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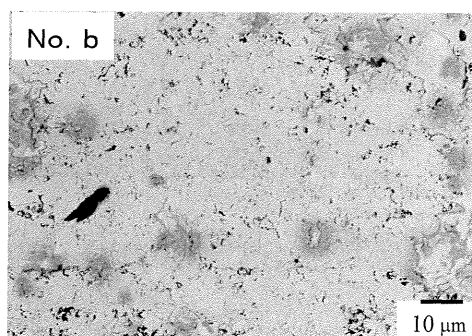
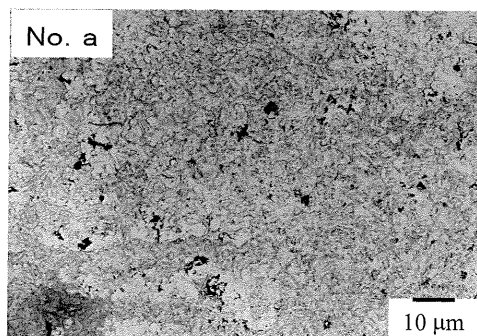
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(54) **METHOD FOR PRODUCING COLD-ROLLED STEEL SHEET, COLD-ROLLED STEEL SHEET,
AND VEHICLE MEMBER**

(57) This invention provides a method of producing a cold-rolled steel sheet being excellent in not only the phosphate treatability but also the corrosion resistance after coating under severe corrosion environment such as hot salt water immersion test or composite cycle corrosion test, wherein a continuously annealed steel sheet after cold rolling preferably comprising 0.5-3.0 mass% of

Si is pickled to remove a Si-containing oxide layer on a surface layer of the steel sheet and further repickled so that a surface covering ratio of an iron-based oxide on the surface of the steel sheet is not more than 40% and preferably a maximum thickness of the iron-based oxide is not more than 150 nm, as well as a cold-rolled steel sheet produced by this method and a member for automobile using the cold-rolled steel sheet.

【Figure 1】



Description

[TECHNICAL FIELD]

[0001] This invention relates to a method of producing a cold-rolled steel sheet as well as a cold-rolled steel sheet and a member for automobile, and more particularly to a method of producing a cold-rolled steel sheet being excellent in not only the phosphate treatability but also the corrosion resistance after coating as evaluated by a hot salt water immersion test or a composite cycle corrosion test, a cold-rolled steel sheet produced by this method as well as a member for automobile using the cold-rolled steel sheet. Moreover, the cold-rolled steel sheet according to the invention can be preferably used in a high-strength cold-rolled steel sheet containing Si and having a tensile strength TS of not less than 590 MPa.

[BACKGROUND ART]

[0002] Recently, it is strongly demanded to improve fuel consumption of an automobile from a viewpoint of the protection of global environment. Also, it is strongly demanded to improve the safety of the automobile from a viewpoint of ensuring the safe of crew members at the time of impact. In order to meet these demands, it is required to simultaneously attain weight reduction and high-strengthening of a vehicle body in the automobile, while the thinning associated with the high strengthening is positively proceeding in cold-rolled steel sheets as a starting material in the member for automobile. However, many members for automobile are manufactured by forming the steel sheet, so that these steel sheets are required to have an excellent formability in addition to the high strength.

[0003] There are various methods for enhancing the strength of the cold-rolled steel sheet. As a method increasing the strength without largely damaging the formability is mentioned a solid-solution strengthening method through addition of Si. However, when a greater amount of Si, particularly not less than 0.5 mass% of Si is added to a cold-rolled steel sheet, it is known that Si-containing oxides such as SiO_2 , Si-Mn based composite oxide and the like are formed on the surface of the steel sheet during slab heating or during annealing after hot rolling or after cold rolling. Since the Si-containing oxide considerably deteriorates the phosphate treatability, the high-strength cold-rolled steel sheets containing a great amount of Si have problems that the phosphate treatability is poor but the coating peeling is easily caused to deteriorate the corrosion resistance after the coating as compared with the commonly used steel sheets when the steel sheet after electrodeposition coating is subjected to severer corrosion environment as in a hot salt water immersion test or a composite cycle corrosion test repeating cycle of wetting-drying.

[0004] As a countermeasure for these problems, for example, Patent Document 1 proposes a high-strength cold-rolled steel sheet obtained by heating a slab at a temperature of higher than 1200°C in hot rolling, descaling under high pressure, polishing the surface of the hot-rolled steel sheet with a nylon brush containing abrasion grains prior to pickling and then immersing in a bath of 9% hydrochloric acid twice to perform pickling to lower the Si concentration on the surface of the steel sheet. Also, Patent Document 2 proposes a high-strength cold-rolled steel sheet wherein the corrosion resistance is improved by rendering line width of Si-containing linear oxide observed in 1-10 μm from the surface of the steel sheet into not more than 300 nm.

[0005] However, in the high-strength cold-rolled steel sheet disclosed in Patent Document 1, even if the Si concentration on the surface of the steel sheet is reduced before the cold rolling, the Si-containing oxide is formed on the surface of the steel sheet by annealing after cold rolling, so that the improvement of the corrosion resistance after coating is not desired. Also, in the high-strength cold-rolled steel sheet disclosed in Patent Document 2, there is no problem in the corrosion resistance under corrosion environment as in a salt spray test defined according to JIS Z2371, but sufficient corrosion resistance after coating is not obtained under severer corrosion environment as in a hot salt water immersion test or a composite cycle corrosion test. That is, the high-strength cold-rolled steel sheet having an excellent corrosion resistance after coating can not be obtained only by reducing the Si concentration on the surface of the steel sheet after hot rolling or by reducing the Si-containing linear oxide.

[0006] As a technique for solving the above problems, Patent Document 3 discloses a technique wherein the Si-containing oxide enriched on the surface of the steel sheet by annealing step or the like is removed by pickling and further an S-based compound is applied to the surface to enhance the reactivity with a phosphate treating solution to thereby improve the phosphate treatability. Also, Patent Document 4 discloses a technique wherein a P-based compound is applied instead of the S-based compound of the above technique.

[PRIOR ART ARTICLES]

[PATENT DOCUMENT]

[0007]

[Patent Document 1] JP-A~2004-204350

[Patent Document 2] JP-A-2004-244698

[Patent Document 3] JP-A-2007-217743

[Patent Document 4] JP-A-2007-246951

[SUMMARY OF THE INVENTION]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

[0008] In recent years, for the purpose of reducing industrial wastes (suppression of sludge formation) and cutting down running cost, it is proceeded to lower the temperature of the phosphate treating solution, and hence the reactivity of the phosphate treating solution to the steel sheet is largely lowered as compared with the conventional phosphate treating conditions. The lowering of the temperature of the treating solution does not come into problem when the surface adjusting technique prior to the phosphate treatment is improved in the common steel sheet having a less addition amount of alloy usually used. However, in the high-strength cold-rolled steel sheet added with a great amount of Si, the reactivity with the phosphate treating solution is considerably deteriorated by the influence of the Si-containing oxide formed on the surface of the steel sheet at an annealing step, so that it is required to enhance the reactivity from the steel sheet side in some way. On the other hand, the techniques disclosed in Patent Documents 3 and 4 are effective to the conventional common steel sheets, but can not expect the sufficient improving effect capable of lowering the temperature of the phosphate treating solution for the high-strength cold-rolled steel sheets containing a great amount of Si.

[0009] The invention is made in view of considering the above problems inherent to the cold-rolled steel sheet containing a great amount of Si and is to provide a method of producing a cold-rolled steel sheet being excellent in not only the phosphate treatability even when using a phosphate treating solution at a lower temperature but also in the corrosion resistance after coating as evaluated by a hot salt water immersion test or a composite cycle corrosion test, a cold-rolled steel sheet produced by this method as well as a member for automobile using the cold-rolled steel sheet.

[MEANS FOR SOLVING PROBLEMS]

[0010] The inventors have made detailed analysis on surface properties of steel sheets after annealing in order to solve the above problems and various studies on a method of enhancing the reactivity between the surface of the steel sheet and the phosphate treating solution. As a result, it has been found that it is very important to subject the continuously annealed steel sheet surface to strong pickling after the cold rolling to thereby remove Si-containing oxide layer formed on the surface of the steel sheet during the annealing but also reduce a ratio of covering the surface of the steel sheet with an iron-based oxide formed on the steel sheet surface by the strong pickling, and consequently the invention has been accomplished.

[0011] That is, the invention proposes a method of producing a cold-rolled steel sheet, comprising steps of cold rolling a steel sheet, continuously annealing, pickling and further repickling it.

[0012] The repickling in the production method of the invention is characterized in that a non-oxidizable acid is used instead of an acid used in the pickling prior to the repickling.

[0013] The non-oxidizable acid in the production method of the invention is characterized to be any of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, oxalic acid and a mixed acid of two or more thereof.

[0014] The non-oxidizable acid in the production method of the invention is characterized to be any of hydrochloric acid with a concentration of 0.1-50 g/L, sulfuric acid with a concentration of 0.1-150 g/L and a mixed acid of 0.1-20 g/L of hydrochloric acid and 0.1-60 g/L of sulfuric acid.

[0015] Also, the production method of the invention is characterized in that the repickling is carried out at a temperature of a repickling solution of 20-70°C for 1-30 seconds.

[0016] Furthermore, the production method of the invention is characterized in that the pickling is carried out with any of nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid and a mixed acid of two or more thereof.

[0017] Moreover, the production method of the invention is characterized in that the pickling is carried out with any of a mixed acid of nitric acid and hydrochloric acid wherein a concentration of nitric acid is more than 50 g/L but not more than 200 g/L and a ratio (HCl/HNO₃) of hydrochloric acid concentration to nitric acid concentration is 0.01-1.0, or a mixed acid of nitric acid and hydrofluoric acid wherein a concentration of nitric acid is more than 50 g/L but not more than 200 g/L and a ratio (HF/HNO₃) of hydrofluoric acid concentration to nitric acid concentration is 0.01-1.0.

[0018] The steel sheet in the production method of the invention is characterized by comprising 0.5-3.0 mass% of Si.

[0019] Also, the steel sheet in the production method of the invention is characterized by having a chemical composition comprising, in addition to Si, C: 0.01-0.30 mass%, Mn: 1.0-7.5 mass%, P: not more than 0.05 mass%, S: not more than

0.01 mass%, Al: not more than 0.06 mass% and the remainder being Fe and inevitable impurities.

