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(54) COLD-ROLLED STEEL SHEET, MANUFACTURING METHOD THEREFOR, AND CAR PART

(57) There are provided a cold-rolled steel sheet having excellent chemical convertibility and high corrosion resistance after coating and a method for producing the cold-rolled steel sheet, and an automotive component.

The method includes performing first pickling with an acid liquid 1) or an acid liquid 2) below on a steel sheet subjected to continuous annealing after cold-rolling and performing second pickling with an acid liquid made of a non-oxidizing acid on the steel sheet:
the acid liquid 1) containing nitric acid and hydrochloric acid, in which the nitric acid has a concentration of more than 50 g/L to 200 g/L or less, a ratio R1 (hydrochloric acid/nitric acid) of a concentration of the hydrochloric acid to the concentration of the nitric acid is 0.01 to 0.25, and a concentration of iron ions is 3 to 50 g/L, and
the acid liquid 2) containing nitric acid and hydrofluoric acid, in which the nitric acid has a concentration of more than 50 g/L to 200 g/L or less, a ratio R2 (hydrofluoric acid/nitric acid) of a concentration of the hydrofluoric acid to the concentration of the nitric acid is 0.01 to 0.25, and a concentration of iron ions is 3 to 50 g/L.

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Description

[Technical Field]

[0001] The present invention relates to a cold-rolled steel sheet and a method for producing the steel sheet, and an automotive component. In particular, the present invention relates to a cold-rolled steel sheet having excellent chemical convertibility and high corrosion resistance after coating, which is evaluated by a hot salt water immersion test or a combined cyclic corrosion test, and a method for producing the steel sheet, and an automotive component.

[Background Art]

[0002] In recent years, from the viewpoint of global environmental conservation, there has been a strong demand for improving vehicle fuel efficiency. Furthermore, from the viewpoint of collision safety of passengers, there has also been a strong demand for increasing the strength of automotive bodies. To satisfy these demands, by increasing the strength and decreasing the thickness of cold-rolled steel sheets serving as a material for automotive components, both a decrease in weight and an increase in strength of automotive bodies have been actively pursued. Many of automotive components are produced by forming a steel sheet, and thus the steel sheet serving as a material for automotive components needs to have excellent formability in addition to high strength.

[0003] The strength of cold-rolled steel sheets can be increased by various methods. Effective means for increasing the strength without considerably impairing the formability is, for example, a solid-solution strengthening method performed by Si addition. However, if a large amount of Si, in particular, 0.5% or more of Si is added to the cold-rolled steel sheet, it is known that a large amount of SiO_2 and a Si-containing oxide such as a Si-Mn composite oxide are formed at an interface between the surface of the steel sheet and oxide scale during slab heating or hot-rolling or during annealing performed after the hot-rolling. This Si-containing oxide considerably degrades the chemical convertibility. Furthermore, if a steel sheet subjected to electrodeposition painting is exposed to a severe corrosive environment such as a salt spray test or a combined cyclic corrosion test in which wetting and drying are repeatedly performed, the coating film readily delaminates, which poses a problem in that the corrosion resistance after coating degrades.

[0004] In view of such problems of Si-containing steel sheets, for example, Patent Literature 1 proposes a high-strength cold-rolled steel sheet in which the Si concentration on the surface of the steel sheet is decreased by heating a slab at a temperature of 1200°C or higher during hot-rolling, performing descaling at high pressure, grinding the surface of the resulting hot-rolled steel sheet using a nylon brush with abrasive grains before pickling, and immersing the steel sheet in a 9% hydrochloric acid tank twice to perform pickling.

[0005] Patent Literature 2 proposes a high-strength cold-rolled steel sheet whose corrosion resistance is improved by controlling the line width of a Si-containing linear oxide observed at a depth of 1 to 10 μm from the steel sheet surface to 300 nm or less.

[0006] Patent Literature 3 proposes a technique for improving the ability to remove oxides by controlling the concentration of iron ions (Fe(II)) in hydrochloric acid to 0.5% to 18%.

[0007] In the high-strength cold-rolled steel sheet described in Patent Literature 1, however, even when the Si concentration on the steel sheet surface is decreased before cold-rolling, a Si-containing oxide is formed on the steel sheet surface due to annealing performed after the cold-rolling. Therefore, the corrosion resistance after coating is not improved.

[0008] In the high-strength cold-rolled steel sheet described in Patent Literature 2, the corrosion resistance is not problematic in a corrosive environment such as a salt spray test specified in JIS Z2371. However, sufficient corrosion resistance after coating is not achieved in a severe corrosive environment such as a hot salt water immersion test or a combined cyclic corrosion test.

[0009] That is, a high-strength cold-rolled steel sheet having excellent corrosion resistance after coating is not obtained only by decreasing the Si concentration on the steel sheet surface after hot-rolling or decreasing the amount of the Si-containing linear oxide.

[0010] In the technique described in Patent Literature 3, SiO_2 is insoluble in hydrochloric acid and cannot be removed even when the concentration of iron ions is controlled to 0.5% to 18%.

[0011] To solve the above problems, Patent Literature 4 discloses a technique for improving the chemical convertibility by removing a Si-containing oxide concentrated on the steel sheet surface through an annealing process or the like by pickling and furthermore providing a S-based compound to the surface to improve the reactivity with a chemical conversion treatment liquid.

[0012] Patent Literature 5 discloses a technique in which a P-based compound is provided instead of the S-based compound in Patent Literature 4.

[0013] Moreover, to solve the above problems, Patent Literature 6 discloses the following technique for improving the reactivity with a chemical conversion treatment liquid to improve the chemical convertibility. At the first stage, pickling is performed using an oxidizing acid to remove SiO_2. At the following second stage, pickling is performed using a non-oxidizing acid to remove an Fe-based oxide formed during the pickling at the first stage.

[Citation List]

[Patent Literature]

[0014]

[PTL 1] Japanese Unexamined Patent Application Publication No. 2004-204350
[PTL 2] Japanese Unexamined Patent Application Publication No. 2004-244698
[PTL 3] Japanese Unexamined Patent Application Publication No. 64-62485
[PTL 4] Japanese Unexamined Patent Application Publication No. 2007-217743
[PTL 5] Japanese Unexamined Patent Application Publication No. 2007-246951
[PTL 6]: Japanese Unexamined Patent Application Publication No. 2012-132092

[Summary of Invention]

[Technical Problem]

[0015] In recent years, the temperature of a chemical conversion treatment liquid has been decreased to reduce the amount of industrial waste (suppress the generation of sludge) and to reduce the operating cost. Thus, the reactivity of the chemical conversion treatment liquid with a steel sheet has been considerably decreased compared with previous chemical conversion conditions. The decrease in the temperature of the chemical conversion treatment liquid does not pose a problem for plain steel sheets, which have been conventionally used and contain only a small amount of alloy, by improving a surface control technique before the chemical conversion treatment, for example. In a high-strength cold-rolled steel sheet containing a large amount of Si, however, the reactivity with the chemical conversion treatment liquid is considerably decreased because of the influence of a Si-containing oxide formed in a surface layer of the steel sheet in the annealing process. Therefore, the reactivity needs to be improved by taking some measures on the steel sheet. The techniques disclosed in Patent Literature 4 and Patent Literature 5 are effective for conventional plain steel sheets, but do not provide a sufficient improvement effect on the decrease in the temperature of the chemical conversion treatment liquid for the high-strength cold-rolled steel sheet containing a large amount of Si. It has been found that, by applying the technique disclosed in Patent Literature 6 to the above techniques, the decrease in the temperature of the chemical conversion treatment liquid can be overcome even in the high-strength cold-rolled steel sheet containing a large amount of Si. In the technique disclosed in Patent Literature 6, however, when the Fe concentration is low, the pickling rate is low and thus the ability to remove a Si-containing oxide is insufficient. Furthermore, when the Fe concentration is high, an iron-based oxide is unfavorably formed, which degrades the chemical convertibility and also the corrosion resistance after coating.

[0016] In view of the foregoing, it is an object of the present invention to provide a cold-rolled steel sheet having excellent chemical convertibility and high corrosion resistance after coating and a method for producing the steel sheet, and to provide an automotive component.

[Solution to Problem]

[0017] To solve the above problems, the inventors have thoroughly studied a method for improving the reactivity between the steel sheet surface and the chemical conversion treatment liquid by analyzing the surface properties of the steel sheet after annealing in detail. As a result, they have found that it is extremely important to pickle, with a strong acid, a surface of the steel sheet subjected to continuous annealing after cold-rolling to remove a Si-containing oxide layer formed in a surface layer of the steel sheet during annealing and also to reduce the steel sheet surface coverage of an iron-based oxide generated on the steel sheet surface as a result of the pickling with a strong acid. Thus, the present invention has been completed.

[0018] The present invention is based on the above findings, and the gist of the present invention is as follows.

[1] A method for producing a cold-rolled steel sheet includes performing first pickling with an acid liquid 1) or an acid liquid 2) below on a steel sheet subjected to continuous annealing after cold-rolling and performing second pickling with an acid liquid made of a non-oxidizing acid on the steel sheet:

the acid liquid 1) containing nitric acid and hydrochloric acid, in which the nitric acid has a concentration of more than 50 gram/liter (hereafter referred to as g/L or g/1) to 200 g/L or less, a ratio R1 (hydrochloric acid/nitric acid)

of a concentration of the hydrochloric acid to the concentration of the nitric acid is 0.01 to 0.25, and a concentration of iron ions is 3 to 50 g/L, and
the acid liquid 2) containing nitric acid and hydrofluoric acid, in which the nitric acid has a concentration of more than 50 g/L to 200 g/L or less, a ratio R2 (hydrofluoric acid/nitric acid) of a concentration of the hydrofluoric acid to the concentration of the nitric acid is 0.01 to 0.25, and a concentration of iron ions is 3 to 50 g/L.

[2] In the method for producing a cold-rolled steel sheet according to [1], the first pickling is performed at a temperature of the acid liquid of 20°C to 70°C for 3 to 30 seconds.
[3] In the method for producing a cold-rolled steel sheet according to [1] or [2], the non-oxidizing acid is at least one of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, and oxalic acid.
[4] In the method for producing a cold-rolled steel sheet according to any one of [1] to [3], the non-oxidizing acid is any one of hydrochloric acid having a concentration of 0.1 to 50 g/L, sulfuric acid having a concentration of 0.1 to 150 g/L, and a mixed acid containing hydrochloric acid having a concentration of 0.1 to 20 g/L and sulfuric acid having a concentration of 0.1 to 60 g/L.
[5] In the method for producing a cold-rolled steel sheet according to any one of [1] to [4], the second pickling is performed at a temperature of the acid liquid of 20°C to 70°C for 1 to 30 seconds.
[6] In the method for producing a cold-rolled steel sheet according to any one of [1] to [5], the cold-rolled steel sheet contains Si in an amount of 0.5 to 3.0 mass%.
[7] In the method for producing a cold-rolled steel sheet according to any one of [1] to [6], the first pickling and the second pickling are continuously performed.
[8] A cold-rolled steel sheet is produced by the method according to any one of [1] to [7], wherein a Si-containing oxide layer in a surface layer of the steel sheet is removed and a surface coverage of an iron-based oxide present on a surface of the steel sheet is 40% or less.
[9] In the cold-rolled steel sheet according to [8], a maximum thickness of the iron-based oxide present on the surface of the steel sheet is 150 nm or less.
[10] An automotive component uses the cold-rolled steel sheet according to [8] or [9].

[Advantageous Effects of Invention]

[0019] The present invention provides a cold-rolled steel sheet having excellent chemical convertibility and high corrosion resistance after coating. According to the production method of the present invention, a cold-rolled steel sheet having excellent chemical convertibility and high corrosion resistance after coating can be easily and stably produced through a typical cold-rolling process and pickling process by simply adjusting the pickling conditions.

[0020] A cold-rolled steel sheet can be provided which has excellent chemical convertibility even when 0.5% to 3.0% of Si is contained or even when the temperature of a chemical conversion treatment liquid is decreased and which has high corrosion resistance after coating even in a severe corrosive environment such as a hot salt water immersion test or a combined cyclic corrosion test. Accordingly, in the present invention, the chemical convertibility and the corrosion resistance after coating of a high-strength cold-rolled steel sheet having a tensile strength TS of 590 MPa or more and containing a large amount of Si can be considerably improved. Thus, the cold-rolled steel sheet according to the present invention can be suitably used for, for example, high-strength components of automotive bodies.

