Br	-	0.3	0.6	0.4	0.2	1.3	-
	KCl	-	-	-	-	-	-	3.35
	KBr	-	-	-	-	-	-	0.13
pH		5.0	5.7	5.1	4.3	6.8	5.8	2.3
Temperature (°C)		42	50	65	55	55	53	50

[Table 2]

[0123]

EP 4 520 857 A1

Table 2

5	No.						Remarks
		Steel sheet surface adjustment process			Cathodic electrolysis process		
		Sulfate ion concentration [g/L]	Amount of aqueous solution [g/m ²]	Holding time [sec]	Electrolytic solution	Electric charge density [C/dm ²]	
10	1	15	7.6	1.5	A	80	Example
	2	50	12.0	3.5	B	100	Example
	3	35	15.6	2.2	C	180	Example
	4	120	4.3	0.5	D	120	Example
15	5	5	22.5	0.4	E	110	Example
	6	100	19.3	1.4	F	72	Example
	7	80	3.3	14.2	A	84	Example
20	8	150	16.5	7.6	B	140	Example
	9	30	16.2	13.7	C	380	Example
	10	80	8.9	2.6	D	300	Example
25	11	65	12.9	0.8	E	100	Example
	12	40	5.4	3.5	F	150	Example
	13	130	8.9	12.6	A	60	Example
30	14	90	11.3	9.0	B	160	Example
	15	20	24.5	3.4	C	120	Example
	16	70	16.7	5.2	D	136	Example
	17	50	10.9	13.6	E	200	Example
35	18	15	6.4	6.6	F	116	Example
	19	140	13.4	5.9	A	52	Example
	20	100	15.8	4.3	B	42	Example
	21	30	7.2	0.6	C	460	Example
40	22	60	14.4	9.8	D	480	Example
	23	80	20.3	0.4	E	320	Example
	24	45	11.5	9.8	F	240	Example
	25	95	13.2	0.2	A	140	Example
45	26	115	8.9	16.3	B	140	Example
	27	130	29.4	3.2	C	150	Example
	28	75	2.5	1.4	D	150	Example
	29	60	27.3	4.6	E	90	Example
50	30	10	1.5	13.4	F	90	Example
	31	20	17.8	0.1	A	130	Example
	32	105	3.6	18.2	B	130	Example
55	33	15	18.0	0.05	C	180	Comparative Example
	34	50	23.2	21.5	D	180	Comparative Example
	35	40	36.5	10.3	E	200	Comparative Example

(continued)

No.						Remarks
	Steel sheet surface adjustment process			Cathodic electrolysis process		
	Sulfate ion concentration [g/L]	Amount of aqueous solution [g/m ²]	Holding time [sec]	Electrolytic solution	Electric charge density [C/dm ²]	
36	80	<u>0.6</u>	2.5	F	190	Comparative Example
37	70	6.7	4.5	G	160	Example
38	60	8.9	17.2	G	160	Example
39	55	<u>57.6</u>	1.5	G	160	Comparative Example
40	<u>TFS (using hexavalent chromium)</u>					Comparative Example

[Table 3]

[0124]

Table 3

No.	Measurement results							Remarks
	Chromium coating weight [mg/m ²]	Chromium oxide coating weight [mg/m ²]	Number of linear regions [/100nm]	Mesh structure	Standard deviation of equivalent circular diameter of mesh [nm]	Average roundness of mesh region	Area ratio of crystalline region [%]	
1	82.8	3.2	12.6	Present	3.0	0.9	12.0	Example
2	103.5	4.3	25.7	Present	2.1	0.8	10.0	Example
3	211.9	15.3	10.5	Present	4.7	0.7	20.0	Example
4	156.7	12.3	34.3	Present	2.1	0.8	13.0	Example
5	110.3	0.5	24.5	Present	2.4	0.9	16.0	Example
6	58.6	19.6	22.8	Present	3.0	0.8	21.0	Example
7	77.3	20.8	15.6	Present	3.2	0.9	9.1	Example
8	142.1	6.5	26.4	Present	2.7	0.9	23.0	Example
9	439.2	32.1	11.6	Present	6.2	0.6	11.0	Example
10	334.6	29.5	21.8	Present	3.1	0.7	0.0	Example
11	93.5	0.2	11.2	Present	5.1	0.6	14.0	Example
12	148.9	10.9	14.5	Present	3.1	0.7	25.0	Example
13	73.9	8.9	21.9	Present	1.9	0.9	2.0	Example
14	154.6	7.4	35.2	Present	1.5	0.9	23.0	Example
15	122.9	13.2	14.2	Present	3.8	0.8	17.0	Example
16	139.5	10.5	11.0	Present	7.6	0.6	5.0	Example
17	191.1	5.3	16.7	Present	4.0	0.7	29.0	Example
18	122.2	2.2	28.7	Present	2.1	0.8	2.0	Example
19	45.2	4.6	30.7	Present	3.1	0.8	12.0	Example