[0020] Furthermore, the steel sheet in the production method of the invention is characterized by containing, in addition to the above chemical composition, one or more selected from Nb: not more than 0.3 mass%, Ti: not more than 0.3 mass%, V: not more than 0.3 mass%, Mo: not more than 0.3 mass%, Cr: not more than 0.5 mass%, B: not more than 0.006 mass% and N: not more than 0.008 mass%.

[0021] Moreover, the steel sheet in the production method of the invention is characterized by containing, in addition to the aforementioned chemical composition, one or more selected from Ni: not more than 2.0 mass%, Cu: not more than 2.0 mass%, Ca: not more than 0.1 mass% and REM: not more than 0.1 mass%.

[0022] The invention is a cold-rolled steel sheet produced by any one of the aforementioned methods, characterized in that a Si-containing oxide layer is removed from a surface layer of the steel sheet by pickling after continuous annealing and a surface covering ratio of an iron-based oxide existing on the surface of the steel sheet after repickling is not more than 40%.

[0023] Also, the cold-rolled steel sheet of the invention is characterized in that a maximum thickness of the iron-based oxide existing on the steel sheet surface after repickling is not more than 150 nm.

[0024] Further, the invention is a member for automobiles, characterized by using a cold-rolled steel sheet as described in any one of the above.

[EFFECT OF THE INVENTION]

[0025] According to the invention, there can be provided a cold-rolled steel sheet which is excellent in the phosphate treatability even when Si is contained as large as 0.5-3.0 mass% and when using a phosphate treating solution at a lower temperature but also is excellent in the corrosion resistance after coating under severer corrosion environment as in a hot salt water immersion test or a composite cycle corrosion test. According to the invention, therefore, it is possible to largely improve the phosphate treatability and corrosion resistance after coating in the high-strength cold-rolled steel sheets containing a greater amount of Si and having a tensile strength TS of not less than 590 MPa, so that it can be preferably used in strong members and the like in a vehicle body of an automobile.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0026]

[FIG. 1] FIG. 1 shows reflection electron microphotographs of steel sheet surfaces of standard cold-rolled steel sheet sample Nos. a and b for determining a surface covering ratio with an iron-based oxide.

[FIG. 2] FIG. 2 shows a histogram of pixel number to gray value in the reflection electron microphotographs of the standard cold-rolled steel sheet sample Nos. a and b.

[FIG. 3] FIG. 3 is a photograph of a section of a coating on a surface of a steel sheet after repickling observed by means of a transmission electron microscope.

[FIG. 4] FIG. 4 is a graph showing energy dispersion type X-ray (EDX) analytical results of an iron-based oxide observed in FIG. 3.

[FIG. 5] FIG. 5 is a graph of depth distribution of O, Si, Mn and Fe on a surface of a test specimen in Comparative Example (No. 1) and Invention Example (No. 9) of Example 1 as measured by GDS.

[EMBODIMENTS FOR CARRYING OUT THE INVENTION]

[0027] First, the basic technical idea of the invention will be described.

In an annealing step using a continuous annealing furnace for recrystallizing a cold-rolled steel sheet after cold rolling to impart desired structure, strength and workability, a non-oxidizing or reducing gas is usually used as an atmosphere gas, and also a dew point is strictly controlled. In the commonly general cold-rolled steel sheet having a less amount of an alloy added, therefore, the oxidation of the steel sheet surface is controlled. However, in the steel sheet containing not less than 0.5 mass% of Si or Mn, even if component or dew point of the atmosphere gas in the annealing is strictly controlled, it can not be avoided that Si, Mn and the like being easily oxidizable as compared with Fe are oxidized to form a Si-containing oxide such as Si oxide (SiO₂), Si-Mn based composite oxide or the like on the surface of the steel sheet. The construction of these oxides varies depending on components of the steel sheet, annealing atmosphere and the like, but both the oxides are typically and frequently existent in a mixture. Also, since the Si-containing oxide is formed not only the surface of the steel sheet but also in the interior of the steel matrix, it is known that the oxide obstructs the etching property on the surface of the steel sheet in the phosphate treatment (treatment with zinc phosphate) made as an underlaying treatment for electrodeposition coating and badly affects the formation of sound phosphate treated coating.

[0028] In recent years, the lowering of the temperature of the phosphate treating solution is proceeding for the purpose

of reducing the sludge amount generated in the phosphate treatment and the running cost, and hence the phosphate treatment is carried out under a condition that the reactivity of the phosphate treating solution to the steel sheet is considerably low as compared with the conventional technique. The change of the phosphate treating condition is not particularly questioned by the improvement of the surface adjusting technique or the like in the conventionally used common steel sheets having a less addition amount of an alloy. In the steel sheet having a greater addition amount of alloying component, particularly a high-strength cold-rolled steel sheet attempted to increase the strength by adding a greater amount of Si, however, the influence of changing the phosphate treating condition as mentioned above is very large. In the cold-rolled steel sheet having a greater amount of Si, therefore, it is required that the surface of the steel sheet itself is activated in correspondence with the deterioration of the phosphate treating condition to enhance the reactivity with the phosphate treating solution.

[0029] The inventors have made various investigations on a method of improving the phosphate treatability for corresponding to the deterioration of the phosphate treating condition as mentioned above. As a result, it has been found out that it is effective to conduct strong pickling of the surface of the cold-rolled steel sheet after continuous annealing with nitric acid or the like as a pickling solution to remove a Si-containing oxide layer formed on the surface of the steel sheet by continuous annealing and the like after cold rolling. The term "Si-containing oxide" used herein means SiO_2 or Si-Mn base composite oxide formed on the surface of the steel sheet or along crystal grain boundary inside the steel sheet in the slab heating or after hot rolling or in annealing after cold rolling. The thickness of the layer containing these Si-containing oxides varied depending upon components of the steel sheet or the annealing condition (temperature, time, atmosphere), but is usually about 1 μm from the surface of the steel sheet. Also, the term "removal of the Si-containing oxide layer" according to the invention means that the pickling is carried out to remove the Si-containing oxide layer to a level that peaks of Si, O do not appear when the surface of the steel sheet is analyzed in depth direction by means of GDS (glow discharge optical emission spectroscopy).

[0030] The reason why a strong acid such as nitric acid or the like is used as the pickling solution is due to the fact that among the Si-containing oxides, Si-Mn based composite oxide is easily dissolved in an acid, but SiO_2 is hardly soluble, and in order to remove the latter, the Si-containing oxide on the surface of the steel sheet should be removed together with the steel matrix.

[0031] According to the inventors' studies, however, it can be seen that the phosphate treatability is largely improved by removing the Si-containing oxide layer existing on the steel sheet surface through strong pickling with nitric acid or the like after the continuous annealing but the phosphate treatability may be deteriorated at moments. As the cause is further investigated, it is newly found that although the Si-containing oxide layer is removed by the strong pickling with nitric acid or the like, Fe dissolved from the surface of the steel sheet by the pickling separately produces an iron-based oxide, which is settled and precipitated on the surface of the steel sheet so as to cover the steel sheet surface to thereby deteriorate the phosphate treatability.

[0032] And, it has been found that in order to suppress the oxidation of the steel sheet surface by the above strong pickling to mitigate the bad influence upon the phosphate treatability, it is important to suppress the formation of the iron-based oxide on the steel sheet surface to reduce the ratio of covering the steel sheet surface with the iron-based oxide to not more than 40% and that it is effective as means for attaining the above to further conduct repickling under adequate conditions after the pickling to dissolve and remove the iron-based oxide precipitated on the surface of the steel sheet.

[0033] Further, the inventors have found that the phosphate treatability is more improved and the corrosion resistance is further improved when the maximum thickness of the iron-based oxide is not more than 150 nm in addition to the fact that the covering ratio of the iron-based oxide generated on the surface of the steel sheet by pickling is not more than 40% and that it is effective as means for attaining the above to conduct the repickling by properly increasing the concentration of the acid used in the repickling.

Moreover, the iron-based oxide in the invention means an oxide composed mainly of iron wherein an atomic concentration ratio of iron is not less than 30% as an element other than oxygen constituting the oxide. The iron-based oxide is existent on the surface of the steel sheet at an uneven thickness, which is different from a natural oxide film existing uniformly and in layer at a thickness of few nm. The iron-based oxide generated on the surface of the cold-rolled steel sheet is confirmed to be amorphous from the observation by means of a transmission electron microscope (TEM) and analysis results of diffraction pattern (analytical diagram) through an electron diffractometry.

The invention is accomplished by conducting further examinations on the above new knowledge.

[0034] The reason why the chemical composition of the cold-rolled steel sheet according to the invention is limited to the above range will be described below.

Si: 0.5-3.0 mass%

[0035] Si is an element effective for attaining the increase of the strength of the steel because the effect of enhancing the strength of steel (solid-solution strengthening ability) is large without largely damaging the workability, but is also an

element adversely exerting on the phosphate treatability and the corrosion resistance after coating. When Si is added as means for attaining a high strength, the addition of not less than 0.5 mass% is necessary. If the Si content is less than 0.5 mass%, the influence due to the deterioration of the phosphate treating conditions is less. On the other hand, when the Si content exceeds 3.0 mass%, the hot rolling property and cold rolling property are largely deteriorated, which is adversely influenced on the productivity and leads to the deterioration of ductility of the steel sheet itself. Therefore, Si is added within a range of 0.5-3.0 mass%. Preferably, it is a range of 0.8-2.5 mass%.

[0036] The cold-rolled steel sheet of the invention is an essential feature to include Si in the above range. The other components are acceptable as far as they are included within composition ranges in the common cold-rolled steel sheet, and are not particularly limited. However, the cold-rolled steel sheet of the invention is preferable to have the following component composition when it is applied to a high-strength cold-rolled steel sheet having a tensile strength of not less than 590 MPa for use in vehicle bodies for automobiles and so on.

C: 0.01-0.30 mass%

[0037] C is an element effective for enhancing the strength of steel and further is an element effective for producing residual austenite having an effect of TRIP (Transformation Induced Plasticity), bainite and martensite. When C content is not less than 0.01 mass%, the above effect is obtained, while when C content is not more than 0.30 mass%, the deterioration of the weldability is not caused. Therefore, C is added preferably within a range of 0.01-0.3 mass%, more preferably within a range of 0.10-0.20 mass%.

Mn: 1.0-7.5 mass%

[0038] Mn is an element having an action for solid-solution strengthening steel to increase the strength and enhance the hardenability and promoting the formation of residual austenite, bainite and martensite. Such effects are developed by the addition of not less than 1.0 mass%. On the other hand, when Mn content is not more than 7.5 mass%, the above effect is obtained without the increase of the cost. Therefore, Mn is added preferably within a range of 1.0-7.5 mass%, more preferably within a range of 2.0-5.0 mass%.