[Brief Description of Drawings]

[0021]

[Fig. 1] Fig. 1 illustrates backscattered electron images of steel sheet surfaces of cold-rolled steel sheet standard samples No. a and No. b for determining the surface coverage of iron-based oxides.
[fig. 2] Fig. 2 illustrates a histogram showing the number of pixels plotted against gray values of the photographs of the backscattered electron images of the cold-rolled steel sheet standard samples No. a and No. b.
[Fig. 3] Fig. 3 is a photograph obtained by observing, with a transmission electron microscope, a cross-section of a coating on a steel sheet surface after pickling with a non-oxidizing acid.
[Fig. 4] Fig. 4 is a graph showing the analysis result of the iron-based oxide observed in Fig. 3 by energy-dispersive X-ray diffractometry (EDX).
[Fig. 5] Fig. 5 illustrates graphs showing depth profiles of 0, Si, Mn, and Fe on surfaces of test specimens in Table 4-1, the depth profiles being measured by GDS.

[Description of Embodiments]

[0022] Hereafter, the present invention will be described in detail. In the following description, the unit of a content of each element of a steel composition is "mass%", which is simply expressed as "%" unless otherwise specified.

[0023] In an annealing process that uses a continuous annealing furnace and is performed to impart desired microstructure, strength, and workability by recrystallizing a cold-rolled steel sheet, a non-oxidizing gas or a reducing gas is normally used as an atmosphere gas, and the dew point is also strictly controlled. Therefore, in typical cold-rolled steel sheets containing only a small amount of alloy, the oxidation of the steel sheet surface is suppressed. In steel sheets containing 0.5% or more of Si or Mn, however, even when the components of the atmosphere gas and the dew point during annealing are strictly controlled, Si, Mn, or the like, which is more easily oxidized than Fe, is oxidized. As a result, silicon oxide (SiO_2) or a Si-containing oxide such as a Si-Mn composite oxide is formed on the steel sheet surface. The composition of such an oxide varies in accordance with the composition of the steel sheet, the annealing atmosphere, or the like, but often varies in accordance with mixed conditions of the composition of the steel sheet and the annealing atmosphere in general. It is known that the Si-containing oxide is formed not only on the steel sheet surface, but also in a steel substrate, which degrades the etching properties of the steel sheet surface in a chemical conversion treatment (zinc phosphate treatment) performed as an underlayer treatment for electrodeposition painting and thus adversely affects the steady formation of a chemical conversion coating.

[0024] In recent years, the temperature of the chemical conversion treatment liquid has been decreased in order to reduce the amount of sludge generated during the chemical conversion treatment and reduce the operating cost. Compared with before, the chemical conversion treatment is performed under conditions in which the reactivity of the chemical conversion treatment liquid with the steel sheet is considerably low. Such a change in chemical conversion conditions does not pose a problem for plain steel sheets, which have been conventionally used and contain only a small amount of alloy, by improving a surface control technique, for example. However, in steel sheets containing a large amount of alloy components, in particular, in high-strength cold-rolled steel sheets whose strength is increased by adding a large amount of Si, the change in the chemical conversion conditions, that is, the decrease in the temperature of the chemical conversion treatment liquid has quite a large influence. Therefore, in cold-rolled steel sheets containing a large amount of Si, the reactivity with the chemical conversion treatment liquid needs to be improved by activating the surface of the steel sheet itself in order to overcome the degradation of chemical conversion conditions.

[0025] The inventors have studied a method for improving the chemical convertibility of the steel sheet to overcome the degradation of chemical conversion conditions described above. As a result, they have found that it is effective to pickle the surface of a cold-rolled steel sheet subjected to continuous annealing using a strong acid such as nitric acid as a pickling solution to remove a Si-containing oxide layer formed in a surface layer of the steel sheet through continuous annealing or the like after cold-rolling. Herein, the Si-containing oxide refers to SiO_2 or a Si-Mn composite oxide formed along grain boundaries on the steel sheet surface or in the steel sheet during slab heating or during annealing after hot-rolling or cold-rolling. The thickness of a layer in which such a Si-containing oxide is present varies depending on the composition of the steel sheet and the annealing conditions (temperature, time, and atmosphere), and is normally about 1 μm from the steel sheet surface. The phrase "to remove a Si-containing oxide layer" in the present invention refers to the removal of a Si-containing oxide layer by performing pickling until peaks of Si and O do not appear when the steel sheet surface is analyzed by GDS (glow discharge spectroscopy) in the depth direction.

[0026] The reason for which a strong acid such as nitric acid is used as the pickling solution is as follows. Among Si-containing oxides, a Si-Mn composite oxide easily dissolves in an acid, but SiO_2 does not easily dissolve in an acid. Therefore, to remove SiO_2, the Si-containing oxide on the steel sheet surface needs to be removed together with the steel substrate.

[0027] However, as a result of studies conducted by the inventors, it has been found that the chemical convertibility is considerably improved by pickling a steel sheet with a strong acid such as nitric acid after continuous annealing to remove a Si-containing oxide layer present on the steel sheet surface, but the chemical convertibility is sometimes not sufficient. The cause thereof has been further studied. Consequently, the following has been additionally found. That is, the Si-based oxide layer is removed by performing pickling with a strong acid such as nitric acid, but Fe eluted from the steel sheet surface as a result of the pickling forms an iron-based oxide, which is different from the Si-based oxide layer. This iron-based oxide is precipitated on the steel sheet surface so as to cover the steel sheet surface, resulting in the degradation of the chemical convertibility.

[0028] The following has also been additionally found. When iron ions (Fe(II) and Fe(III)) are present to some extent in an acid liquid containing nitric acid or the like, the dissolution rate of iron increases and thus the Si-containing oxide layer is effectively removed. When the concentration of iron ions (Fe(II) and Fe(III)) is excessively high, the amount of the iron-based oxide formed increases, which rather degrades the chemical convertibility. The concentration of iron ions in the present invention refers to the total concentration of Fe(II) ions and Fe(III) ions because, in the acid liquid containing nitric acid, which has a strong oxidation power, the eluted Fe(II) ions relatively quickly change to Fe(III) ions by the nitric acid.

[0029] As a result of the above studies, it is important to remove the Si-containing oxide layer present on the steel sheet surface while the generation of the iron-based oxide on the steel sheet surface is suppressed by performing pickling with an acid liquid containing nitric acid or the like and iron ions in an appropriate iron ion concentration.

[0030] As a result of further studies, it has been found that, to reduce the adverse effect on the chemical convertibility, it is important to suppress the generation of the iron-based oxide on the steel sheet surface and to control the surface coverage of the iron-based oxide on the steel sheet surface to 40% or less. It has also been found that the iron-based oxide present on the steel sheet surface can be dissolved and removed by performing pickling with a non-oxidizing acid after the pickling with a strong acid.

[0031] In the present invention, the first pickling is performed using a strong acid to remove the Si-containing oxide layer present on the steel sheet surface while suppressing the generation of the iron-based oxide on the steel sheet surface. Subsequently, the second pickling is performed using a non-oxidizing acid to control the surface coverage of the iron-based oxide present on the steel sheet surface to 40% or less.

[0032] The inventors have also found that when the coverage of the iron-based oxide generated on the steel sheet surface is controlled to 40% or less by pickling and the maximum thickness of the iron-based oxide is controlled to 150 nm or less, the chemical convertibility is further improved and the corrosion resistance is also further improved. They have also found that the maximum thickness of the iron-based oxide is effectively controlled to 150 nm or less by appropriately setting pickling conditions (concentration, temperature, and time) and non-oxidative pickling conditions (acid concentration, temperature, and time).

[0033] The iron-based oxide in the present invention refers to an oxide mainly containing iron at an atomic concentration ratio of 30% or more among elements other than oxygen constituting the oxide. This iron-based oxide is present with an uneven thickness on the steel sheet surface and is different from a natural oxide film present in the form of a layer with a uniform thickness of several nanometers. The iron-based oxide generated on the surface of the cold-rolled steel sheet is found to be amorphous from the observation with a transmission electron microscope (TEM) and the analysis result of a diffraction pattern obtained by electron diffraction analysis.

[0034] The present invention has been completed based on the above new findings and further studies.

[0035] Next, a method for producing a cold-rolled steel sheet according to the present invention will be described.

[0036] In the present invention, for example, a steel sheet obtained by heating a steel material (slab) containing Si in an amount of 0.5% to 3.0% and performing hot-rolling, cold-rolling, and continuous annealing is subjected to first pickling using an acid liquid 1) or an acid liquid 2) below and then subjected to second pickling using an acid liquid made of a non-oxidizing acid.

The acid liquid 1) containing nitric acid and hydrochloric acid, wherein the nitric acid has a concentration of more than 50 g/L and 200 g/L or less, the ratio R1 (hydrochloric acid/nitric acid) of the concentration of the hydrochloric acid to the concentration of the nitric acid is 0.01 to 0.25, and the concentration of iron ions (total of Fe(II) and Fe(III)) is 3 to 50 g/L.

The acid liquid 2) containing nitric acid and hydrofluoric acid, wherein the nitric acid has a concentration of more than 50 g/L and 200 g/L or less, the ratio R2 (hydrofluoric acid/nitric acid) of the concentration of the hydrofluoric acid to the concentration of the nitric acid is 0.01 to 0.25, and the concentration of iron ions (total of Fe(II) and Fe(III)) is 3 to 50 g/L.

[0037] By performing such pickling, the chemical convertibility and the corrosion resistance after coating are considerably improved.

First pickling conditions

[0038] A large amount of Si-containing oxides such as SiO_2 and a Si-Mn composite oxide are generated in a surface layer of the steel sheet after continuous annealing. In this state, the chemical convertibility and the corrosion resistance after coating are considerably degraded. In the production method according to the present invention, the first pickling is performed by pickling a cold-rolled steel sheet after annealing using an acid liquid containing nitric acid and hydrochloric acid or an acid liquid containing nitric acid or hydrofluoric acid to remove a Si-containing oxide layer on the steel sheet surface together with the steel substrate.

[0039] Among the Si-containing oxides, the Si-Mn composite oxide easily dissolves in an acid, but the SiO_2 does not easily dissolve in an acid. Therefore, to remove the Si-containing oxide including SiO_2, an oxide layer needs to be removed together with the steel substrate of the steel sheet by performing pickling with a strong acid. In the present invention, nitric acid, which has a strong oxidation power, is used as an acid for the acid liquid. An acid liquid containing nitric acid and hydrochloric acid or an acid liquid containing nitric acid and hydrofluoric acid is used. It is also effective to add a pickling accelerator to the acid liquid or perform electrolysis in a combined manner to facilitate the dissolution of the steel substrate.

[0040] As described above, Fe eluted from the steel sheet surface by pickling forms an iron-based oxide, and this iron-based oxide is precipitated on the steel sheet surface so as to cover the steel sheet surface. Consequently, the chemical convertibility is sometimes degraded. To prevent this and to reduce the load on the second pickling, the amount of the iron-based oxide generated on the steel sheet surface is preferably suppressed. For the above reasons, the following pickling conditions are specified.

[0041] To effectively remove the Si-containing oxide, when the acid liquid containing nitric acid and hydrochloric acid is used, the concentration of the nitric acid is set to more than 50 g/L and 200 g/L or less. Furthermore, the nitric acid and the hydrochloric acid, which has an effect of breaking an oxide film, are mixed so that the ratio R1 (hydrochloric acid/nitric acid) of the concentration of the hydrochloric acid to the concentration of the nitric acid is 0.01 to 0.25. The concentration of iron ions (total of Fe(II) and Fe(III)) is 3 to 50 g/L. When the acid liquid containing nitric acid and hydrofluoric acid is used, the concentration of the nitric acid is set to more than 50 g/L and 200 g/L or less. Furthermore, the nitric acid and the hydrofluoric acid, which has an effect of breaking an oxide film, are mixed so that the ratio R2 (hydrofluoric acid/nitric acid) of the concentration of the hydrofluoric acid to the concentration of the nitric acid is 0.01 to 0.25. The concentration of iron ions (total of Fe(II) and Fe(III)) is 3 to 50 g/L. If the concentration of the nitric acid is 50 g/L or less, a long time is required for pickling, which increases the facility length and thus increases the facility cost. If the concentration of the nitric acid is more than 200 g/L, the eluted iron is oxidized to generate an iron-based oxide. This iron-based oxide is precipitated on the steel sheet surface, which adversely affects the chemical convertibility and the corrosion resistance after coating. If R1 or R2 is more than 0.25 or the concentration of iron ions (total of Fe(II) and Fe(III)) is less than 3 g/L, a desired pickling rate is not achieved, and thus the Si-containing oxide cannot be efficiently removed. If R1 or R2 is less than 0.01 or the Fe concentration is more than 50 g/L, a desired pickling rate is achieved, but a large amount of iron-based oxide is formed on the steel sheet surface because of a large amount of iron ions in the pickling solution. Thus, the iron-based oxide cannot be completely removed during the second pickling. Consequently, the chemical convertibility and the corrosion resistance cannot be improved.