EP 4 520 857 A1

(continued)

No.	Measurement results							Remarks
	Chromium coating weight [mg/m ²]	Chromium oxide coating weight [mg/m ²]	Number of linear regions [/100nm]	Mesh structure	Standard deviation of equivalent circular diameter of mesh [nm]	Average roundness of mesh region	Area ratio of crystalline region [%]	
20	36.3	7.8	26.2	Present	2.1	0.9	14.0	Example
21	473.1	5.4	15.6	Present	2.5	0.9	17.0	Example
22	506.9	6.5	18.8	Present	1.8	0.9	19.0	Example
23	313.5	37.8	20.4	Present	4.1	0.5	12.0	Example
24	221.1	42.5	11.3	Present	3.0	0.7	11.0	Example
25	163.5	12.2	8.3	Present	11.0	0.8	23.0	Example
26	160.2	8.3	8.4	Present	12.0	0.8	22.0	Example
27	146.3	1.5	7.6	Not present	-	-	16.0	Example
28	140.3	2.3	7.8	Not present	-	-	15.0	Example
29	100.9	3.6	6.2	Not present	-	-	21.0	Example
30	101.4	3.8	6.0	Not present	-	-	23.0	Example
31	141.3	6.5	5.4	Present	19.0	0.5	14.0	Example
32	138.5	6.3	5.5	Present	18.0	0.6	15.0	Example
33	194.3	16.9	<u>4.3</u>	Present	18.0	0.4	22.0	Comparative Example
34	193.5	15.2	<u>3.7</u>	Present	19.0	0.5	20.0	Comparative Example
35	209.5	15.4	<u>0.1</u>	Not present	-	-	22.0	Comparative Example
36	211.3	4.9	<u>0.0</u>	Not present	-	-	25.0	Comparative Example
37	111.4	5.6	13.4	Present	9.0	0.9	17.0	Example
38	105.6	6.7	8.9	Present	13.0	0.9	10.0	Example
39	107.9	6.3	<u>3.2</u>	Not present	-	-	18.0	Comparative Example
40	121.3	11.3	<u>0.0</u>	Not present	-	-	100.0	Comparative Example

[Table 4]

[0125]

EP 4 520 857 A1

Table 4

	No.	Corrosion resistance at BPA-free painted worked part				Remarks
		(1) Cysteine	(2) Lactic acid	(3) Citric acid	(4) Salt + Acetic acid	
5	1	5.0	5.0	5.0	2.5	Example
	2	5.0	5.0	5.0	2.5	Example
	3	5.0	5.0	5.0	2.5	Example
10	4	5.0	5.0	5.0	2.5	Example
	5	5.0	5.0	5.0	2.5	Example
	6	5.0	5.0	5.0	2.5	Example
	7	5.0	5.0	5.0	2.5	Example
15	8	5.0	5.0	5.0	2.5	Example
	9	5.0	5.0	5.0	2.5	Example
	10	5.0	5.0	5.0	2.5	Example
20	11	5.0	5.0	5.0	2.5	Example
	12	5.0	5.0	5.0	2.5	Example
	13	5.0	5.0	5.0	2.5	Example
	14	5.0	5.0	5.0	2.5	Example
25	15	5.0	5.0	5.0	2.5	Example
	16	5.0	5.0	5.0	2.5	Example
	17	5.0	5.0	5.0	2.5	Example
30	18	5.0	5.0	5.0	2.5	Example
	19	5.0	5.0	4.5	2.0	Example
	20	5.0	5.0	4.0	2.0	Example
35	21	5.0	5.0	4.5	2.0	Example
	22	5.0	5.0	4.0	2.0	Example
	23	5.0	5.0	4.5	2.0	Example
	24	5.0	5.0	4.0	2.0	Example
40	25	5.0	5.0	4.5	2.0	Example
	26	5.0	5.0	4.5	2.0	Example
	27	5.0	5.0	4.5	2.0	Example
	28	5.0	5.0	4.5	2.0	Example
45	29	5.0	5.0	4.0	2.0	Example
	30	5.0	5.0	4.0	2.0	Example
	31	5.0	5.0	4.0	2.0	Example
50	32	5.0	5.0	4.0	2.0	Example
	33	1.5	1.5	2.5	0.5	Comparative Example
	34	1.5	1.5	2.5	0.5	Comparative Example
	35	1.0	1.5	2.0	0.5	Comparative Example
55	36	1.0	1.0	1.0	0.0	Comparative Example
	37	5.0	5.0	4.5	2.0	Example
	38	5.0	5.0	4.0	2.0	Example