P: not more than 0.05 mass%

[0039] P is an element damaging no drawability though the solid-solution strengthening ability is large and is also an element effective for attaining a high strength, so that it is preferable to be included in an amount of not less than 0.005 mass%. However, P is an element damaging the spot weldability, but there is no problem when it is not more than 0.05 mass%. Therefore, P is preferably not more than 0.05 mass%, more preferably not more than 0.02 mass%.

S: not more than 0.01 mass%

[0040] S is an impurity element inevitably incorporated, and is a harmful element which is precipitated in steel as MnS to deteriorate the stretch-flanging property. In order to prevent the deterioration of the stretch-flanging property, S is preferably not more than 0.01 mass%, more preferably not more than 0.005 mass%, further preferably not more than 0.003 mass%.

Al: not more than 0.06 mass%

[0041] Al is an element added as a deoxidizer at steel-making step, and is also an element effective for separating non-metallic inclusion, which deteriorates the stretch-flanging property, as a slug, so that it is preferable to be included in an amount of not less than 0.01 mass%. When Al content is not more than 0.06 mass%, the above effect is obtained without the increase of cost for material. Therefore, Al is preferable to be not more than 0.06 mass%, More preferably, it is a range of 0.02-0.06 mass%.

[0042] In addition to the above components, the cold-rolled steel sheet of the invention may contain one or more selected from Nb: not more than 0.3 mass%, Ti: not more than 0.3 mass%, V: not more than 0.3 mass%, Mo: not more than 0.3 mass%, Cr: not more than 0.5 mass%, B: not more than 0.006 mass% and N: not more than 0.008 mass%. Nb, Ti and V are elements forming carbide and nitride to suppress ferrite growth at a heating stage in the annealing and finely divide the structure to improve the formability, particularly stretch-flanging property, and also Mo, Cr and B are elements improving the hardenability of steel and promoting the formation of bainite and martensite, so that they can be added within the above ranges. Also, N is an element forming nitrides with Nb, Ti and V or solid-soluting in steel to contribute to the increase of the strength of steel, so that when it is not more than 0.008 mass%, a greater amount of the nitride is not formed, and hence the breakage due to the formation of voids in the press forming can be suppressed

to obtain the above effect.

[0043] In addition to the above components, the cold-rolled steel sheet of the invention may contain one or more selected from Ni: not more than 2.0 mass%, Cu: not more than 2.0 mass%, Ca: not more than 0.1 mass% and REM: not more than 0.1 mass%.

Ni and Cu promote the formation of the low-temperature transformation phase to develop the effect of increasing the strength of steel, so that they can be added within the above ranges. Also, Ca and REM are elements controlling the form of the sulfide base inclusion to improve the stretch-flanging property of the steel sheet, so that they can be added within the above ranges.

In the cold-rolled steel sheet of the invention, the remainder other than the above components is Fe and inevitable impurities. However, other components may be optionally added within a scope of not damaging the action and effect of the invention.

[0044] The surface properties of the cold-rolled steel sheet of the invention will be described below.

As mentioned above, the cold-rolled steel sheet of the invention is necessary to have a steel sheet surface obtained after the removal of Si-containing oxide layer such as SiO_2 or Si-Mn based composite oxide formed on the surface layer of the steel sheet during annealing. For this end, it is necessary to conduct strong pickling with nitric acid or the like to dissolve and remove the Si-containing oxide formed on the surface of the steel sheet and in the grain boundary portion in the vicinity of the surface together with the steel matrix.

[0045] Furthermore, in the cold-rolled steel sheet of the invention, it is necessary to reduce the ratio of covering the surface of the steel sheet with iron-based oxide generated on the steel sheet surface by the strong pickling with nitric acid or the like to not more than 85% as an area ratio in addition to the removal of the Si-containing oxide layer. When the surface covering ratio exceeds 85%, the dissolving reaction of iron in the phosphate treatment is inhibited to suppress the crystal growth of phosphate such as zinc phosphate or the like. However, in case of using a phosphate treating solution of a lower temperature, the covering ratio of not more than 85% is insufficient in cold-rolled steel sheets used in applications requiring an extremely severe corrosion resistance after coating such as leg members for vehicle bodies particularly subjected to severe corrosion, so that it should be further reduced to not more than 40%, preferably not more than 35%.

[0046] In the invention, the surface covering ratio of the iron-based oxide is determined as follows:

The surface of the steel sheet after the pickling is observed at about 5 fields with a ultra-low acceleration voltage scanning type electron microscope (ULV-SEM) capable of detecting information of an extremely surface layer under conditions of acceleration voltage: 2 kV, operating distance: 3.0 mm and magnification: about 1000 times and spectroscopy is conducted with an energy dispersion type X-ray spectrometer (EDX) to obtain a reflection electron image. The reflection electron image is binarized with an image analysis software, e.g. Image J to measure an area ratio of a black portion. The measured results on the fields can be averaged to obtain a surface covering ratio of the iron-based oxide. Moreover, as the ultra-low acceleration voltage scanning type electron microscope (ULV-SEM) may be mentioned, for example, ULTRA 55 made by SEISS, and as the energy dispersion type X-ray spectrometer (EDX) may be mentioned, for example, NSS 312E made by Thermo Fisher.

[0047] Here, threshold value in the binarization will be described.

A steel slab of Steel symbol G shown in Table 3 of the following example is subjected to hot rolling, cold rolling and continuous annealing under conditions of No. 8 in Table 4 of the following example to obtain a cold-rolled steel sheet of 1.8 mm in thickness, and then the cold-rolled steel sheet after the continuous annealing is subjected to pickling and repickling under conditions shown in Table 1, washed with water, dried and subjected to 0.7% temper rolling to obtain two cold-rolled steel sheets of Nos. a and b having different iron-based oxide amounts on their steel sheet surfaces. Then, the cold-rolled steel sheet of No. a is a standard sample having a large amount of iron-based oxide and the cold-rolled steel sheet of No. b is a standard sample having a small amount of iron-based oxide, and each of these steel sheets is observed with the scanning type electron microscope under the aforementioned conditions to obtain a reflection electron image. FIG. 1 shows photographs of reflection electron images of steel sheets Nos. a and b, and FIG. 2 shows a histogram of pixel number to a gray value in the photographs of the reflection electron images of the steel sheets Nos. a and b. In the invention, a gray value (Y point) corresponding to an intersecting point (X point) of the histograms of Nos. a and b shown in FIG. 2 is defined as a threshold value. Incidentally, when the surface covering ratio of the iron-based oxide in the steel sheets Nos. a and b is determined with the above threshold value, it is 85.3% in the steel sheet No. a and 25.8% in the steel sheet No. b.

[0048] Table 1

[0049] In order to more improve the phosphate treatability and hence the corrosion resistance in the cold-rolled steel sheet of the invention, it is preferable that the maximum thickness of the iron-based oxide is not more than 150 nm in addition that the covering ratio of the iron-based oxide produced on the steel sheet surface by repickling is not more than 40%. When the maximum thickness of the iron-based oxide is not more than 150 nm, the dissolving reaction of

iron through the phosphate treatment is not inhibited locally and also the precipitation of crystal of phosphate such as zinc phosphate or the like is not inhibited locally. More preferably, it is not more than 130 nm.

[0050] The maximum thickness of the iron-based oxide is measured as follows.

First, 10 extraction replicas are prepared from the surface of the steel sheet after the pickling by a focused ion beam (FIB) work for observing a section of about 8 μm relative to the widthwise direction of the steel sheet. Then, the section of 8 μm in the each replica is continuously shot by means of a transmission electron microscope (TEM) provided with an energy dispersion type X-ray spectrometer (EDX) capable of checking local information of the section at an acceleration voltage of 200 kV and a magnification of 100000 times. As an example, FIG. 3 is a photograph showing a section of a covering layer existing on the surface of the steel sheet and generated by pickling as observed by TEM, and FIG. 4 shows analytical results of the covering layer by EDX. As seen from FIG. 4, the covering layer is an iron-based oxide composed mainly of iron. Therefore, the interval between a line A showing a surface of the steel sheet and a line B showing a thickest portion of an oxide layer shown by the photograph of the section in FIG. 3 is measured with respect to the 10 replicas, and a maximum thickness among them is a maximum thickness of the iron-based oxide. Moreover, the size and numbers of the replicas, measuring conditions by TEM and the like as mentioned above are merely exemplified, and may be properly modified as a matter of course.

[0051] The production method of the cold-rolled steel sheet according to the invention will be described below.

The production method of the cold-rolled steel sheet of the invention is necessary to be a method wherein a steel material (slab) having Si: 0.5-3.0 mass% is heated, hot rolled, cold rolled, continuously annealed and then strong-pickled with nitric acid or the like to remove Si-containing oxide layer on a surface layer portion of the steel sheet and further repickled to render a surface covering ratio of an iron-based oxide not more than 40% generated on the steel sheet surface by the above strong pickling. Further, it is preferable to be a method wherein a maximum thickness of the iron-based oxide can be made to not more than 150 nm. Therefore, the procedure ranging from the steel-making step to the continuous annealing step after the cold rolling can be carried out according to the usual manner, but the pickling after the continuous annealing is preferable to be conducted under the following conditions.

Pickling conditions after continuous annealing

[0052] On the surface layer of the steel sheet after the continuous annealing is produced a greater amount of the Si-containing oxide such as SiO_2 , Si-Mn based composite oxide or the like, so that the phosphate treatability and the corrosion resistance after coating are considerably deteriorated. In the production method of the invention, therefore, it is necessary that the cold-rolled steel sheet after the annealing is strongly pickled with nitric acid or the like, whereby the Si-containing oxide layer on the surface of the steel sheet is removed with the steel matrix.

[0053] As previously mentioned, Si-Mn based composite oxide among the Si-containing oxides is easily dissolved in an acid, but SiO_2 is insoluble in an acid. Therefore, in order to remove the Si-containing oxide including SiO_2 , it is necessary to remove the oxide layer together with the steel matrix of the steel sheet by the strong pickling. As the acid usable in the strong pickling can be preferably used nitric acid as a strong oxidizable acid, but hydrofluoric acid, hydrochloric acid, sulfuric acid or the like may be used as long as the Si-containing oxide layer can be removed, so that the kind of the acid is particularly no matter. Also, it is effective to add a pickling promoting agent to the acid, or to co-use an electrolytic treatment to promote the dissolution of the steel matrix.