[0042] Herein, the concentration of iron ions (total of Fe(II) and Fe(III)) is maintained to 3 to 50 g/L by, for example, the following method. When the concentration exceeds 50 g/L, dilution is performed by adding nitric acid and hydrochloric acid. Alternatively, a method for decreasing the amount of iron in an acid using an iron-removing apparatus may be employed.

[0043] Furthermore, the maximum thickness of the iron-based oxide can be controlled to 150 nm or less by appropriately setting the pickling conditions (concentration, temperature, and time). When the first pickling is performed at a temperature of the acid liquid of 20°C to 70°C for 3 to 30 seconds, the maximum thickness of the iron-based oxide is controlled to 150 nm or less. Consequently, the chemical convertibility is further improved, and the corrosion resistance is also further improved.

Second pickling conditions

[0044] The first pickling with a strong acid is not sufficient to stably control the surface coverage of the iron-based oxide generated on the steel sheet surface to 40% or less. In the present invention, therefore, second pickling is performed in order to decrease, with certainty, the amount of the iron-based oxide generated on the steel sheet surface as a result of the first pickling. That is, pickling is performed using an acid liquid made of a non-oxidizing acid to dissolve and remove the iron-based oxide.

[0045] The non-oxidizing acid is at least one of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, and oxalic acid. Any of them may be used, and hydrochloric acid and sulfuric acid commonly used in the iron industry can be preferably used. Among them, hydrochloric acid can be suitably used because hydrochloric acid is a volatile acid and thus a residue such as a sulfate ion is not easily left on the steel sheet surface subjected to washing with water unlike sulfuric acid, and hydrochloric acid has a large effect of breaking an oxide due to a chloride ion. Alternatively, a mixed acid containing hydrochloric acid and sulfuric acid may be used.

[0046] In particular, for the purpose of preventing the degradation of the steel sheet surface quality due to lack of removal of the iron-based oxide and excess pickling, any one of hydrochloric acid having a concentration of 0.1 to 50 g/L, sulfuric acid having a concentration of 0.1 to 150 g/L, and a mixed acid containing hydrochloric acid having a concentration of 0.1 to 20 g/L and sulfuric acid having a concentration of 0.1 to 60 g/L is preferably used.

[0047] The second pickling is preferably performed at a temperature of the acid liquid of 20°C to 70°C for 1 to 30 seconds. When the temperature of the pickling solution is 20°C or higher and the treatment time is 1 second or more, the iron-based oxide left on the steel sheet surface is sufficiently removed. When the temperature of the pickling solution is 70°C or lower and the treatment time is 30 seconds or less, the steel sheet surface is not excessively dissolved and another surface oxide film is not formed.

[0048] To obtain a steel sheet having better chemical convertibility and higher corrosion resistance, the maximum thickness of the iron-based oxide present on the steel sheet surface after the pickling is preferably decreased to 150 nm or less with certainty. To achieve this, the concentration of the acid liquid made of a non-oxidizing acid is preferably increased to an appropriate value. For example, when hydrochloric acid is used, the concentration of the hydrochloric acid is preferably 3 to 50 g/L. When sulfuric acid is used, the concentration of the sulfuric acid is preferably 8 to 150 g/L. When a pickling solution prepared by mixing hydrochloric acid and sulfuric acid is used, a mixed acid containing hydrochloric acid having a concentration of 3 to 20 g/L and sulfuric acid having a concentration of 8 to 60 g/L is preferably used. When the concentration is within the above range, the thickness of the iron-based oxide can be decreased to 150 nm or less with certainty, and thus the chemical convertibility and the corrosion resistance after coating are improved. Furthermore, when the concentration is within the above range, the steel sheet surface is not excessively dissolved and another surface oxide film is not formed.

[0049] As described above, after continuous annealing, the first pickling and the second pickling are performed. Subsequently, an ordinary process such as temper rolling is performed to obtain a product sheet (cold-rolled steel sheet).

[0050] In the present invention, the pickling method, that is, a method for contacting a steel sheet with the acid liquid described in the present invention is not particularly limited. There may be a method for spraying the acid liquid onto a steel sheet or a method for immersing a steel sheet in the acid liquid.

[0051] The first pickling and the second pickling are preferably performed in a continuous manner. This prevents the steel sheet from naturally oxidizing after the first pickling, and an end product can be obtained at a time. Thus, production can be performed at low cost.

[0052] Next, the composition of the cold-rolled steel sheet according to the present invention will be described.

[0053] In the present invention, the cold-rolled steel sheet preferably has such a composition that high strength sufficient for chassis parts and the like of automobiles and good chemical convertibility can be achieved.

[0054] The Si content is preferably 0.5% to 3.0%. Si has a large effect (solid-solution strengthening ability) of increasing the strength of steel without considerably impairing the workability. Therefore, Si is an element effective for increasing the strength of steel, but is also an element that adversely affects the chemical convertibility and the corrosion resistance after coating. For the above reason, the Si content is preferably 0.5% or more. If the Si content is more than 3.0%, the hot rollability and the cold rollability are considerably degraded, which may adversely affect the productivity or degrade the ductility of the steel sheet itself. Accordingly, when Si is added, the Si content is preferably 0.5% to 3.0% and more preferably 0.8% to 2.5%.

[0055] Components other than Si are allowable as long as the contents of the components are within the ranges of typical cold-rolled steel sheets. Herein, when the cold-rolled steel sheet according to the present invention is applied to a high-strength cold-rolled steel sheet having a tensile strength TS of 590 MPa or more and used for automotive bodies and the like, the suitable composition except for Si is preferably as follows.

C: 0.01% to 0.30%

[0056] C is an element effective for increasing the strength of steel and also an element effective for generating retained austenite having a TRIP (transformation induced plasticity) effect, bainite, and martensite. When the C content is 0.01% or more, the above effects are produced. When the C content is 0.30% or less, the weldability does not degrade. Accordingly, the C content is preferably 0.01% to 0.30% and more preferably 0.10% to 0.20%.

Mn: 1.0% to 7.5%

[0057] Mn is an element that increases the strength of steel through solid-solution strengthening, improves the hardenability, and facilitates the generation of retained austenite, bainite, and martensite. When the Mn content is 1.0% or more, such effects are produced. When the Mn content is 7.5% or less, the above effects are produced without increasing the cost. Accordingly, the Mn content is preferably 1.0% to 7.5% and more preferably 2.0% to 5.0%.

P: 0.05% or less

[0058] P is an element that does not degrade the drawability despite its high solid-solution strengthening ability and that is effective for increasing the strength. Therefore, the P content is preferably 0.005% or more. Although P is an element that degrades the spot weldability, no problem is posed when the P content is 0.05% or less. Accordingly, the P content is preferably 0.05% or less and more preferably 0.02% or less.

S: 0.01% or less

[0059] S is an impurity element that unavoidably mixes and a harmful component that precipitates in steel in the form of MnS to degrade the stretch flangeability of the steel sheet. To prevent the degradation of stretch flangeability, the S content is preferably 0.01% or less and more preferably 0.005% or less.

Al: 0.01% to 0.06%

[0060] Al is an element that is added as a deoxidizer in a steelmaking process and that is effective for separating a nonmetal inclusion which degrades the stretch flangeability in the form of slag. Therefore, the Al content is preferably 0.01% or more. When the Al content is 0.06% or less, the above effects can be produced without increasing the raw material cost. Accordingly, the Al content is preferably 0.01% to 0.06% and more preferably 0.02% to 0.06%.

[0061] In the cold-rolled steel sheet according to the present invention, the balance other than the above components is Fe and unavoidable impurities. However, the addition of other components is not necessarily denied as long as the advantageous effects of the present invention are not impaired.

[0062] Next, the surface properties of the cold-rolled steel sheet according to the present invention will be described.

[0063] As described above, the cold-rolled steel sheet according to the present invention has a steel sheet surface from which the Si-containing oxide layer, such as SiO_2 and a Si-Mn composite oxide, formed in the surface layer of the steel sheet during annealing has been removed.

[0064] In the cold-rolled steel sheet according to the present invention, in addition to the removal of the Si-containing oxide layer, the surface coverage of the iron-based oxide present on the steel sheet surface needs to be decreased to 40% or less. This is because if the surface coverage is more than 40%, the dissolution reaction of iron in the chemical conversion treatment is inhibited, which suppresses the growth of conversion crystals of zinc phosphate or the like. However, in the case where a chemical conversion treatment liquid whose temperature is decreased is used, a coverage of 40% or less is insufficient for cold-rolled steel sheets used for parts, such as chassis parts of vehicles that severely corrode, required to have very high corrosion resistance after coating. Therefore, the surface coverage needs to be further decreased to 35% or less. The surface coverage is preferably 35% or less.

[0065] In the present invention, the surface coverage of the iron-based oxide is determined by the following method.

[0066] A steel sheet surface subjected to pickling is observed for about five fields at an acceleration voltage of 2 kV at a working distance of 3.0 mm with about 1000-fold magnification using an ultra-low-voltage scanning electron microscope (ULV-SEM) that can detect information regarding an outermost surface layer. Spectroscopic analysis is performed using an energy-dispersive X-ray diffractometer (EDX) to obtain a backscattered electron image. The backscattered electron image is processed using image analysis software such as Image J. Specifically, the backscattered electron image is converted into a binary representation to measure the area fraction of a black portion. By averaging the measured values in the fields, the surface coverage of the iron-based oxide can be obtained. An example of the ultra-low-voltage scanning electron microscope (ULV-SEM) is ULTRA 55 manufactured by SEISS. An example of the energy-dispersive X-ray diffractometer (EDX) is NSS312E manufactured by Thermo Fisher.

[0067] The threshold of the binary conversion will be described. A steel slab shown in Table 1 is subjected to hot-rolling, cold-rolling, and continuous annealing under the conditions shown in Table 2 to obtain a cold-rolled steel sheet having a sheet thickness of 1.8 mm. Subsequently, the cold-rolled steel sheet after the continuous annealing is pickled under the conditions shown in Table 3, washed with water, dried, and then temper-rolled at an elongation percentage of 0.7% to obtain two cold-rolled steel sheets No. a and No. b containing different amounts of iron-based oxides on the steel sheet surfaces. Subsequently, the cold-rolled steel sheet No. a is defined as a standard sample containing a large amount of iron-based oxide, and the cold-rolled steel sheet No. b is defined as a standard sample containing a small amount of iron-based oxide. Each of the steel sheets is observed using a scanning electron microscope under the above conditions to obtain a backscattered electron image. Fig. 1 illustrates photographs of the backscattered electron images of the steel sheets No. a and No. b. Fig. 2 illustrates a histogram showing the number of pixels plotted against gray values of the photographs of the backscattered electron images of the steel sheets No. a and No. b. In the present invention, the gray value (Y point) corresponding to an intersection point (X point) of the histogram No. a and the histogram No. b in Fig. 2 is defined as a threshold. The surface coverages of the iron-based oxides on the steel sheets No. a and No. b were actually determined using the threshold. The surface coverage was 85.3% in the steel sheet No. a and 25.8% in the steel sheet No. b.