(continued)

No.	Corrosion resistance at BPA-free painted worked part				Remarks
	(1) Cysteine	(2) Lactic acid	(3) Citric acid	(4) Salt + Acetic acid	
39	1.5	1.5	1.0	0.5	Comparative Example
40	5.0	5.0	4.0	2.0	Comparative Example

Claims

1. A surface-treated steel sheet comprising:

a steel sheet; and
a chromium-containing layer disposed on a surface of the steel sheet on at least one side, wherein when the chromium-containing layer is observed from a surface direction, linear regions in which an element smaller in atomic number than chromium is concentrated are present, and the number of the linear regions is 5.0 or more per 100 nm.

2. The surface-treated steel sheet according to claim 1, wherein the linear regions have a mesh-like connected structure.

3. The surface-treated steel sheet according to claim 2, wherein a standard deviation of an equivalent circular diameter of the mesh is 30 nm or less.

4. The surface-treated steel sheet according to claim 2 or 3, wherein average roundness of the mesh is 0.5 to 1.0.

5. The surface-treated steel sheet according to any one of claims 1 to 4, wherein a chromium coating weight of the chromium-containing layer is 40.0 mg/m² to 500.0 mg/m² per one side.

6. The surface-treated steel sheet according to any one of claims 1 to 5, wherein a chromium oxide coating weight of the chromium-containing layer is 40.0 mg/m² or less per one side.

7. The surface-treated steel sheet according to any one of claims 1 to 6, wherein an area ratio of a crystalline region when the chromium-containing layer is observed from the surface direction is 30 % or less.

8. A production method for a surface-treated steel sheet that includes: a steel sheet; and a chromium-containing layer disposed on a surface of the steel sheet on at least one side, the production method comprising:

bringing the steel sheet into contact with an aqueous solution containing sulfate ions, and holding the steel sheet in a state in which 1.0 g/m² to 30.0 g/m² of the aqueous solution is present on the surface of the steel sheet for 0.1 seconds to 20.0 seconds; and
subjecting the steel sheet to cathodic electrolysis treatment in an electrolytic solution containing 0.05 mol/L or more of trivalent chromium ions.

9. The production method for a surface-treated steel sheet according to claim 8, wherein the electrolytic solution is prepared by mixing a trivalent chromium ion source, a carboxylic acid compound, and water, adjusting pH to 4.0 to 7.0, and adjusting temperature to 40 °C to 70 °C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/016772

A. CLASSIFICATION OF SUBJECT MATTER*C25D 11/38*(2006.01)i; *C25D 9/10*(2006.01)i

FI: C25D11/38 301Z; C25D9/10

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)

C25D11/38; C25D9/10

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)

JSTPlus/JMEDPlus/JST7580 (JDreamIII); Scopus

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2021-38429 A (OTEC CO., LTD.) 11 March 2021 (2021-03-11)	1-9
A	JP 6-340998 A (NIHON PARKERIZING CO., LTD.) 13 December 1994 (1994-12-13)	1-9
A	JP 6-108265 A (NIPPON STEEL CORP.) 19 April 1994 (1994-04-19)	1-9
A	JP 10-130891 A (TEIKOKU PISTON RING CO., LTD.) 19 May 1998 (1998-05-19)	1-9

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

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“&” document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/016772

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2021-38429 A	11 March 2021	(Family: none)	
JP 6-340998 A	13 December 1994	(Family: none)	
JP 6-108265 A	19 April 1994	(Family: none)	
JP 10-130891 A	19 May 1998	US 6013380 A	
		EP 841413 A1	

REFERENCES CITED IN THE DESCRIPTION

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