[0054] Moreover, in order to remove the Si-containing oxide layer from the surface layer of the steel sheet after the continuous annealing and mitigate the load of the following repickling, it is preferable to suppress the amount of the iron-based oxide generated on the steel sheet surface by the strong pickling after the continuous annealing and before the repickling. For this end, it is preferable to conduct the pickling with a pickling solution having a nitric acid concentration of more than 50 g/L but not more than 200 g/L wherein hydrochloric acid having an effect of breaking the oxide is mixed so that a ratio R (HCl/HNO_3) of hydrochloric acid concentration to nitric acid concentration is a range of 0.01-1.0 or hydrofluoric acid is mixed so that a ratio (HF/HNO_3) of hydrofluoric acid concentration to nitric acid concentration is a range of 0.01-1.0. In case of using the above pickling solution, it is preferable that a temperature of the pickling solution is 20-70°C and a pickling time is 3-30 seconds.

Repickling conditions after the pickling

[0055] However, when only the strong pickling is carried out with the pickling solution obtained by mixing nitric acid and hydrofluoric acid or nitric acid and hydrochloric acid as mentioned above, it is difficult to stably control the surface covering ratio of the iron-based oxide generated on the surface of the steel sheet to not more than 40%. In the invention, therefore, in order to more surely reduce the iron-based oxide generated on the surface of the steel sheet by the strong pickling, the iron-based oxide is dissolved and removed by further repickling the steel sheet pickled after the continuous annealing with a non-oxidizable acid.

[0056] The non-oxidizable acid usable in the repickling includes hydrochloric acid, sulfuric acid, phosphoric acid,

pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, oxalic acid and a mixed acid of two or more thereof. Any of these may be used, but hydrochloric acid or sulfuric acid commonly used in the iron-making industry may be preferably used. Among them, hydrochloric acid is preferable because it is a volatile acid and hardly remains a residue on the steel sheet surface after washing with water different from sulfuric acid retaining sulfuric acid root and is large in the effect of breaking the oxide by chloride ion. Also, a mixed acid of hydrochloric acid and sulfuric acid may be used.

[0057] When hydrochloric acid is used as the pickling solution in the repickling, it is preferable that a concentration of hydrochloric acid is 0.1-50 g/L, while in case of using sulfuric acid, it is preferable that a concentration of sulfuric acid is 0.1-150 g/L. Also, when the mixed acid of hydrochloric acid and sulfuric acid is used in the repickling, it is preferable to use a mixed acid having a hydrochloric acid concentration of 0.1-20 g/L and a sulfuric acid concentration of 0.1-60 g/L. Also, the repickling of the invention is preferable to be conducted at a temperature of a repickling solution of 20-70°C for a treating time of 1-30 seconds even in case of using any of the repickling solutions. When the concentration of the repickling solution is more than the above lower limit and the liquid temperature is not lower than 20°C and the treating time is not less than 1 second, it is sufficient to remove the iron-based oxide existing on the steel sheet surface, while when the concentration of the repickling solution is not more than the above upper limit and the temperature is not higher than 70°C and the treating time is not more than 30 seconds, the dissolution of the steel sheet surface becomes not excessive and a new surface oxide film is not formed.

[0058] In order to obtain steel sheets being more excellent in the phosphate treatability and corrosion resistance, it is preferable that the maximum thickness of the iron-based oxide existing on the steel sheet surface after the pickling is surely thinned to not more than 150 nm. For this end, it is preferable to properly increase the concentration of the pickling solution used in the repickling. For example, it is preferable that when hydrochloric acid is used in the repickling, the concentration of hydrochloric acid is 3-50 g/L, while when sulfuric acid is used in the repickling, the concentration of sulfuric acid is 8-150 g/L. On the other hand, when a mixture of hydrochloric acid and sulfuric acid is used as a pickling solution in the repickling, it is preferable to use a mixed acid having a hydrochloric acid concentration of 3-20 g/L and a sulfuric acid concentration of 8-60 g/L. In any case, when the acid concentration is within the above range, the iron-based oxide can be surely thinned to not more than 150 nm, whereby the phosphate treatability and the corrosion resistance after coating are improved. Also, when the acid concentration is within the above range, the dissolution of the steel sheet surface becomes not excessive, and hence new surface oxide film is never formed.

[0059] The cold-rolled steel sheet, wherein the covering ratio of the steel sheet surface with the iron-based oxide is made to not more than 40% by pickling and repickling after the continuous annealing as mentioned above, or alternately the cold-rolled steel sheet, wherein the maximum thickness of the iron-based oxide is made to not more than 150 nm, is subsequently subjected to usual treating steps such as temper rolling and the like to provide products.

[Example 1]

[0060] A steel comprising C: 0.125 mass%, Si: 1.5 mass%, Mn: 2.6 mass%, P: 0.019 mass%, S: 0.008 mass%, Al: 0.040 mass% and the remainder being Fe and inevitable impurities is prepared according to common refining process such as melting in a converter, degassing treatment and the like and continuously cast into a steel material (slab). Then, the slab is reheated to a temperature of 1150-1170°C, hot rolled at a terminating temperature of finish rolling of 850-880°C and coiled at a temperature of 500-550°C to obtain a hot-rolled steel sheet having a thickness of 3~5mm. Then, the hot-rolled steel sheet is pickled to remove scales and thereafter cold rolled to obtain a cold-rolled steel sheet having a thickness of 1.8 mm. Next, the cold-rolled steel sheet is subjected to such a continuous annealing that it is heated to a soaking temperature of 750-780°C and held at this temperature for 40-50 seconds and then cooled at a rate of 20-30°C/second from the soaking temperature to a cooling stop temperature of 350-400°C and held at the cooling stop temperature range for 100-120 seconds, and then the steel sheet is pickled and further repickled under conditions shown in Table 2, washed with water, dried and subjected to a temper rolling at a stretching ratio of 0.7% to obtain cold-rolled steel sheets Nos. 1-85 shown in Table 2.

[0061] A test specimen is sampled from each of the above cold-rolled steel sheets and observed at 5 fields of the steel sheet surface with a scanning type electron microscope of ultra-low acceleration voltage (ULV-SEM; made by SEISS; ULTRA 55) at an acceleration voltage of 2 kV, an operating distance of 3.0 mm and a magnification of 1000 times. And analyzed with an energy dispersion X-ray spectrometer (EDX; made by Thermo Fisher; NSS 312E) to obtain a reflection electron image. The reflection electron image is binarized with an image analyzing software (Image J) with respect to gray value (Y-point) corresponding to intersect point (X-point) and threshold value defined in histograms of the aforementioned standard samples Nos. a and b to measure an area ratio of a black portion. The values measured at 5 fields are averaged as a surface covering ratio of iron-based oxide.

[0062] Also, a test specimen is sampled from each of the above cold-rolled steel sheets and subjected to a phosphate treatment and a coating treatment under the following conditions and then subjected to three corrosion tests of hot salt water immersion test, salt water spray test and composite cycle corrosion test to evaluate a corrosion resistance after

coating. Further, a distribution of O, Si, Mn and Fe in depth direction on the surface of the test specimen sampled from each cold-rolled steel sheet is measured with GDS.

(1) Phosphate treating conditions

[0063] The test specimen sampled from each cold-rolled steel sheet is subjected to a phosphate treatment with a degreasing agent: FC-E2011, a surface regulator: PL-X and a phosphate treating agent: PALBOND PB-L3065, which are made by Nihon Parkerizing Co., Ltd., so as to provide a phosphate coating adhered amount of 1.7-3.0 g/m² under two conditions of the following standard condition and comparative condition of lowering the phosphate treating temperature to a low temperature.

<Standard condition>

[0064]

- Degreasing step: treating temperature 40°C, treating time 120 seconds
- Spray degreasing, surface regulating step: pH 9.5, Treating temperature room temperature, treating time 20 seconds
- Phosphate treating step: temperature of phosphate treating solution 35°C, treating time 120 seconds

<Low temperature condition>

[0065] Condition of lowering the temperature of the phosphate treating solution in the above standard condition to 33°C

(2) Corrosion test

[0066] The surface of the test specimen subjected to the phosphate treatment is electrodeposited with an electrodeposition paint : V-50 made by Nippon Paint Co., Ltd. so as to have a coating thickness of 25 μm and then subjected to the following three corrosion tests.

<Hot salt water immersion test>

[0067] The test specimen (n = 1) subjected to the phosphate treatment and electrodeposition is provided on its surface with a crosscut flaw of 45 mm in length by means of a cutter, and thereafter immersed in a solution of 5 mass% NaCl (60°C) for 360 hours, washed with water, and dried. After an adhesive tape is attached to a cut flaw portion, a test of peeling off the tape is carried out to measure a maximum peeled full width combining either side of the cut flaw portion. When the maximum peeled full width is not more than 5.0 mm, the corrosion resistance can be evaluated to be good in the hot salt water immersion test.

<Salt water spray test (SST)>

[0068] The test specimen (n = 1) subjected to the phosphate treatment and electrodeposition is provided on its surface with a crosscut flaw of 45 mm in length by means of a cutter, and thereafter subjected to a salt water spray test with an aqueous solution of 5 mass% NaCl for 1200 hours according to a neutral salt water spray test defined in JIS Z2371: 2000, and then a tape peeling test on a crosscut flaw portion is conducted to measure a maximum peeled full width combining either side of the cut flaw portion. When the maximum peeled full width is not more than 4.0 mm, the corrosion resistance can be evaluated to be good in the salt water spray test.

<Composite cycle corrosion test (CCT)>

[0069] The test specimen (n = 1) subjected to the phosphate treatment and electrodeposition is provided on its surface with a crosscut flaw of 45 mm in length by means of a cutter, and thereafter subjected to a corrosion test that one cycle of salt water spraying (aqueous solution of 5 mass% NaCl: 35°C, relative humidity: 98%) for 2 hours → drying (60°C, relative humidity: 30%) for 2 hours → wetting (50°C, relative humidity: 95%) for 2 hours is repeated 120 cycles, washed with water and dried, and then a tape peeling test on a cut flaw portion is conducted to measure a maximum peeled full width combining either side of the cut flaw portion. When the maximum peeled full width is not more than 6.0 mm, the corrosion resistance can be evaluated to be good in the composite cycle corrosion test.