[Table 1]

Chemical composition (mass%)						
C	Si	Mn	P	S	Al	Si/Mn
0.14	1.65	1.33	0.018	0.002	0.035	1.24

[Table 2]

No.	Heating temperature (°C)	Hot-rolling conditions			Cold-rolling reduction ratio (%)	Continuous annealing conditions						Strength
		Finishing temperature (°C)	Cooling rate (°C/s)	Coiling temperature (°C)		Heating temperature (°C)	Holding time (s)	Coaling rate (°C/s)	Cooling stop temperature (°C)	Holding time (s)	Cooling rate (°C/s)	TS (MPa)
1	1150	850	33	550	60	750	30	20	400	100	50	624

[Table 3]

Steel sheet	First pickling conditions			Second pickling conditions			Surface coverage of iron-based oxide (%)
	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	
a	Nitric acid: 250 + Hydrochloric acid: 25	40	10	-	-	-	85.3
b	Nitric acid: 150 + Hydrochloric acid: 15	40	10	Hydrochloric acid: 10	40	30	25.8

[0068] To further improve the chemical convertibility and also the corrosion resistance, the surface coverage of the iron-based oxide on the steel sheet surface after the second pickling is preferably 40% or less and also the maximum thickness of the iron-based oxide is preferably 150 nm or less. When the maximum thickness of the iron-based oxide is 150 nm or less, the dissolution reaction of iron in the chemical conversion treatment is not locally inhibited, and the precipitation of conversion crystals of zinc phosphate or the like is not locally suppressed. The maximum thickness is more preferably 130 nm or less.

[0069] The maximum thickness of the iron-based oxide is determined as follows.

[0070] First, ten extraction replicas that allow the observation of a cross-section having a length of about 8 μm in the width direction of the steel sheet are prepared from the steel sheet surface after the pickling by focused ion beam (FIB) machining. Subsequently, the cross-section (8 μm) of each replica is continuously captured at an acceleration voltage of 200 kV with 100,000-fold magnification using a transmission electron microscope (TEM) equipped with an energy-dispersive X-ray diffractometer (EDX) with which the local information of a cross-section can be investigated.
As one example, Fig. 3 is a photograph obtained by observing, with a transmission electron microscope (TEM), the cross-section of a coating layer generated on the steel sheet surface as a result of the first pickling. Fig. 4 illustrates the EDX analysis result of the coating layer.
As is clear from Fig. 4, the coating layer is found to be formed of an iron-based oxide. The distance between the line A that indicates a steel sheet substrate and the line B that indicates the thickest portion of the iron-based oxide layer in the cross-sectional photograph of Fig. 3 is measured for all the ten replicas. The largest distance is defined as the maximum thickness of the iron-based oxide. Note that the size and number of replicas, the measurement conditions with a TEM, and the like are merely examples, and may be obviously changed appropriately.

[0071] The thus-obtained cold-rolled steel sheet has excellent chemical convertibility and high corrosion resistance after coating evaluated by a hot salt water immersion test or a combined cyclic corrosion test, and therefore can be suitably used for automotive components.

[Example 1]

[0072] The present invention will be further described in detail based on Examples.

[0073] A steel containing C: 0.125%, Si: 1.5%, Mn: 2.6%, P: 0.019%, S: 0.008%, and Al: 0.040%, with the balance being Fe and unavoidable impurities, was refined through typical refining processes such as a converter process and degassing and continuously cast to obtain a steel material (slab). Subsequently, the slab was reheated to a temperature of 1150°C to 1170°C, then hot-rolled at a finishing temperature of 850°C to 880°C, and coiled at a temperature of 500°C to 550°C to obtain a hot-rolled steel sheet having a sheet thickness of 3 to 4 mm. Then, the hot-rolled steel sheet was pickled to remove scales and then cold-rolled to obtain a cold-rolled steel sheet having a sheet thickness of 1.8 mm. Then, the cold-rolled steel sheet was subjected to continuous annealing in which the steel sheet was heated to a soaking temperature of 750°C to 780°C and held for 40 to 50 seconds, then cooled from the soaking temperature to a cooling stop temperature of 350°C to 400°C at 20 to 30°C/s, and held in the cooling stop temperature range for 100 to 120 seconds. Subsequently, the steel sheet surface was pickled under the conditions shown in Table 4-1 and Table 4-2, washed with water, dried, and then temper-rolled at an elongation percentage of 0.7% to obtain cold-rolled steel sheets Nos. 2 to 80 in Table 4-1 and Table 4-2.

[0074] A test specimen was collected from each of the cold-rolled steel sheets. The steel sheet surface was observed for five fields at an acceleration voltage of 2 kV at a working distance of 3.0 mm with 1000-fold magnification using an ultra-low-voltage scanning electron microscope (ULV-SEM, manufactured by SEISS, ULTRA 55). Spectroscopic analysis was performed using an energy-dispersive X-ray diffractometer (EDX, manufactured by Thermo Fisher, NSS312E) to obtain a backscattered electron image. The backscattered electron image was processed using image analysis software (Image J). The gray value (Y point) corresponding to an intersection point (X point) of the histograms of the standard samples No. a and No. b described above was defined as a threshold. The backscattered electron image was converted into a binary representation to measure the area fraction of a black portion. The average of the measured values in the five fields was used as the surface coverage of the iron-based oxide.

[0075] Furthermore, a test specimen was collected from each of the cold-rolled steel sheets. The test specimen was subjected to a chemical conversion treatment and a coating treatment under the conditions below and then subjected to three corrosion tests of a hot salt water immersion test, a salt spray test, and a combined cyclic corrosion test. Thus, the corrosion resistance after coating was evaluated. Moreover, the depth profiles of 0, Si, Mn, and Fe were measured by GDS for the surface of the test specimen collected from each of the cold-rolled steel sheets.

(1) Chemical conversion conditions

[0076] The test specimen collected from each of the cold-rolled steel sheets was subjected to a chemical conversion treatment so that the chemical conversion coating had a coating weight of 1.7 to 3.0 g/m^2. The chemical conversion treatment was performed using a degreasing agent FC-E2011, a surface controlling agent PL-X, and a chemical conversion treatment agent Palbond PB-L3065 manufactured by Nihon Parkerizing Co., Ltd. under two conditions below which are standard conditions and comparative conditions in which the temperature of the chemical conversion treatment liquid was decreased.

<Standard conditions>

[0077]

- Degreasing process: treatment temperature 40°C, treatment time 120 seconds
- Spray degreasing, surface controlling process: pH 9.5, treatment temperature room temperature, treatment time 20 seconds
- Chemical conversion process: temperature of chemical conversion treatment liquid 35°C, treatment time 120 seconds

<Low-temperature conditions>

[0078] The temperature of the chemical conversion treatment liquid in the standard conditions was decreased to 33°C.

(2) Corrosion test

[0079] Electrodeposition painting was performed on the surface of the test specimen subjected to the above chemical conversion treatment using an electrodeposition paint V-50 manufactured by NIPPONPAINT Co., Ltd. so that a layer having a thickness of 25 μm was formed. The test specimen was subjected to the three corrosion tests below.

<Hot salt water immersion test>

[0080] The surface of the test specimen (n = 1) subjected to the chemical conversion treatment and the electrodeposition painting was cut with a cutter to form a crosscut mark having a length of 45 mm. The test specimen was then immersed in a 5 mass% NaCl solution (60°C) for 360 hours, washed with water, and dried. Subsequently, a tape peel-off test was performed by attaching an adhesive tape to a cut mark portion and then peeling off the adhesive tape. The maximum total width of peeling on both left and right sides of the cut mark portion was measured. When the maximum total width of peeling is 5.0 mm or less, the corrosion resistance in the hot salt water immersion test is evaluated to be good.

<Salt spray test (SST)>

[0081] The surface of the test specimen (n = 1) subjected to the chemical conversion treatment and the electrodeposition painting was cut with a cutter to form a crosscut mark having a length of 45 mm. The test specimen was then subjected to a salt spray test for 1200 hours using a 5 mass% aqueous NaCl solution in conformity with a neutral salt spray test specified in JIS Z2371:2000. Subsequently, a tape peel-off test was performed on a crosscut mark portion. The maximum total width of peeling on both left and right sides of the cut mark portion was measured. When the maximum total width of peeling is 4.0 mm or less, the corrosion resistance in the salt spray test is evaluated to be good.

<Combined cyclic corrosion test (CCT)>

[0082] The surface of the test specimen (n = 1) subjected to the chemical conversion treatment and the electrodeposition painting was cut with a cutter to form a crosscut mark having a length of 45 mm. The test specimen was subjected to a corrosion test in which 120 cycles each including salt spraying (5 mass% aqueous NaCl solution: 35°C, relative humidity: 98%) x 2 hours → drying (60°C, relative humidity: 30%) x 2 hours → wetting (50°C, relative humidity: 95%) x 2 hours were repeatedly performed. The test specimen was washed with water and dried. Subsequently, a tape peel-off test was performed on a cut mark portion. The maximum total width of peeling on both left and right sides of the cut mark portion was measured. When the maximum total width of peeling is 6.0 mm or less, the corrosion resistance in the combined cyclic corrosion test is evaluated to be good.

[0083] Table 4-1 and Table 4-2 show the results of the tests together with the conditions of the tests.

[Table 4-1]

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/ Nitric acid) R2 (Hydrofluoric acid/ Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Temperature of chemical conversion treatment liquid				
										35°C			33°C	
										Hol sait water Immersion test	Sail spray test	Combined cyclic corrosion lest		
2	Nitric acid 130 + Hydrochloric acid: 15	R1 = 0.12	3.3	40	10	-	-	-	73.1	6.4	5.6	7.9	8.4	Comparative Example
3			3.5			Hydrochloric acid: 0.1	40	1	39.2	4.8	4.0	5.9	5.9	Invention Example
4								10	36.1	4.6	3.9	5.5	5.5	Invention Example
5								30	30.5	4.5	3.5	5.1	5.2	Invention Example
6			3.2			Hydrochloric acid: 15	20	1	38.9	4.8	4.0	5.8	5.7	Invention Example
7								10	35.7	4.7	3.6	5.4	5.6	Invention Example
8								30	31.5	4.6	3.5	5.3	5.2	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/ Nitric acid) R2 (Hydrofluoric acid/ Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Temperature of chemical conversion treatment liquid				
										35°C			33°C	
										Hol sait water Immersion test	Sail spray test	Combined cyclic corrosion lest		
9			3.5			Hydrochloric acid: 15	40	1	34.9	4.5	3.6	5.3	5.7	Invention Example
10								10	31.0	4.5	3.6	4.9	5.2	Invention Example
11								30	25.6	4.1	3.1	4.3	4.6	Invention Example
12			3.9			Hydrochloric acid: 15	70	1	30.6	4.3	3.4	4.8	4.9	Invention Example
13								10	25.0	4.2	3.3	4.4	4.6	Invention Example
14								30	22.1	4.1	3.0	4.1	4.3	Invention Example
15			3.7			Hydrochloric acid: 50	40	1	29.2	4.2	3.4	4.8	4.7	Invention Example
16								10	25.9	4.1	3.2	4.4	4.5	Invention Example
17								30	21.9	3.9	3.0	3.9	3.9	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/ Nitric acid) R2 (Hydrofluoric acid/ Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Temperature of chemical conversion treatment liquid				
										35°C			33°C	
										Hol sait water Immersion test	Sail spray test	Combined cyclic corrosion lest		
18			3.1			Hydrochloric acid: 75	40	1	37.6	4.8	4.0	5.7	5.7	Invention Example
19								10	37.1	4.7	4.0	5.7	5.8	Invention Example
20								30	36.5	4.6	3.9	5.8	5.7	Invention Example
21	Nitric acid: 130 + Hydrofluoric acid: 15	R2 = 0.12	3.7	40	10	Hydrochloric acid: 0.1	40	1	37.2	4.7	3.8	5.8	5.9	Invention Example
22								10	36.5	4.6	3.6	5.8	5.9	Invention Example
23								30	35.1	4.5	3.6	5.5	5.7	Invention Example
24			3.9			Hydrochloric acid: 15	20	1	38.2	4.7	3.8	5.8	5.8	Invention Exampia
25								10	35.9	4.7	3.7	5.7	5.8	Invention Example
26								30	34.3	4.6	3.7	5.7	5.7	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/ Nitric acid) R2 (Hydrofluoric acid/ Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Temperature of chemical conversion treatment liquid				
										35°C			33°C	
										Hol sait water Immersion test	Sail spray test	Combined cyclic corrosion lest		
27			3.5			Hydrochloric acid: 15	40	1	35.1	4.6	3.9	5.7	5.7	Invention Example
28								10	33.3	4.6	3.7	5.7	5.7	Invention Example
29								30	31.9	4.5	3.6	5.5	5.5	Invention Example
30			3.6			Hydrochloric acid: 15	70	1	34.6	4.7	3.8	5.8	5.8	Invention Example
31								10	34.2	4.6	3.7	5.7	5.7	Invention Example
32								30	32.8	4.5	3.7	5.6	5.7	Invention Example
33			3.4			Hydrochloric acid: 50	40	1	34.5	4.6	3.9	5.7	5.8	Invention Example
34								10	33.2	4.5	3.8	5.7	5.7	Invention Example
35								30	31.5	4.5	3.8	5.7	5.7	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/ Nitric acid) R2 (Hydrofluoric acid/ Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Temperature of chemical conversion treatment liquid				
										35°C			33°C	
										Hol sait water Immersion test	Sail spray test	Combined cyclic corrosion lest		
36			31			Hydrochloric acid. 75	40	1	39.5	4.7	3.9	5.9	5.8	Invention Example
37								10	39.0	4.8	3.9	5.8	5.7	Invention Example
38								30	38.3	4.5	3.8	5.8	5.6	Invention Example