[0070] The test results are also shown in Table 2. As seen from these results, the steel sheets of Invention Examples subjected to the pickling and repickling under the conditions adequate for the invention after the continuous annealing

are small in the maximum peeled full width on all of the hot salt water immersion test, salt water spray test and composite cycle corrosion test and show the good corrosion resistance after coating. Particularly, all of the cold-rolled steel sheets having the surface covering ratio of the iron-based oxide of not more than 40% are excellent in the corrosion resistance after coating under severe corrosion environment. Moreover, as the distribution in depth direction of O, Si, Mn and Fe on the surface of each steel sheet in Table 2 is measured with GDS, it has been confirmed that in the steel sheets pickled under the conditions adequate for the invention, peaks of Si and O do not appear and the Si-containing oxide layer is removed sufficiently. As a reference, FIG. 5 shows the profile in depth direction of O, Si, Mn and Fe as surface-analyzed with GDS with respect to the test specimens of Comparative Example No. 1 and Invention Example No. 9 in Table 2.

[0071] Table 2-1

[0072] Table 2-2

[0073] Table 2-3

[Example 2]

[0074] Each of steels A-X having a chemical composition shown in Table 3 is prepared according to common refining process such as melting in a converter, degassing treatment and the like and continuously cast into a steel slab. The steel slab is hot rolled under hot rolling conditions shown in Table 4 to obtain a hot-rolled steel sheet having a thickness of 3-4 mm, which is pickled to remove scales on the surface of the steel sheet and thereafter cold rolled to obtain a cold-rolled steel sheet having a thickness of 1.8 mm. Next, the cold-rolled steel sheet is continuously annealed under the conditions shown in Table 4, pickled and repickled under conditions shown in Table 5, washed with water, dried and subjected to a temper rolling at a stretching ratio of 0.7% to obtain cold-rolled steel sheets Nos. 1-39.

[0075] Table 3

[0076] Table 4-1

[0077] Table 4-2

[0078] Table 5-1

[0079] Table 5-2

[0080] A test specimen is sampled from each of the cold-rolled steel sheets and subjected to the following tensile test and test for the corrosion resistance after coating after the surface covering ratio of iron-based oxide on the steel sheet surface after the repickling is measured in the same manner as in Example 1. Also, the distribution in depth direction of O, Si, Mn and Fe on the surface of the test specimen sampled from each of the cold-rolled steel sheets is measured with GDS.

(1) Mechanical properties

[0081] A tensile test specimen of JIS No. 5 ($n = 1$) sampled in a direction (C-direction) parallel to the rolling direction according to JIS Z2201:1998 is subjected to a tensile test according to JIS Z2241:1998 to measure tensile strength TS.

(2) Corrosion resistance after coating

[0082] A test specimen is prepared by subjecting the test specimen sampled from each of the cold-rolled steel sheet to phosphate treatment and electrodeposition under the same conditions as in Example 1 and then subjected to three corrosion tests of hot salt water immersion test, salt water spray test (SST) and composite cycle corrosion test (CCT) likewise Example 1 to evaluate the corrosion resistance after coating.

[0083] The results of the above tests are shown in Tables 4 and 5. As seen from these results, the high-strength cold-rolled steel sheets of Invention Examples containing Si of not less than 0.5 mass% and pickled and repickled under the conditions adequate for the invention to render the surface covering ratio of the iron-based oxide into not more than 40% are excellent in the corrosion resistance after coating but also have a tensile strength TS of not less than 590 MPa. Moreover, as the distribution in depth direction of O, Si, Mn and Fe is measured with GDS, it has been confirmed that in all of the steel sheets pickled under the conditions adequate for the invention, peaks of Si and O do not appear and the Si-containing oxide layer is removed sufficiently.

[Example 3]

[0084] A steel comprising C: 0.125 mass%, Si: 1.5 mass%, Mn: 2.6 mass%, P: 0.019 mass%, S: 0.008 mass%, Al: 0.040 mass% and the remainder being Fe and inevitable impurities is melted and continuously cast into a steel material (slab). The slab is reheated to a temperature of 1150-1170°C, hot rolled at a terminating temperature of finish rolling of 850-880°C and coiled at a temperature of 500-550°C to obtain a hot-rolled steel sheet having a thickness of 3-4 mm.. The hot-rolled steel sheet is pickled to remove scales and thereafter cold rolled to obtain a cold-rolled steel sheet having

a thickness of 1.8 mm. Next, the cold-rolled steel sheet is subjected to such a continuous annealing that it is heated to a soaking temperature of 750-780°C and held at this temperature for 40-50 seconds and then cooled at a rate of 20-30°C/second from the soaking temperature to a cooling stop temperature of 350-400°C and held at the cooling stop temperature range for 100-120 seconds, and then the steel sheet is pickled and repickled under conditions shown in Table 6, washed with water, dried and subjected to a temper rolling at a stretching ratio of 0.7% to obtain cold-rolled steel sheets Nos. 1-61 shown in Table 6.

[0085] A test specimen is sampled from each of the above cold-rolled steel sheets to measure a surface covering ratio and maximum thickness of iron-based oxide generated on the surface of the steel sheet by pickling through the aforementioned methods.

[0086] Also, the test specimen is sampled from each of the above cold-rolled steel sheets and subjected to phosphate treatment and coating treatment under the following conditions and then subjected to three corrosion tests of hot salt water immersion test, salt water spray test and composite cycle corrosion test to evaluate the corrosion resistance after coating. Further, the distribution in depth direction of O, Si, Mn and Fe on the surface of the test specimen sampled from each of the cold-rolled steel sheets is measured with GDS.

(1) Phosphate treating conditions

[0087] The test specimen sampled from each cold-rolled steel sheet is subjected to a phosphate treatment with a degreasing agent: FC-E2011, a surface regulator: PL-X and a phosphate treating agent: PALBOND PB-L3065, which are made by Nihon Parkerizing Co., Ltd., so as to provide a phosphate coating adhered amount of 1.7-3.0 g/m² under two conditions of the following standard condition and comparative condition of lowering the phosphate treating temperature to a low temperature.

<Standard condition>

[0088]

- Degreasing step: treating temperature 40°C, treating time 120 seconds
- Spray degreasing, surface regulating step: pH 9.5, Treating temperature room temperature, treating time 20 seconds
- Phosphate treating step: temperature of phosphate treating solution 35°C, treating time 120 seconds

<Low temperature condition>

[0089] Condition of lowering the temperature of the phosphate treating solution in the above standard condition to 33°C

(2) Corrosion test

[0090] The surface of the test specimen subjected to the phosphate treatment is electrodeposited with an electrodeposition paint : V-50 made by Nippon Paint Co., Ltd. so as to have a coating thickness of 25 μm and then subjected to the following three corrosion tests under more strict conditions than the one with Example 1.

<Hot salt water immersion test>

[0091] The test specimen (n = 1) subjected to the phosphate treatment and electrodeposition is provided on its surface with a crosscut flaw of 45 mm in length by means of a cutter, and thereafter immersed in a solution of 5 mass% NaCl (60°C) for 480 hours, washed with water, and dried. After an adhesive tape is attached to a cut flaw portion, a test of peeling off the tape is carried out to measure a maximum peeled full width combining either side of the cut flaw portion. When the maximum peeled full width is not more than 5.0 mm, the corrosion resistance can be evaluated to be good in the hot salt water immersion test.

<Salt water spray test (SST)>

[0092] The test specimen (n = 1) subjected to the phosphate treatment and electrodeposition is provided on its surface with a crosscut flaw of 45 mm in length by means of a cutter, and thereafter subjected to a salt water spray test with an aqueous solution of 5 mass% NaCl for 1400 hours according to a neutral salt water spray test defined in JIS Z2371: 2000, and then a tape peeling test on a crosscut flaw portion is conducted to measure a maximum peeled full width combining either side of the cut flaw portion. When the maximum peeled full width is not more than 4.0 mm, the corrosion resistance can be evaluated to be good in the salt water spray test.

<Composite cycle corrosion test (CCT)>

[0093] The test specimen (n = 1) subjected to the phosphate treatment and electrodeposition is provided on its surface with a crosscut flaw of 45 mm in length by means of a cutter, and thereafter subjected to a corrosion test that one cycle of salt water spraying (aqueous solution of 5 mass% NaCl: 35°C, relative humidity: 98%) for 2 hours → drying (60°C, relative humidity: 30%) for 2 hours → wetting (50°C, relative humidity: 95%) for 2 hours is repeated 150 cycles, washed with water and dried, and then a tape peeling test on a cut flaw portion is conducted to measure a maximum peeled full width combining either side of the cut flaw portion. When the maximum peeled full width is not more than 6.0 mm, the corrosion resistance can be evaluated to be good in the composite cycle corrosion test.

[0094] The test results are also shown in Table 6. As seen from these results, the steel sheets of Invention Examples, wherein the surface of the steel sheet after annealing is subjected to the pickling and repickling under the conditions that the surface covering ratio of the iron-based oxide on the surface of the steel sheet after repickling is not more than 40% and the maximum thickness of the iron-based oxide is not more than 150 nm, are small in the maximum peeled full width on all of the hot salt water immersion test, salt water spray test and composite cycle corrosion test and show the very good corrosion resistance after coating. Moreover, as the distribution in depth direction of O, Si, Mn and Fe is measured with GDS, it has been confirmed that in the steel sheets pickled under the conditions adequate for the invention, peaks of Si and O do not appear and the Si-containing oxide layer is removed sufficiently.

[0095] Table 6-1

[0096] Table 6-2

[0097] Table 6-3

[INDUSTRIAL APPLICABILITY]

[0098] The cold-rolled steel sheets produced according to the invention not only are excellent in the corrosion resistance after coating but also have a high strength and a good workability, so that they can be preferably used as not only a starting material used in members of the automotive vehicle body but also a starting material for applications requiring the same properties such as household electrical goods, building members and so on.

[Table 1]

Steel sheet	Pickling conditions			Repickling conditions			Surface covering ratio of iron-based oxide (%)
	Acid concentration (g/l)	Temperature (°C)	Treating time (Seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (Seconds)	
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

【Table 2-1】

No.	Pickling condition			Repickling condition			Surface properties	Full width peeled after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Surface covering ratio of iron-based oxide (%)	Temperature of phosphate treating solution				
								35°C			33°C	
								Hot salt water Immersion test	Salt water Spray test	Composite cycle corrosion test		
1	Nitric acid : 150 + Hydrochloric acid : 15	40	10	—	—	—	<u>72.6</u>	6.3	5.5	7.9	8.3	Comparative example
2				Hydrochloric acid : 0.1	40	1	39.5	4.9	4.0	5.8	5.8	Invention example
3						10	35.3	4.6	3.8	5.6	5.6	Invention example
4						30	30.4	4.4	3.6	5.0	5.0	Invention example
5				Hydrochloric acid : 10	20	1	39.1	4.9	4.0	5.8	5.8	Invention example
6						10	36.1	4.8	3.7	5.4	5.5	Invention example
7						30	32.3	4.6	3.6	5.2	5.0	Invention example
8				Hydrochloric acid : 10	40	1	35.2	4.6	3.7	5.3	5.6	Invention example
9						10	30.3	4.5	3.6	4.8	5.0	Invention example
10						30	25.9	4.0	3.1	4.4	4.5	Invention example
11				Hydrochloric acid : 10	70	1	30.9	4.4	3.5	4.8	4.9	Invention example
12						10	25.1	4.0	3.2	4.1	4.5	Invention example
13						30	22.3	3.7	3.0	4.0	4.1	Invention example
14				Hydrochloric acid : 50	40	1	30.1	4.3	3.5	4.8	4.8	Invention example
15						10	26.2	4.1	3.2	4.3	4.5	Invention example
16						30	21.2	3.5	3.0	3.6	3.6	Invention example
17				Hydrochloric acid : 100	40	1	<u>49.8</u>	5.5	4.4	6.7	6.8	Comparative example
18						10	<u>54.5</u>	5.7	4.7	7.1	7.4	Comparative example
19						30	<u>59.8</u>	5.9	5.1	7.3	7.6	Comparative example
20	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Hydrochloric acid : 0.1	40	1	39.7	4.9	3.9	5.9	5.8	Invention example
21						10	36.1	4.8	3.8	5.4	5.4	Invention example
22						30	32.1	4.2	3.5	5.0	5.0	Invention example
23				Hydrochloric acid : 10	20	1	39.5	5.0	4.0	5.6	5.6	Invention example
24						10	37.2	4.7	3.9	5.6	5.4	Invention example
25						30	33.6	4.6	3.6	5.3	5.1	Invention example
26				Hydrochloric acid : 10	40	1	36.2	4.8	3.8	5.5	5.8	Invention example
27						10	32.4	4.6	3.7	5.3	5.5	Invention example
28						30	28.3	4.2	3.5	4.8	4.6	Invention example
29				Hydrochloric acid : 10	70	1	32.1	4.6	3.6	5.0	5.3	Invention example
30						10	26.8	4.2	3.3	4.5	4.6	Invention example
31						30	24.1	3.9	3.2	4.2	4.3	Invention example
32				Hydrochloric acid : 50	40	1	31.2	4.3	3.5	4.6	5.0	Invention example
33						10	25.6	4.0	3.3	4.1	4.6	Invention example
34						30	22.3	3.7	3.1	3.6	4.2	Invention example
35				Hydrochloric acid : 100	40	1	<u>45.9</u>	5.3	4.2	6.2	6.4	Comparative example
36						10	<u>55.3</u>	5.8	4.7	7.1	7.3	Comparative example
37						30	<u>62.1</u>	6.0	5.1	7.3	7.7	Comparative example

【Table 2 - 2】

No.	Pickling condition			Repickling condition			Surface properties	Full width peeled after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Surface covering ratio of iron-based oxide (%)	Temperature of phosphate treating solution				
								35°C			33°C	
								Hot salt water Immersion test	Salt water Spray test	Composite cycle corrosion test		
38	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Sulfuric acid : 0.1	40	1	39.5	4.8	4.0	5.7	5.9	Invention example
39						10	35.3	4.7	3.9	5.6	5.7	Invention example
40						30	30.4	4.6	3.7	5.1	5.2	Invention example
41				Sulfuric acid : 75	20	1	39.1	4.8	4.1	5.9	5.9	Invention example
42						10	36.1	4.7	3.8	5.6	5.6	Invention example
43						30	32.3	4.5	3.7	5.2	5.4	Invention example
44				Sulfuric acid : 75	40	1	35.2	4.8	3.9	5.6	5.6	Invention example
45						10	30.3	4.6	3.6	5.2	5.1	Invention example
46						30	25.9	4.3	3.3	4.8	4.8	Invention example
47				Sulfuric acid : 75	70	1	30.9	4.6	3.8	5.2	5.2	Invention example
48						10	25.1	4.2	3.5	4.7	4.7	Invention example
49						30	22.3	3.9	3.2	4.5	4.6	Invention example
50				Sulfuric acid : 150	40	1	30.1	4.6	3.5	5.2	5.2	Invention example
51						10	26.2	4.3	3.3	4.6	4.8	Invention example
52						30	21.2	4.0	3.2	4.2	4.5	Invention example
53				Sulfuric acid : 200	40	1	<u>49.9</u>	5.4	4.4	6.6	6.8	Comparative example
54						10	<u>55.0</u>	5.7	4.7	7.1	7.4	Comparative example
55						30	<u>62.1</u>	6.0	5.2	7.4	7.6	Comparative example
56	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Sulfuric acid : 0.1	40	1	39.7	5.0	3.8	5.9	6.0	Invention example
57						10	36.1	4.7	3.7	5.7	5.8	Invention example
58						30	32.1	4.7	3.6	5.5	5.6	Invention example
59				Sulfuric acid : 75	20	1	39.5	4.9	4.2	6.0	6.0	Invention example
60						10	37.2	4.8	4.0	5.8	5.8	Invention example
61						30	33.6	4.5	3.7	5.6	5.6	Invention example
62				Sulfuric acid : 75	40	1	36.2	4.8	3.9	5.6	5.7	Invention example
63						10	32.4	4.6	3.6	5.3	5.4	Invention example
64						30	28.3	4.5	3.5	4.9	5.2	Invention example
65				Sulfuric acid : 75	70	1	32.1	4.5	3.7	5.3	5.3	Invention example
66						10	26.8	4.3	3.4	4.6	4.9	Invention example
67						30	24.1	4.2	3.3	4.4	4.7	Invention example
68				Sulfuric acid : 150	40	1	31.2	4.5	3.6	5.2	5.3	Invention example
69						10	25.6	4.2	3.5	4.8	4.7	Invention example
70						30	22.3	4.2	3.3	4.4	4.6	Invention example
71				Sulfuric acid : 200	40	1	<u>50.1</u>	5.4	4.5	6.6	6.8	Comparative example
72						10	<u>55.3</u>	5.8	4.8	7.2	7.5	Comparative example
73						30	<u>61.5</u>	5.9	5.2	7.4	7.7	Comparative example

【Table 2 - 3】

No.	Pickling condition			Repickling condition			Surface properties	Full width peeled after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Surface covering ratio of iron-based oxide (%)	Temperature of phosphate treating solution				
								35°C			33°C	
								Hot salt water Immersion test	Salt water Spray test	Composite cycle corrosion test		
74	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrochloric acid : 5 + Sulfuric acid : 5	40	1	35.5	4.5	3.7	5.4	5.8	Invention example
75						10	30.6	4.4	3.5	4.9	5.0	Invention example
76						30	26.3	3.9	3.2	4.6	4.6	Invention example
77	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrochloric acid : 10 + Sulfuric acid : 50	40	1	33.2	4.4	3.6	5.3	5.8	Invention example
78						10	30.1	4.2	3.5	4.9	5.0	Invention example
79						30	25.6	3.8	3.3	4.5	4.5	Invention example
80	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Hydrochloric acid : 5 + Sulfuric acid : 5	40	1	35.7	4.6	3.8	5.4	5.7	Invention example
81						10	30.9	4.5	3.6	4.9	5.3	Invention example
82						30	27.0	4.1	3.2	4.7	4.8	Invention example
83	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Hydrochloric acid : 5 + Sulfuric acid : 5	40	1	34.6	4.5	3.8	5.2	5.6	Invention example
84						10	30.1	4.4	3.5	5.0	5.2	Invention example
85						30	26.5	4.1	3.1	4.6	4.7	Invention example

[Table 3]

steel Symbol	Chemical composition (mass %)								
	C	Si	Mn	P	s	Al	Si/Mn	Nb, Ti, V, Mo, Cr, B, N	Ni, Cu, Ca, REM
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	-	-
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	-	-
N	0.06	1.28	2.12	0.025	0.003	0.040	0.60	Nb:0.1, Ti:0.2	Cu:0.15
O	0.18	1.21	1.97	0.015	0.002	0.035	0.61	V:0.1, Mo:0.2	Ni:0.13
P	0.18	1.56	2.58	0.010	0.002	0.030	0.60	Cr:0.2, B:0.005	Ca:0.003

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(continued)

steel Symbol	Chemical composition (m a s s%)								
	C	Si	Mn	P	s	Al	Si/Mn	Nb, Ti, V, Mo, Cr, B, N	Ni, Cu, Ca, REM
Q	0.13	1.32	1.32	0.030	0.001	0.040	1.00	N:0.007	REM:0.002
R	0.07	1.26	2.10	0.025	0.002	0.040	0.60	Nb:0.1	-
S	0.06	1.28	2.12	0.025	0.003	0.040	0.60	Nb:0.1, Ti: 0.2	-
T	0.17	1.23	1.99	0.015	0.002	0.050	0.62	-	Ni:0.13
U	0.18	1.22	1.97	0.015	0.003	0.040	0.62	-	Ni:0.13, Ca: 0.003
V	0.18	1.21	1.98	0.015	0.002	0.035	0.61	V:0.1	N:0.13
W	0.18	1.56	2.58	0.010	0.002	0.030	0.60	Mo:0.1, Cr: 0.2, B:0.005	Ca:0.003
X	0.13	1.32	1.32	0.030	0.001	0.040	1.00	Nb:0.1, N: 0.007	Cu:0.2, REM:0.002
Y	0.01	0.02	0.25	0.020	0.012	0.040	0.08	-	-
Z	0.11	0.45	1.50	0.020	0.003	0.030	0.30	-	-