[Table 4-2]

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio	Concentration of iron ions (g/l)	Temperature	Treatment time	Acid concentration	temperature	Treatment time	Surface coverage of iron-based oxide	Temperature of chemical treatment liquid				
		R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)		(°C)	(s)	(g/l)	(°C)	(s)	(%)	35°C			33°C	
										Hot salt waler immersion test	Sail spray test	Combined corrosion	cyclic test	
39	Nitric acid: 130 + Hydrochloric acid: 15	Rt = 0.12	3.1	40	10	Sulfuric acid: 0.1	40	1	36.9	4.9	4.0	5.5	5.8	Invention Example
40								10	36.2	4.8	3.9	5.5	5.7	Invention Example
41								30	30.1	4.6	3.8	5.2	5.3	Invention Example
42			3.8			Sulfuric acid: 50	20	1	39.3	4.7	4.0	5.9	5.8	Invention Example
43								10	36.7	4.7	3.9	5.6	55	Invention Example
44								30	33.3	4.6	3.8	5.1	5.3	Invention Example
45			3.5			Sulfuric acid: 50	40	1	35.1	4.9	3.7	5.6	5.7	Invention Example
46								10	30.2	4.5	3.5	5.3	5.2	Invention Example
47								30	25.8	4.4	3.3	4.9	4.9	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio	Concentration of iron ions (g/l)	Temperature	Treatment time	Acid concentration	temperature	Treatment time	Surface coverage of iron-based oxide	Temperature of chemical treatment liquid				
		R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)		(°C)	(s)	(g/l)	(°C)	(s)	(%)	35°C			33°C	
										Hot salt waler immersion test	Sail spray test	Combined corrosion	cyclic test	
48			3.3			Sulfuric acid:50	70	1	30.8	4.4	3.7	5.2	5.1	Invention Example
49								10	25.2	4.3	3.5	4.9	4.8	Invention Example
50								30	21.3	4.1	3.2	4.6	47	Invention Example
51			3.5			Sulfuric acid: 150	40	1	30.2	4.9	3.6	5.1	5.1	Invention Example
52								10	26.4	4.2	3.3	4.6	4.7	Invention Example
53								30	21.6	4.3	3.2	4.3	4.6	Invention Example
54			4.1			Sulfuric acid: 200	40	1	38.5	4.9	4.0	5.9	5.9	Invention Example
55								10	38.3	4.7	3.8	5.7	5.8	Invention Example
56								30	37.2	4.7	3.6	5.7	5.8	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio	Concentration of iron ions (g/l)	Temperature	Treatment time	Acid concentration	temperature	Treatment time	Surface coverage of iron-based oxide	Temperature of chemical treatment liquid				
		R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)		(°C)	(s)	(g/l)	(°C)	(s)	(%)	35°C			33°C	
										Hot salt waler immersion test	Sail spray test	Combined corrosion	cyclic test	
57	Nitric acid: 130 + Hydrofluoric acid: 15	R2 = 0.12	3.5	40	10	Sulfuric add: 0.1	40	1	36.5	4.8	4.0	5.8	5.9	Invention Example
58								10	38.3	4.7	3.9	5.7	5.6	Invention Example
59								30	38.0	4.7	3.9	5.7	5.8	Invention Example
60			4.3			Sulfuric acid: 50	20	1	37.2	4.8	3.8	5.8	6.9	Invention Example
61								10	37.1	4.7	3.8	5.7	5.9	Invention Example
82								30	36.5	4.6	3.7	5.6	5.8	Invention Example
63			4.2			Sulfuric acid: 50	40	1	36.1	4.9	3.9	5.8	5.8	Invention Example
64								10	35.7	4.7	3.8	5.8	5.8	Invention Example
65								30	35.5	4.6	3.7	5.7	5.7	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Temperature of chemical treatment liquid				
										35°C			33°C	
										Hot salt waler immersion test	Sail spray test	Combined corrosion	cyclic test	
66			3.4			Sulfuric acid. 50	70	1	35.1	4.8	3.8	5.7	5.9	Invention Example
67								10	34.8	4.8	3.8	5.6	5.7	Invention Example
68								30	34.5	4.6	3.7	5.6	5.7	Invention Example
69			3.1			Sulfuric acid: 150	40	1	33.2	4.7	3.8	5.7	5.8	Invention Example
70								10	33.1	4.7	3.7	5.6	5.8	Invention Example
71								30	32.5	4.6	3.7	5.5	5.5	Invention Example
72			3.8			Sulfuric acid: 200	40	1	39.3	4.6	4.0	5.9	5.9	Invention Example
73								10	39.1	4.8	4.0	5.9	5.8	Invention Example
74								30	38.8	4.7	3.9	5.6	5.7	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Acid ratio	Concentration of iron ions (g/l)	Temperature	Treatment time	Acid concentration	temperature	Treatment time	Surface coverage of iron-based oxide	Temperature of chemical treatment liquid				
		R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)		(°C)	(s)	(g/l)	(°C)	(s)	(%)	35°C			33°C	
										Hot salt waler immersion test	Sail spray test	Combined corrosion	cyclic test	
75	Nitric acid: 130 + Hydrochloric acid: 15	R1 = 0.12	3.2	40	10	Hydrochloric acid: 10 +Sulfuric acid: 10	40	1	35.4	4.3	3.9	5.5	5.7	Invention Example
76								10	30.5	4.2	3.7	5.0	5.0	Invention Example
77								30	26.2	4.1	3.3	47	4.7	Invention Example
78	Nitric acid: sdd: 130 + Hydrochloric acid: 15	R1 = 0.12	3.9	40	10	Hydrochloric acid: 20 + Sulfuric acid: 50	40	1	33.4	4.3	3.7	5.2	5.8	Invention Example
79								10	30.7	4.2	3.5	4.9	5.2	Invention Example
80								30	25.6	3.9	3.4	4.6	4.7	Invention Example

[0084] As is clear from Table 4-1 and Table 4-2, the steel sheets of Invention Examples that were pickled under the conditions of the present invention after continuous annealing had a small maximum total width of peeling in any of the hot salt water immersion test, the salt spray test, and the combined cyclic corrosion test. Thus, the steel sheets of Invention Examples had excellent chemical convertibility and high corrosion resistance after coating. In particular, all the cold-rolled steel sheets having a surface coverage of the iron-based oxide of 40% or less had excellent corrosion resistance after coating in a severe corrosive environment. The depth profiles of O, Si, Mn, and Fe on each of the steel sheet surfaces in Table 4-1 and Table 4-2 were measured by GDS. It was confirmed that peaks of Si and 0 did not appear for the steel sheets pickled under the conditions of the present invention, and thus the Si-containing oxide layer was sufficiently removed. For reference, Fig. 5 illustrates depth profiles of O, Si, Mn, and Fe obtained when the test specimen No. 2 of Comparative Example and the test specimen No. 9 of Invention Example in Table 4-1 were subjected to surface analysis by GDS.

[Example 2]

[0085] Steels A to O having compositions shown in Table 5 were refined through typical refining processes such as a converter process and degassing and continuously cast to obtain steel slabs. Each of the steel slabs was hot-rolled under the hot-rolling conditions shown in Table 6 to obtain a hot-rolled steel sheet having a sheet thickness of 3 to 4 mm. The hot-rolled steel sheet was pickled to remove scales on the steel sheet surface and then cold-rolled to obtain a cold-rolled steel sheet having a sheet thickness of 1.8 mm. Subsequently, the cold-rolled steel sheet was subjected to continuous annealing and pickling under the conditions shown in Tables 6 and 7, then washed with water, dried, and temper-rolled at an elongation percentage of 0.7% to obtain each of cold-rolled steel sheets Nos. 81 to 111.

[0086] A test specimen was collected from each of the thus-obtained cold-rolled steel sheets. The surface coverage of the iron-based oxide on the steel sheet surface after pickling was measured in the same manner as in Example 1. Then, the test specimen was subjected to a tensile test and a test for corrosion resistance after coating described below. Furthermore, the depth profiles of O, Si, Mn, and Fe on the surface of the test specimen collected from each of the cold-rolled steel sheets were measured by GDS.

(1) Mechanical properties

[0087] A tensile test was performed in conformity with JIS Z2241:1998 using a JIS No. 5 tensile test specimen (n = 1) specified in JIS Z2201:1998 and collected in a direction (C direction) perpendicular to the rolling direction. Thus, the tensile strength TS was measured.

(2) Corrosion resistance after coating

[0088] A test specimen collected from each of the cold-rolled steel sheets was subjected to a chemical conversion treatment and electrodeposition painting under the same conditions as in Example 1. The test specimen was subjected to three corrosion tests of a hot salt water immersion test, a salt spray test (SST), and a combined cyclic corrosion test (CCT) in the same manner as in Example 1. Thus, the corrosion resistance after coating was evaluated.

[0089] Table 7 shows the results of the tests (the tensile strength TS is shown in Table 6).

[Table 5]

Steel Symbol	Chemical composition (mass%)						Si/Mn
	C	Si	Mn	P	S	Al	
A	0.11	1.25	1.55	0.018	0.001	0.032	0.81
B	0.15	1.30	1.80	0.019	0.002	0.033	0.72
C	0.15	1.20	1.95	0.017	0.001	0.033	0.62
D	0.09	1.45	1.40	0.017	0.002	0.028	1.04
E	0.18	1.11	1.36	0.018	0.001	0.032	0.82
F	0.16	1.41	1.23	0.017	0.001	0.041	1.15
G	0.14	1.65	1.33	0.018	0.002	0.035	1.24
H	0.12	1.45	2.10	0.017	0.001	0.042	0.69
I	0.17	0.90	1.40	0.017	0.002	0.044	0.64

(continued)

Steel Symbol	Chemical composition (mass%)						Si/Mn
	C	Si	Mn	P	S	Al	
J	0.13	1.20	1.89	0.018	0.001	0.041	0.63
K	0.15	1.20	1.85	0.017	0.001	0.034	0.65
L	0.03	1.25	3.25	0.018	0.001	0.005	0.38
M	0.22	3.30	1.15	0.018	0.001	0.027	2.87
O	0.11	0.45	1.50	0.020	0.003	0.030	0.30

[Table 6]

No.	Steel Symbol	Heating temperature (°C)	Hot-rolling conditions			Cold-rolling	Continuous annealing conditions						Tensile strength TS (MPa)
			Finishing temperature (°C)	Cooling rate (°C/s)	Coiling temperature (°C)	Reduction ratio (%)	Heating temperature (°C)	Holding time (s)	Cooling rate (°C/s)	Cooling stop temperature (°C)	Holding time (s)	Cooling rate (°C/s)	
81	A	1150	850	25	620	60	780	45	20	350	100	40	623
82	B	1150	820	31	400	60	780	40	20	400	100	50	822
83	C	1150	820	31	400	60	780	40	20	400	100	50	821
84	D	1140	850	26	600	60	760	50	20	350	100	45	816
85	E	1150	840	33	530	60	730	40	20	350	110	40	625
86	F	1150	850	30	580	55	750	35	20	400	110	50	833
87	G	1150	850	25	620	60	750	50	20	350	120	50	631
88	G	1150	850	33	550	60	750	30	20	400	100	50	635
89	G	1150	850	33	550	60	750	30	20	400	100	50	633
90	G	1150	850	33	550	60	750	30	20	400	100	50	633
91	G	1150	850	33	550	60	750	30	20	400	100	50	632
92	G	1150	850	33	550	60	750	30	20	400	100	50	635
93	G	1150	850	33	550	60	750	30	20	400	100	50	639
94	G	1150	850	33	550	60	750	30	20	400	100	50	636
95	G	1150	850	33	550	60	750	30	20	400	100	50	632
96	G	1150	850	33	550	60	750	30	20	400	100	50	634
97	G	1150	850	33	550	60	750	30	20	400	100	50	631
98	G	1150	850	33	550	60	750	30	20	400	100	50	634
99	H	1130	820	28	570	60	780	50	15	370	150	50	838
100	I	1150	840	34	530	55	780	50	15	350	120	55	821
101	J	1140	850	28	600	60	770	60	20	300	100	45	835
102	K	1150	850	25	620	60	780	45	20	350	100	40	649
103	L	1100	850	33	550	60	750	50	20	450	150	50	958

(continued)

No.	Steel	Heating temperature (°C)	Hot-rolling conditions			Cold-rolling	Continuous annealing conditions						Tensile strength TS (MPa)
	Symbol		Finishing temperature (°C)	Cooling rate (°C/s)	Coiling temperature (°C)	Reduction ratio (%)	Heating temperature (°C)	Holding time (s)	Cooling rate (°C/s)	Cooling stop temperature (°C)	Holding time (s)	Cooling rate (°C/s)	
104	L	1100	850	33	550	60	750	50	20	450	150	50	957
105	L	1100	850	33	550	60	750	50	20	450	150	50	961
106	L	1100	850	33	550	60	750	50	20	450	150	50	961
107	L	1100	850	33	550	60	750	50	20	450	150	50	962
108	M	1120	830	31	550	55	720	50	15	410	190	50	1131
109	O	990	690	25	540	75	750	35	20	400	100	50	754
110	O	970	710	28	540	70	750	35	20	400	100	50	793
111	O	960	700	27	550	75	750	35	I 20	400	100	50	805

[Table 7]

No.	Steel	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Symbol	Acid concentration (g/l)	Acid ratio	Concentration of iron Ions (g/l)	Temperature	Treatment time	Acid concentration (g/l)	Temperature	Treatment time	Surface coverage of iron based oxide	Temperature of chemical conversion treatment liquid: 35°C			33°C	
			Rt (Hydrochloric acid/Nitricacid) R2 (Hydrafluoric acid/Nitric acid)		(°C)	(s)		(°C)	(s)	(%)	Hot salt water immersion test	Salt spray test	Combined cyclic corrosion test		
81	A	Nitric acid: 130 + Chloric acid: 15	R1 =0.12	5.9	40	10	Chloric acid: 10	40	10	31.5	4.3	3.8	4.6	4.7	Invention Example
82	B			32.3	40	10	Chloric acid: 10	40	10	38.3	4.7	3.9	4.9	4.8	Invention Example
83	C	Nitric acid: 130 + Chloric acid: 15	R1 =0.12	6.2	40	10	Chloric acid: 10	40	10	31.2	4.4	3.5	4.6	5.1	Invention Example
84	O			6.1	40	10	Chloric acid: 10	40	10	30.5	4.3	3.9	4.8	5.2	Invention Example
85	E			7.3	40	10	Chloric acid: 10	40	10	30.1	4.2	3.9	4.7	5.1	Invention Example
86	F			8.2	40	10	Chloric acid: 10	40	10	30.3	4.4	3.6	4.8	5.1	Invention Example
87	G			5.9	40	10	Chloric acid: 10	10	1	33.2	4.8	3.9	4.7	5.2	Invention Example
88	G			6.9	40	10	Chloric acid: 10	40	1	34.3	4.4	3.9	5.1	5.4	Invention Example
89	G			6.8	40	10	Chloric acid: 10	40	30	26.9	4.2	3.1	4.4	4.5	Invention Example

(continued)

No.	Steel	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Symbol	Acid concentration (g/l)	Acid ratio	Concentration of iron Ions (g/l)	Temperature	Treatment time	Acid concentration (g/l)	Temperature	Treatment time	Surface coverage of iron based oxide	Temperature of chemical conversion treatment liquid: 35°C			33°C	
			Rt (Hydrochloric acid/Nitric acid) R2 (Hydrafluoric acid/Nitric acid)		(°C)	(s)		(°C)	(s)	(%)	Hot salt water immersion test	Salt spray test	Combined cyclic corrosion test		
90	G			53.2	40	10	Chloric acid: 10	40	10	52.9	5.9	4.9	7.5	7.6	Comparative Example
91	G			4.9	40	10	Sulfuric acid: 75	40	30	26.7	4.1	3.2	4.7	4.8	Invention Example
92	G			5.8	40	10	Chloric acid: 100	40	10	31.3	4.5	3.8	5.2	5.5	Invention Example
93	G	Nitric acid: 130 + Hydrofluoric acid: 15	R2 = 0.12	4.2	40	10	Chloric acid: 10	10		33.3	4.4	3.8	5.1	5.4	Invention Example
94	G			4.5	40	10	Chloric acid: 10	40	1	33.2	4.3	4	5	5.3	Invention Example
95	G			6.3	40	10	Chloric acid: 10	40	30	27.8	4.3	3.3	4.3	4.5	Invention Example
96	G			52.1	40	10	Chloric acid: 10	40	10	53.9	5.9	5.8	7.4	7.5	Comparative Example
97	G			7.2	40	10	Sulfuric acid: 75	40	30	26.5	4.1	3.9	4.5	4.7	Invention Example

(continued)

No.	Steel	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Symbol	Acid concentration (g/l)	Acid ratio	Concentration of iron Ions (g/l)	Temperature	Treatment time	Acid concentration (g/l)	Temperature	Treatment time	Surface coverage of iron based oxide	Temperature of chemical conversion treatment liquid: 35°C			33°C	
			Rt (Hydrochloric acid/Nitricacid) R2 (Hydrafluoric acid/Nitric acid)		(°C)	(s)		(°C)	(s)	(%)	Hot salt water immersion test	Salt spray test	Combined cyclic corrosion test		
98	G			5.8	40	10	Chloric acid: 100	40	10	31.5	4.5	3.9	5.3	5.6	Invention Example
99	H	Nitric acid: 130 + Chloric acid: 15	R1 = 0.12	11.1	40	10	Chloric acid: 10	40	10	35.1	4.5	3.9	4.7	5.3	Invention Example
100	I			9.2	40	10	Chloric acid: 10	40	10	31.5	4.4	3.9	4.9	5.5	Invention Example
101	J			8.3	40	10	Chloric acid: 10	40	10	31.3	4.5	3.9	4.8	5.3	Invention Example
102	K			6.6	40	10	Chloric acid: 10	40	10	30.5	4.2	3.9	4.6	5.3	Invention Example
103	L			5.9	40	10	Sulfuric acid: 75	10	1	32.9	4.4	3.7	4.7	5.5	Invention Example
104	L			13.5	40	10	Sulfuric acid: 75	40	1	36.2	4.4	3.9	5.2	5.5	Invention Example
105	L			12.1	40	10	Sulfuric acid: 75	40	30	29.8	4.2	3.5	4.8	5.6	Invention Example
106	L			3	40	10	Chloric acid: 10	40	30	26.1	4.5	3.1	5.2	5.3	Invention Example

(continued)

No.	Steel	First pickling conditions					Second pickling conditions			Surface properties	Total width of peeling after corrosion test (mm)				Remarks
	Symbol	Acid concentration (g/l)	Acid ratio	Concentration of iron Ions (g/l)	Temperature	Treatment time	Acid concentration (g/l)	Temperature	Treatment time	Surface coverage of iron based oxide	Temperature of chemical conversion treatment liquid: 35°C			33°C	
			Rt (Hydrochloric acid/Nitric acid) R2 (Hydrafluoric acid/Nitric acid)		(°C)	(s)		(°C)	(s)	(%)	Hot salt water immersion test	Salt spray test	Combined cyclic corrosion test		
107	L			4.5	40	10	Sulfuric acid: 200	40	10	32.5	4.3	3.8	5.3	5.5	Invention Example
108	M			5.2	40	10	Chloric acid: 10	40	10	32.6	4.3	3.7	5.1	5.4	Invention Example
109	N	Nitric acid : 100 +Chloric acid : 5	R1=0.05	23.1	40	10	Chloric acid : 10	40	10	29.9	4.3	3.7	4.9	5.2	Invention Example
110	N			15.2	40	10	Chloric acid : 10	40	10	30.5	4.4	3.7	4.9	5.3	Invention Example
111	N	Nitric acid 150 +Chloric acid : 15	R1=0.10	36	40	10	Chloric acid : 10	40	10	31.2	4.2	3.6	4.6	5.2	Invention Example
109	O	Nitric acid: 100 + Chloric acid: 5	R1=0.05	4.6	40	10	Chloric acid: 10	40	10	35.3	4.4	3.9	5.2	5.3	Invention Example
110	O			4.8	40	10	Chloric acid: 10	40	10	36.2	4.3	3.9	5.2	5.3	Invention Example
111	O	Nitric acid· 150 + Chloric acid: 15	R1=0.10	6.2	40	10	Chloric acid: 10	40	10	30.2	4.2	3.8	4.9	5.2	Invention Example

[0090] As is clear from Table 6 and Table 7, the high-strength cold-rolled steel sheets of Invention Examples that contained 0.5% or more of Si and pickled under the conditions of the present invention to decrease the surface coverage of the iron-based oxide on the steel sheet surface to 40% or less had not only excellent chemical convertibility and high corrosion resistance after coating, but also high strength with a tensile strength TS of 590 MPa or more. The depth profiles of 0, Si, Mn, and Fe were measured by GDS. It was confirmed that peaks of Si and O did not appear for all the steel sheets pickled under the conditions of the present invention, and thus the Si-containing oxide layer was sufficiently removed.

[Example 3]

[0091] A steel containing C: 0.125%, Si: 1.5%, Mn: 2.6%, P: 0.019%, S: 0.008%, and Al: 0.040%, with the balance being Fe and unavoidable impurities, was refined and continuously cast to obtain a steel material (slab). The slab was reheated to a temperature of 1150°C to 1170°C, then hot-rolled at a finishing temperature of 850°C to 880°C, and coiled at a temperature of 500°C to 550°C to obtain a hot-rolled steel sheet having a sheet thickness of 3 to 4 mm. The hot-rolled steel sheet was pickled to remove scales and then cold-rolled to obtain a cold-rolled steel sheet having a sheet thickness of 1.8 mm. Then, the cold-rolled steel sheet was subjected to continuous annealing in which the steel sheet was heated to a soaking temperature of 750°C to 780°C and held for 40 to 50 seconds, then cooled from the soaking temperature to a cooling stop temperature of 350°C to 400°C at 20 to 30°C/s, and held in the cooling stop temperature range for 100 to 120 seconds. Subsequently, the steel sheet surface was pickled under the conditions shown in Table 8, washed with water, dried, and then temper-rolled at an elongation percentage of 0.7% to obtain cold-rolled steel sheets Nos. 112 to 149 in Table 8.

[0092] A test specimen was collected from each of the cold-rolled steel sheets. The surface coverage and maximum thickness of the iron-based oxide generated on the steel sheet surface as a result of the pickling were measured by the above-described methods.

[0093] Furthermore, a test specimen was collected from each of the cold-rolled steel sheets. The test specimen was subjected to a chemical conversion treatment and a coating treatment under the conditions below and then subjected to three corrosion tests of a hot salt water immersion test, a salt spray test, and a combined cyclic corrosion test. Thus, the corrosion resistance after coating was evaluated. Moreover, the depth profiles of O, Si, Mn, and Fe were measured by GDS for the surface of the test specimen collected from each of the cold-rolled steel sheets.

(1) Chemical conversion conditions

[0094] The test specimen collected from each of the cold-rolled steel sheets was subjected to a chemical conversion treatment so that the chemical conversion coating had a coating weight of 1.7 to 3.0 g/m^2. The chemical conversion treatment was performed using a degreasing agent FC-E2011, a surface controlling agent PL-X, and a chemical conversion treatment agent Palbond PB-L3065 manufactured by Nihon Parkerizing Co., Ltd. under two conditions below which are standard conditions and comparative conditions in which the temperature of the chemical conversion treatment liquid was decreased.