【Table 4-1】

No.	Steel symbol	Heating Temperature (°C)	Hot rolling conditions			Cold rolling reduction (%)	Continuous annealing conditions						Strength T S (MPa)	Remarks
			Finish Temperature (°C)	Cooling rate (°C/s)	Coiling temperature (°C)		Heating temperature (°C)	Holding time (Second)	Cooling rate (°C/s)	Cooling stop temperature (°C)	Holding time (second)	Cooling rate (°C/s)		
1	A	1150	850	25	620	60	780	45	20	350	100	40	625	Invention example
2	B	1150	820	31	400	60	780	40	20	400	100	50	821	Invention example
3	B	1150	820	31	400	60	780	40	20	400	100	50	819	Invention example
4	C	1140	850	26	600	60	760	50	20	350	100	45	814	Invention example
5	D	1150	840	33	530	60	730	40	20	350	110	40	623	Invention example
6	E	1150	850	30	580	55	750	35	20	400	110	50	836	Invention example
7	F	1150	850	25	620	60	750	50	20	350	120	50	634	Invention example
8	G	1150	850	33	550	60	750	30	20	400	100	50	632	Comparative example
9	G	1150	850	33	550	60	750	30	20	400	100	50	635	Invention example
10	G	1150	850	33	550	60	750	30	20	400	100	50	631	Invention example
11	G	1150	850	33	550	60	750	30	20	400	100	50	633	Invention example
12	G	1150	850	33	550	60	750	30	20	400	100	50	634	Comparative example
13	H	1130	820	28	570	60	780	50	15	370	150	50	840	Invention example
14	I	1150	840	34	530	55	780	50	15	350	120	55	812	Invention example
15	J	1140	850	28	600	60	770	60	20	300	100	45	836	Invention example
16	K	1150	850	25	620	60	780	45	20	350	100	40	650	Invention example
17	L	1100	850	33	550	60	750	50	20	450	150	50	960	Comparative example
18	L	1100	850	33	550	60	750	50	20	450	150	50	959	Invention example
19	L	1100	850	33	550	60	750	50	20	450	150	50	963	Invention example
20	L	1100	850	33	550	60	750	50	20	450	150	50	962	Invention example
21	L	1100	850	33	550	60	750	50	20	450	150	50	961	Comparative example
22	M	1120	830	31	550	55	720	50	15	410	190	50	1124	Comparative example

【Table 4-2】

No.	Steel symbol	Heating temperature (°C)	Hot rolling conditions			Cold rolling reduction (%)	Continuous annealing conditions						Strength T S (MPa)	Remarks
			Finish temperature (°C)	Cooling rate (°C/s)	Cooling temperature (°C)		Heating Temperature (°C)	Holding time (Seconds)	Cooling rate (°C/s)	Cooling stop temperature (°C)	Holding time (Seconds)	Cooling rate (°C/s)		
23	N	1120	830	33	550	60	750	30	20	400	100	50	613	Invention example
24	O	1150	850	32	560	60	750	35	20	350	100	50	776	Invention example
25	P	1130	840	33	550	55	780	30	20	400	110	50	1152	Invention example
26	Q	1140	850	33	580	60	750	40	20	400	120	45	586	Invention example
27	R	1120	830	33	550	60	750	30	20	400	100	50	611	Invention example
28	S	1120	830	32	550	60	750	35	20	410	100	50	621	Invention example
29	T	1150	850	32	560	60	750	35	20	350	100	50	773	Invention example
30	U	1140	850	33	550	60	750	35	20	400	100	50	785	Invention example
31	V	1150	850	32	550	60	750	40	20	380	100	50	770	Invention example
32	W	1130	840	33	550	55	780	30	20	400	110	50	1156	Invention example
33	X	1140	850	33	580	60	750	40	20	400	120	45	585	Invention example
34	Y	910	630	22	550	80	750	40	20	370	100	50	285	Invention example
35	Y	905	650	24	560	83	750	40	20	400	100	50	279	Invention example
36	Y	910	640	24	550	85	750	35	20	400	100	50	290	Invention example
37	Z	990	690	25	540	75	750	35	20	400	100	50	785	Invention example
38	Z	970	710	28	540	70	750	35	20	400	100	50	790	Invention example
39	Z	960	700	27	550	75	750	35	20	400	100	50	803	Invention example

【Table 5-1】

No.	Steel symbol	Pickling conditions		Repickling conditions			Surface properties	Full width peeled after corrosion test(mm)				Remarks
		Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)		Temperature of phosphate treating solution : 35°C	Hot salt water immersion test	Salt water spray test	33°C Composite cycle corrosion test	
1	A	Nitric Acid : 150 +	40	10	Hydrochloric Acid : 1	40	30.1	4.4	4.4	3.7	4.8	Invention example
2	B	Hydrochloric Acid : 15	40	10	Hydrochloric Acid : 10	40	30.5	4.3	4.3	3.7	4.6	Invention example
3	B	Nitric Acid : 50 + Hydrofluoric acid : 50	40	10	Hydrochloric Acid : 10	40	30.2	4.5	4.5	3.8	5.1	Invention example
4	C	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrochloric Acid : 10	40	29.9	4.4	4.4	3.6	4.7	Invention example
5	D		40	10	Hydrochloric Acid : 10	40	30.7	4.4	4.4	3.9	4.9	Invention example
6	E		40	10	Hydrochloric Acid : 10	40	30.2	4.3	4.3	3.8	4.8	Invention example
7	F		40	10	Hydrochloric Acid : 10	40	30.3	4.6	4.6	3.5	4.8	Invention example
8	G		40	10	Hydrochloric Acid : 10	10	<u>74.3</u>	6.5	6.5	5.3	7.7	Comparative example
9	G		40	10	Hydrochloric Acid : 10	40	35.5	4.5	4.5	3.9	5.2	Invention example
10	G		40	10	Hydrochloric Acid : 10	40	25.8	4.0	4.0	3.0	4.5	Invention example
11	G		40	10	Sulfuric Acid : 75	40	26.4	4.3	4.3	3.3	4.8	Invention example
12	G		40	10	Hydrochloric Acid : 100	40	<u>54.5</u>	5.7	5.7	4.7	7.1	Comparative example
13	H		40	10	Hydrochloric Acid : 10	40	30.5	4.2	4.2	3.9	4.8	Invention example
14	I		40	10	Hydrochloric Acid : 10	40	30.8	4.2	4.2	3.8	5.0	Invention example
15	J		40	10	Hydrochloric Acid : 10	40	29.8	4.3	4.3	3.9	4.9	Invention example
16	K		40	10	Hydrochloric Acid : 10	40	30.1	4.1	4.1	4.0	4.7	Invention example
17	L		40	10	Sulfuric Acid : 75	10	<u>75.2</u>	6.4	6.4	5.5	7.8	Comparative example
18	L		40	10	Sulfuric Acid : 75	40	35.3	4.4	4.4	3.9	5.3	Invention example
19	L		40	10	Sulfuric Acid : 75	40	25.5	4.4	4.4	3.3	4.9	Invention example
20	L		40	10	Hydrochloric Acid : 10	40	25.4	4.5	4.5	3.2	5.0	Invention example
21	L		40	10	Sulfuric Acid : 200	40	<u>55.0</u>	5.7	5.7	4.7	7.1	Comparative example
22	M		40	10	Hydrochloric Acid : 10	40	<u>41.2</u>	5.2	5.2	4.1	6.3	Comparative example

【Table 5-2】

No.	Steel symbol	Pickling conditions		Repickling conditions			Surface properties	Full width peeled after corrosion test(mm)				Remarks		
		Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)		Treating time (seconds)	Temperature of phosphate treating solution : 35°C					
									Hot salt water immersion test	Salt water spray test	Composite cycle corrosion test			
23	N	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrochloric acid : 10	40	10	30.8	4.4	3.9	5.1	5.2	Invention example	
24	O		40	10	Hydrochloric acid : 10	40	10	31.3	4.3	3.9	5.1	5.3	Invention example	
90	P		40	10	Hydrochloric acid : 10	40	10	30.9	4.4	3.7	5.0	5.2	Invention example	
26	Q		40	10	Hydrochloric acid : 10	40	10	31.0	4.4	3.8	4.9	5.1	Invention example	
27	R		40	10	Hydrochloric acid : 10	40	10	30.7	4.4	3.8	5.2	5.3	Invention example	
28	S		40	10	Hydrochloric acid : 10	40	10	31.1	4.4	4.0	5.1	5.2	Invention example	
29	T		Hydrochloric acid : 15	40	10	Hydrochloric acid : 10	40	10	31.4	4.3	3.8	5.2	5.3	Invention example
30	U			40	10	Hydrochloric acid : 10	40	10	31.4	4.3	3.8	5.3	5.3	Invention example
31	V			40	10	Hydrochloric acid : 10	40	10	30.9	4.4	3.9	5.2	5.3	Invention example
32	W			40	10	Hydrochloric acid : 10	40	10	30.5	4.2	3.7	5.1	5.1	Invention example
33	X	Nitric acid : 50 + Hydrochloric acid : 5	40	10	Hydrochloric acid : 10	40	10	31.4	4.3	3.9	4.9	5.2	Invention example	
34	Y		40	10	Hydrochloric acid : 10	40	10	29.8	4.2	3.6	4.7	5.2	Invention example	
35	Y		40	10	Hydrochloric acid : 10	40	10	29.3	4.3	3.5	4.7	5.2	Invention example	
36	Y	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrochloric acid : 10	40	10	28.3	4.1	3.5	4.5	5.1	Invention example	
37	Z	Nitric acid : 50 + Hydrochloric acid : 5	40	10	Hydrochloric acid : 10	40	10	37.4	4.4	3.9	5.3	5.4	Invention example	
38	Z		40	10	Hydrochloric acid : 10	40	10	35.3	4.3	3.9	5.3	5.3	Invention example	
39	Z	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrochloric acid : 10	40	10	29.9	4.4	3.7	4.7	5.2	Invention example	