<Standard conditions>

[0095]

- Degreasing process: treatment temperature 40°C, treatment time 120 seconds
- Spray degreasing, surface controlling process: pH 9.5, treatment temperature room temperature, treatment time 20 seconds
- Chemical conversion process: temperature of chemical conversion treatment liquid 35°C, treatment time 120 seconds

<Low-temperature conditions>

[0096] The temperature of the chemical conversion treatment liquid in the standard conditions was decreased to 33°C.

(2) Corrosion test

[0097] Electrodeposition painting was performed on the surface of the test specimen subjected to the above chemical conversion treatment using an electrodeposition paint V-50 manufactured by NIPPONPAINT Co., Ltd. so that a layer having a thickness of 25 μm was formed. The test specimen was subjected to the three corrosion tests below under more strict conditions than those of Example 1.

<Hot salt water immersion test>

[0098] The surface of the test specimen (n = 1) subjected to the chemical conversion treatment and the electrodeposition painting was cut with a cutter to form a crosscut mark having a length of 45 mm. The test specimen was then immersed in a 5 mass% NaCl solution (60°C) for 480 hours, washed with water, and dried. Subsequently, a tape peel-off test was performed by attaching an adhesive tape to a cut mark portion and then peeling off the adhesive tape. The maximum total width of peeling on both left and right sides of the cut mark portion was measured. When the maximum total width of peeling is 5.0 mm or less, the corrosion resistance in the hot salt water immersion test is evaluated to be good.

<Salt spray test (SST)>

[0099] The surface of the test specimen (n = 1) subjected to the chemical conversion treatment and the electrodeposition painting was cut with a cutter to form a crosscut mark having a length of 45 mm. The test specimen was then subjected to a salt spray test for 1400 hours using a 5 mass% aqueous NaCl solution in conformity with a neutral salt spray test specified in JIS Z2371:2000. Subsequently, a tape peel-off test was performed on a crosscut mark portion. The maximum total width of peeling on both left and right sides of the cut mark portion was measured. When the maximum total width of peeling is 4.0 mm or less, the corrosion resistance in the salt spray test is evaluated to be good.

<Combined cyclic corrosion test (CCT)>

[0100] The surface of the test specimen (n = 1) subjected to the chemical conversion treatment and the electrodeposition painting was cut with a cutter to form a crosscut mark having a length of 45 mm. The test specimen was subjected to a corrosion test in which 150 cycles each including salt spraying (5 mass% aqueous NaCl solution: 35°C, relative humidity: 98%) x 2 hours → drying (60°C, relative humidity: 30%) x 2 hours → wetting (50°C, relative humidity: 95%) x 2 hours were repeatedly performed. The test specimen was washed with water and dried. Subsequently, a tape peel-off test was performed on a cut mark portion. The maximum total width of peeling on both left and right sides of the cut mark portion was measured. When the maximum total width of peeling is 6.0 mm or less, the corrosion resistance in the combined cyclic corrosion test is evaluated to be good.

[0101] Table 8 shows the results of the tests.

[Table 8]

No.	First pickling conditions					Second pickling conditions			Surface properties		Total width of peeling after corrosion lest (mm)				Remarks
	Acid concentration (g/l)	Acid ratio	Concentration of iron ions	Temperature	Treatment time	Acid concentration	Temperature	Treatment time	Surface coverage of iron-based oxide (%)	Maximum thickness of iron based oxide (nm)	Temperature of chemical conversion treatment liquid: 35°C			33°C	
		R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)	(g/l)	(°C)	(s)	(g/l)	(°C)	(s)			Hot salt water immersion test	Salt spray test	Combined cyclic corrosion lest		
112	Nitric acid: 130 * Chloric acid: 15	R1 = 0.12	5.2	40	10	-	-	-	73.2	214	8.5	5.8	8.2	8.4	Comparative Example
113			6.4	40	10	Chloric acid: 0.1	40	1	39.4	158	5.0	4.0	6.0	5.9	Invention Example
114			3.8					10	36.1	158	4.9	4.0	5.9	6.0	Invention Example
115			7.2					30	31.1	158	4.9	3.9	5.9	6.0	Invention Example
116			5.5	40	10	Chloric acid. 15	40	1	38.5	144	4.9	3.9	5.9	5.9	Invention Example
117			3.2					10	32.5	139	4.8	3.9	5.7	5.7	Invention Example
118			12.1					10	34.3	142	4.9	4.0	5.9	6.0	Invention Example
119			25.3					10	35.2	145	4.8	3.9	5.8	5.9	Invention Example
120			40.3					10	36.1	148	4.9	4.0	5.9	5.9	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties		Total width of peeling after corrosion lest (mm)				Remarks
	Acid concentration (g/l)	Acid ratio	Concentration of iron ions	Temperature	Treatment time	Acid concentration	Temperature	Treatment time	Surface coverage of iron-based oxide (%)	Maximum thickness of iron based oxide (nm)	Temperature of chemical conversion treatment liquid: 35°C			33°C	
		R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)	(g/l)	(°C)	(s)	(g/l)	(°C)	(s)			Hot salt water immersion test	Salt spray test	Combined cyclic corrosion lest		
121			52.1	40	10	Chloric acid. 50	40	10	45.3	172	6.2	6.2	8.1	6.3	Comparative Example
122			3.2					30	28.2	144	4.8	4.0	5.7	5.9	Invention Example
123			5.8					1	30.3	93	4.3	3.6	5.1	5.3	Invention Example
124			3.8					10	27.1	69	4.2	3.4	4.9	5.2	Invention Example
125			10.1					30	21.5	85	4.0	3.1	4.7	4.9	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties		Total width of peeling after corrosion lest (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Maximum thickness of iron based oxide (nm)	Temperature of chemical conversion treatment liquid: 35°C			33°C	
											Hot salt water immersion test	Salt spray test	Combined cyclic corrosion lest		
126	Nitric acid: 130 + Hydrofluoric acid: +-	R2 = 0.12	3.5	40	10	Chloric acid: 0.1	40	1	38.3	148	4.9	4.0	5.6	5.9	Invention Example
127			4.2					10	35.2	147	4.8	4.0	5.7	6.0	Invention Example
128			6.9					30	30.5	145	4.3	3.8	5.5	5.8	Invention Example
129			3.3			Chloric acid. 50	40	1	37.2	95	4.5	4.0	5.0	5.6	Invention Example
130			4.5					10	34.5	67	4.5	3.9	4.9	5.5	Invention Example
131			5.3					30	29.8	80	4.3	3.7	4.9	5.3	Invention Example
132			5.6			Chloric acid: 150	40	1	36.5	83	4.3	4.0	4.8	5.2	Invention Example
133			8.2					10	32.5	80	4.1	3.5	4.7	5.2	Invention Example
134			5.8					30	28.5	78	4.0	3.1	4.6	5.0	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties		Total width of peeling after corrosion lest (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Maximum thickness of iron based oxide (nm)	Temperature of chemical conversion treatment liquid: 35°C			33°C	
											Hot salt water immersion test	Salt spray test	Combined cyclic corrosion lest		
135	Nitric acid: 130+Chloric acid 15	R1 = 0.12	7.5	40	10	Sulfuricacid: 0.1	40	1	39.2	149	4.9	3.9	5.9	5.9	Invention Example
136			3.5					10	35.1	145	4.8	4.0	5.8	6.0	Invention Example
137			6.2					30	30.3	141	4.8	4.0	5.9	6.0	Invention Example
138			6.7			Sulfuricacid: 50	40	1	37.5	148	4.8	3.9	5.9	6.0	Invention Example
139			9.1					10	32.1	144	4.8	3.9	5.8	5.7	Invention Example
140			8.2					30	28.6	139	4.7	3.7	5.6	5.8	Invention Example
141			7.5			Sulfuricacid: 150	40	1	30.5	92	4.3	3.9	5.7	5.5	Invention Example
142			6.3					10	26.9	88	4.3	3.6	5.5	5.3	Invention Example
143			3.3					30	24.3	85	4.1	3.3	5.2	5.1	Invention Example

(continued)

No.	First pickling conditions					Second pickling conditions			Surface properties		Total width of peeling after corrosion lest (mm)				Remarks
	Acid concentration (g/l)	Acid ratio R1 (Hydrochloric acid/Nitric acid) R2 (Hydrofluoric acid/Nitric acid)	Concentration of iron ions (g/l)	Temperature (°C)	Treatment time (s)	Acid concentration (g/l)	Temperature (°C)	Treatment time (s)	Surface coverage of iron-based oxide (%)	Maximum thickness of iron based oxide (nm)	Temperature of chemical conversion treatment liquid: 35°C			33°C	
											Hot salt water immersion test	Salt spray test	Combined cyclic corrosion lest		
144	Nitric acid: aCid: 130 + Chloric acid: 15	R1 = 0.12	6.2	40	10	Chloric acid 10 + Sulfuric acid: 10	40	1	35.2	149	4.9	3.9	5.8	5.9	Invention Example
145			5.8					10	31.5	146	4.9	3.9	5.9	6.0	Invention Example
146			6.6					30	29.3	143	4.8	4.0	5.7	6.0	Invention Example
147	Nitric acid: 130 + Chloric acid 15	R1 = 0.12	5.7	40	10	Chloric acid 20 + Sulfuric acid: 50	40	1	33.3	148	4.7	3.9	5.9	6.0	Invention Example
148			5.1					10	29.2	145	4.8	3.8	5.8	5.7	Invention Example
149			9.2					30	26.1	142	4.8	3.8	5.7	5.8	Invention Example

[0102] As is clear from Table 8, the steel sheets of Invention Examples in which the steel sheet surface after annealing was pickled so that the surface coverage of the iron-based oxide on the steel sheet surface after the second pickling was 40% or less and the maximum thickness of the iron-based oxide was 150 nm or less had a small maximum total width of peeling in any of the hot salt water immersion test, the salt spray test, and the combined cyclic corrosion test performed under strict conditions in which the test time was longer than that in Example 1. Thus, the steel sheets of Invention Examples had very high corrosion resistance after coating. The depth profiles of 0, Si, Mn, and Fe were measured by GDS. It was confirmed that peaks of Si and O did not appear for all the steel sheets pickled under the conditions of the present invention, and thus the Si-containing oxide layer was sufficiently removed.

[Industrial Applicability]

[0103] The cold-rolled steel sheet produced in the present invention is capable of having not only excellent chemical convertibility and high corrosion resistance after coating, but also high strength. The steel sheet can be suitably used as a material for automotive components and also a material for parts required to have the same characteristics in the field of household appliances, building, and the like.

Claims

1. A method for producing a cold-rolled steel sheet, comprising:

    performing first pickling with an acid liquid 1) or an acid liquid 2) below on a steel sheet subjected to continuous annealing after cold-rolling; and
    performing second pickling with an acid liquid made of a non-oxidizing acid on the steel sheet,

    the acid liquid 1) containing nitric acid and hydrochloric acid, wherein the nitric acid has a concentration of more than 50 g/L to 200 g/L or less, a ratio R1 (hydrochloric acid/nitric acid) of a concentration of the hydrochloric acid to the concentration of the nitric acid is 0.01 to 0.25, and a concentration of iron ions is 3 to 50 g/L, and
    the acid liquid 2) containing nitric acid and hydrofluoric acid, wherein the nitric acid has a concentration of more than 50 g/L to 200 g/L or less, a ratio R2 (hydrofluoric acid/nitric acid) of a concentration of the hydrofluoric acid to the concentration of the nitric acid is 0.01 to 0.25, and a concentration of iron ions is 3 to 50 g/L.

2. The method for producing a cold-rolled steel sheet according to Claim 1, wherein the first pickling is performed at a temperature of the acid liquid of 20°C to 70°C for 3 to 30 seconds.

3. The method for producing a cold-rolled steel sheet according to Claim 1 or 2, wherein the non-oxidizing acid is at least one of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, and oxalic acid.

4. The method for producing a cold-rolled steel sheet according to any one of Claims 1 to 3, wherein the non-oxidizing acid is any one of hydrochloric acid having a concentration of 0.1 to 50 g/L, sulfuric acid having a concentration of 0.1 to 150 g/L, and a mixed acid containing hydrochloric acid having a concentration of 0.1 to 20 g/L and sulfuric acid having a concentration of 0.1 to 60 g/L.

5. The method for producing a cold-rolled steel sheet according to any one of Claims 1 to 4, wherein the second pickling is performed at a temperature of the acid liquid of 20°C to 70°C for 1 to 30 seconds.

6. The method for producing a cold-rolled steel sheet according to any one of Claims 1 to 5, wherein the cold-rolled steel sheet contains Si in an amount of 0.5 to 3.0 mass%.

7. The method for producing a cold-rolled steel sheet according to any one of Claims 1 to 6, wherein the first pickling and the second pickling are continuously performed.

8. A cold-rolled steel sheet produced by the method according to any one of Claims 1 to 7, wherein a Si-containing oxide layer in a surface layer of the steel sheet is removed and a surface coverage of an iron-based oxide present on a surface of the steel sheet is 40% or less.

9. The cold-rolled steel sheet according to Claim 8, wherein a maximum thickness of the iron-based oxide present on

the surface of the steel sheet is 150 nm or less.

10. An automotive component using the cold-rolled steel sheet according to Claim 8 or 9.

FIG. 1

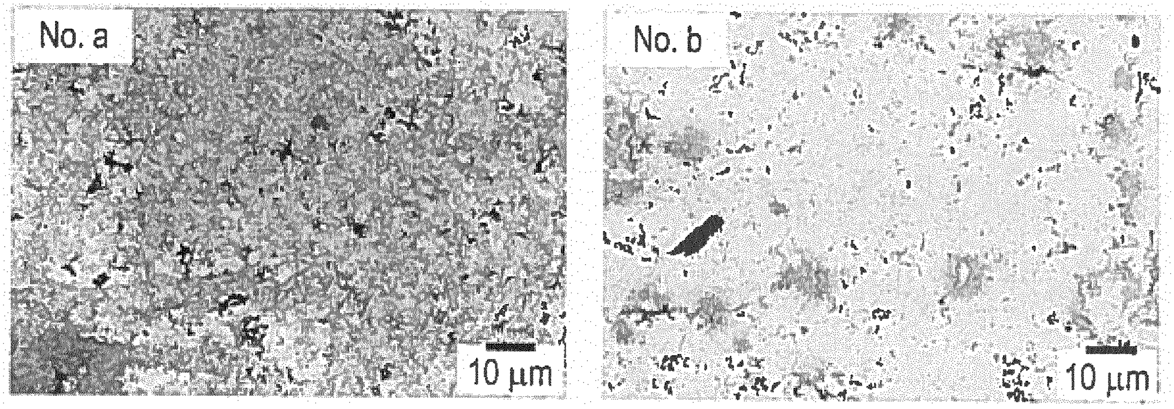


FIG. 2

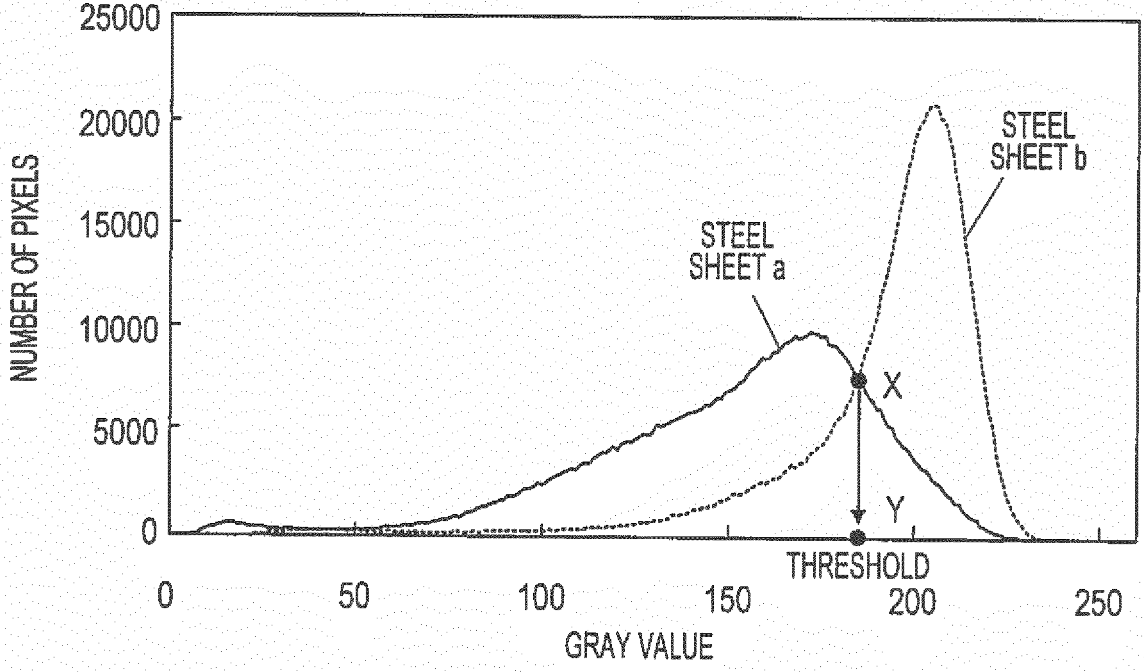


FIG. 3

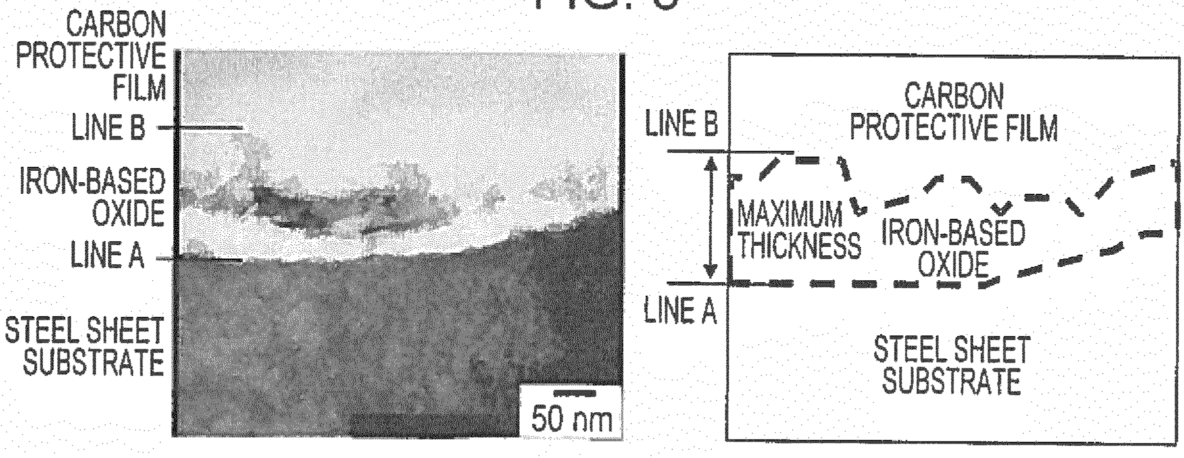
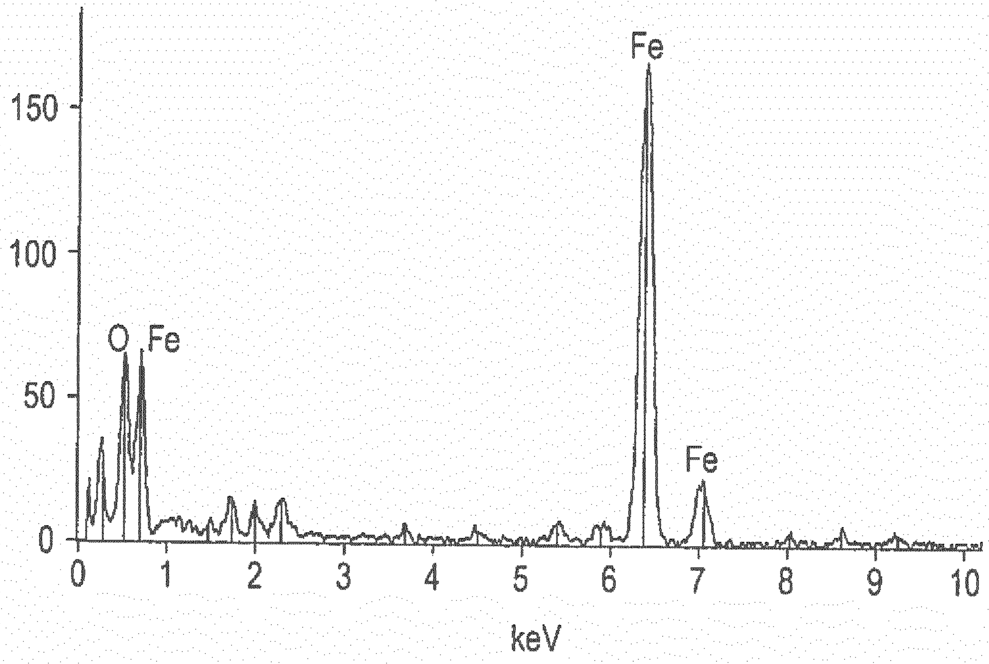


FIG. 4


150
100
50
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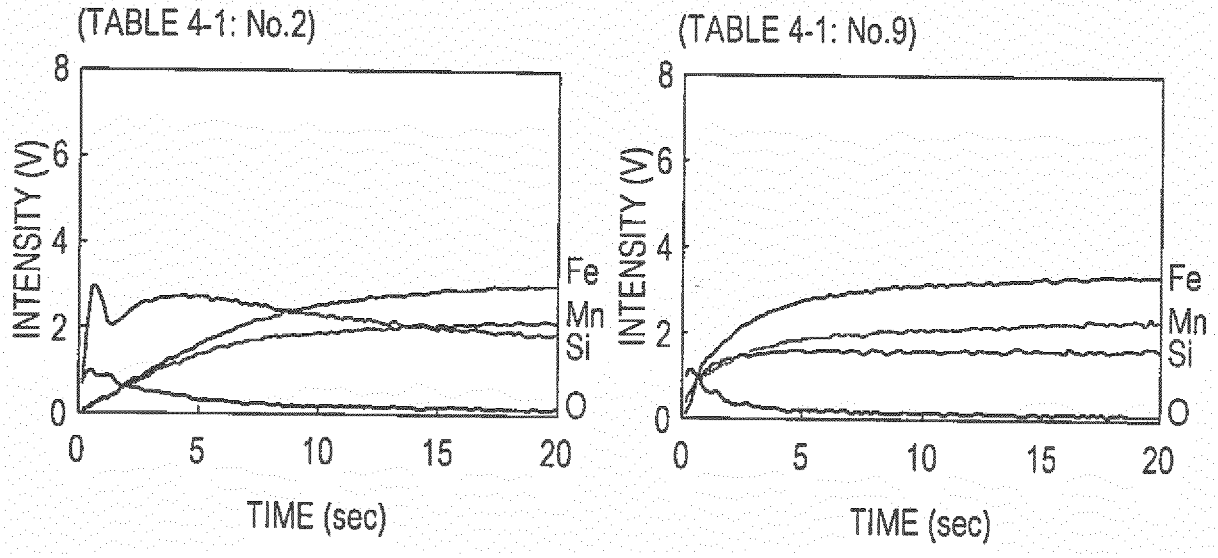
1
2
3
4
5
6
7
8
9
10
keV
O
Fe
Fe
Fe

FIG. 5


(TABLE 4-1: No.2)
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6
4
2
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0
5
10
15
20
TIME (sec)
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Mn
Si
O
(TABLE 4-1: No.9)
INTENSITY (V)
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6
4
2
0
0
5
10
15
20
TIME (sec)
Fe
Mn
Si
O

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/000777

A. CLASSIFICATION OF SUBJECT MATTER
C23G1/08(2006.01)i, *C21D9/46*(2006.01)n, *C22C38/00*(2006.01)n, *C22C38/06*(2006.01)n

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)
C23G1/08, C21D9/46, C22C38/00, C22C38/06

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

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.
Y	JP 2013-173976 A (JFE Steel Corp.), 05 September 2013 (05.09.2013), claims; paragraphs [0012], [0035], [0036] (Family: none)	1-10
Y	WO 2013/108785 A1 (JFE Steel Corp.), 25 July 2013 (25.07.2013), paragraphs [0035], [0045] & JP 5482968 B & KR 10-2014-0099320 A & CN 104053820 A & EP 2806051 A1 & US 2015/0013716 A	1-10

☐ 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 08 May 2015 (08.05.15)	Date of mailing of the international search report 19 May 2015 (19.05.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

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- JP 2012132092 A **[0014]**