【Table 6—1】

No.	Peckling condition			Repickling condition			Surface properties		Full width peeled after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Surface covering ratio of iron-based oxide (%)	Maximum thickness of iron-based oxide (nm)	Temperature of phosphate treating solution : 35°C			33°C	
									Hot salt water Immersion test	Salt water Spray test	Composite cycle corrosion test		
1		40	10	—	—	—	72.6	214	6.5	5.8	8.2	8.4	Comparative example
2		40	10	Hydrofluoric acid : 0.1	40	1	39.5	158	5.2	4.3	6.2	6.3	Invention example
3						10	35.3	157	5.2	4.1	6.1	6.3	Invention example
4						30	30.4	162	5.3	4.2	6.3	6.4	Invention example
5	Nitric acid : 150 +	40	10	Hydrofluoric acid : 3	40	1	38.2	149	4.9	4.0	5.9	5.9	Invention example
6						10	33.1	148	5.0	3.9	5.8	5.9	Invention example
7						30	27.8	144	4.8	4.0	5.7	5.9	Invention example
8		Hydrochloric acid : 15	40	10	Hydrofluoric acid : 10	40	1	35.2	119	4.7	3.8	5.5	5.6
9	10						30.3	114	4.7	3.7	5.6	5.4	Invention example
10	30						25.9	124	4.8	3.8	5.6	5.6	Invention example
11			40	10	Hydrofluoric acid : 50	40	1	30.1	91	4.4	3.6	5.1	5.2
12		10					26.2	88	4.3	3.4	4.9	5.2	Invention example
13		30					21.2	83	4.2	3.1	4.6	4.4	Invention example
14			40	10	Hydrofluoric acid : 0.1	40	1	39.7	163	5.3	4.4	6.3	6.2
15	10						36.1	167	5.5	4.3	6.3	6.4	Invention example
16	30						32.1	159	5.4	4.4	6.2	6.2	Invention example
17	Nitric acid : 50 +		40	10	Hydrofluoric acid : 3	40	1	37.8	148	5.0	3.9	5.9	6.0
18		10					34.3	147	4.8	3.9	5.8	6.0	Invention example
19		30					28.5	149	4.9	4.0	5.8	5.9	Invention example
20		Hydrofluoric acid : 50	40	10	Hydrofluoric acid : 10	40	1	36.2	146	4.9	4.0	5.9	5.9
21	10						32.4	144	4.9	3.9	5.7	6.0	Invention example
22	30						28.3	148	4.8	3.9	5.9	6.0	Invention example
23			40	10	Hydrofluoric acid : 50	40	1	31.2	115	4.5	3.7	5.5	5.5
24		10					25.6	120	4.6	3.8	5.6	5.4	Invention example
25		30					22.3	119	4.4	3.8	5.5	5.6	Invention example

【Table 6—2】

No.	Peckling condition			Repickling condition			Surface properties		Full width peeled after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Surface covering ratio of iron-based Oxide (%)	Maximum thickness of iron-based oxide (n.m)	Temperature of phosphate treating solution : 35°C			Composite cycle corrosion test	
									Hot salt water Immersion test	Salt water Spray test			
26	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Sulfuric acid : 0.1	40	1	39.5	165	5.4	4.4	6.2	6.4	Invention example
27						10	35.3	168	5.5	4.4	6.4	6.5	Invention example
28						30	30.4	170	5.7	4.5	6.3	6.5	Invention example
29				Sulfuric acid : 8	40	1	38.5	148	4.9	4.0	5.8	5.9	Invention example
30						10	33.1	146	4.8	3.9	5.8	5.7	Invention example
31						30	27.6	149	4.8	3.8	5.7	5.9	Invention example
32				Sulfuric acid : 75	40	1	35.2	121	4.6	3.9	5.6	5.7	Invention example
33						10	30.3	118	4.6	3.7	5.5	5.4	Invention example
34						30	25.9	117	4.4	3.6	5.6	5.8	Invention example
35				Sulfuric acid : 150	40	1	30.1	90	4.6	3.6	5.2	5.2	Invention example
36	10	26.2	81			4.3	3.4	5.0	4.9	Invention example			
37	30	21.2	86			4.4	3.3	4.7	5.0	Invention example			
38	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Sulfuric acid : 0.1	40	1	39.7	170	5.6	4.6	6.4	6.5	Invention example
39						10	36.1	169	5.5	4.6	6.6	6.8	Invention example
40						30	32.1	174	5.8	4.7	6.7	6.8	Invention example
41				Sulfuric acid : 8	40	1	38.7	149	4.8	4.0	5.9	6.0	Invention example
42						10	33.9	148	4.9	3.9	5.8	5.9	Invention example
43						30	27.4	148	5.0	4.0	5.8	5.9	Invention example
44				Sulfuric acid : 75	40	1	36.2	145	4.9	4.0	5.8	5.9	Invention example
45						10	32.4	148	4.8	3.9	5.9	5.8	Invention example
46						30	28.3	147	4.8	3.9	5.7	6.0	Invention example
47				Sulfuric acid : 150	40	1	31.2	118	4.6	3.6	5.5	5.6	Invention example
48	10	25.6	115			4.4	3.7	5.4	5.7	Invention example			
49	30	22.3	113			4.5	3.5	5.3	5.4	Invention example			

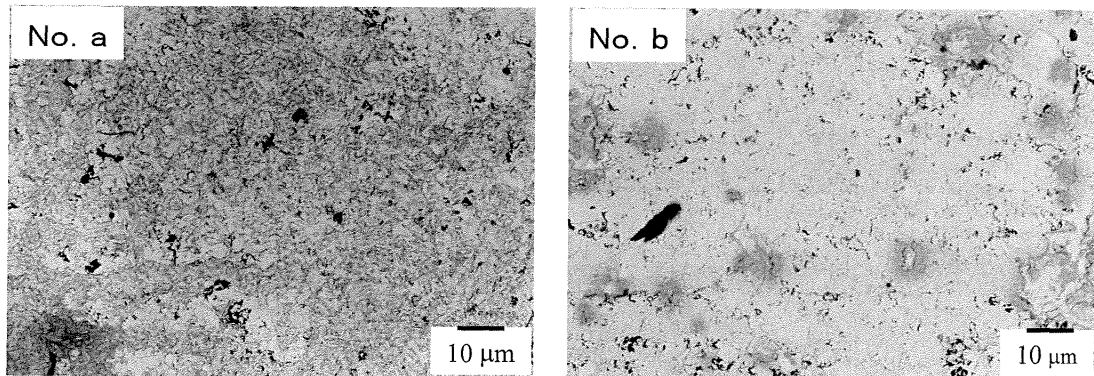
【Table 6 — 3】

No.	Peckling condition			Repickling condition			Surface properties		Full width peeled after corrosion test (mm)				Remarks
	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Acid concentration (g/l)	Temperature (°C)	Treating time (seconds)	Surface covering ratio of iron-based Oxide (%)	Maximum thickness of iron-based oxide (nm)	Temperature of phosphate treating solution : 35°C				
									Hot salt water Immersion test	Salt water Spray test	Composite cycle corrosion test	33°C	
50	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrofluoric acid : 5 + Sulfuric acid : 5	40	1	35.5	152	5.1	4.1	6.1	6.2	Invention example
51							30.6	155	5.1	4.2	6.2	6.2	Invention example
52							30	26.3	154	5.2	4.2	6.3	6.4
53	Nitric acid : 150 + Hydrochloric acid : 15	40	10	Hydrofluoric acid : 3 + Sulfuric acid : 8	40	1	34.3	146	4.8	3.9	5.9	5.9	Invention example
54							29.5	145	4.8	3.8	5.9	5.7	Invention example
55							30	25.6	143	4.6	3.7	5.7	5.8
56	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Hydrofluoric acid : 5 + Sulfuric acid : 5	40	1	36.5	155	5.2	4.2	6.2	6.2	Invention example
57							31.6	158	5.3	4.4	6.3	6.2	Invention example
58							30	28.4	156	5.3	4.2	6.3	6.4
59	Nitric acid : 50 + Hydrofluoric acid : 50	40	10	Hydrofluoric acid : 3 + Sulfuric acid : 8	40	1	35.7	148	4.9	3.8	5.9	5.9	Invention example
60							30.9	147	4.9	4.0	5.9	5.8	Invention example
61							30	27.0	148	5.0	3.9	5.8	6.0

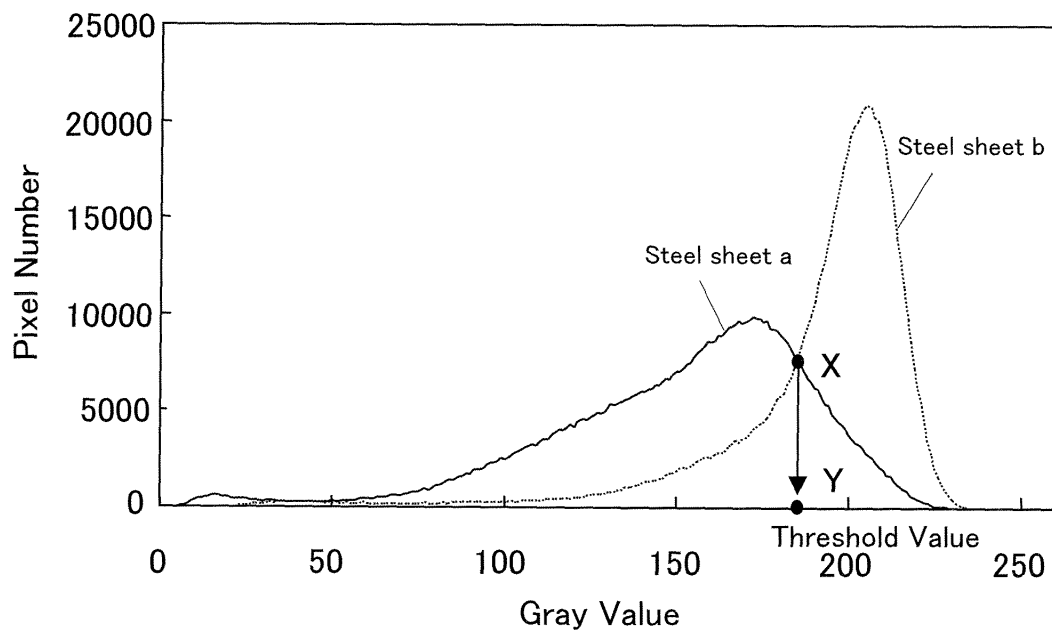
Claims

1. A method of producing a cold-rolled steel sheet, comprising steps of cold rolling a steel sheet, continuously annealing, pickling and further repickling it.
2. A method of producing a cold-rolled steel sheet according to claim 1, wherein the repickling uses a non-oxidizable acid different from an acid used in the pickling before repickling.
3. A method of producing a cold-rolled steel sheet according to claim 2, wherein the non-oxidizable acid is any of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, oxalic acid and a mixed acid of two or more thereof.
4. A method of producing a cold-rolled steel sheet according to claim 2, wherein the non-oxidizable acid is any of hydrochloric acid with a concentration of 0.1-50 g/L, sulfuric acid with a concentration of 0.1-150 g/L and a mixed acid of 0.1-20 g/L of hydrochloric acid and 0.1-60 g/L of sulfuric acid.
5. A method of producing a cold-rolled steel sheet according to any one of claims 1 to 4, wherein the repickling is carried out at a temperature of a repickling solution of 20-70°C for 1-30 seconds.
6. A method of producing a cold-rolled steel sheet according to any one of claims 1 to 5, wherein the pickling is carried out with any of nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid and a mixed acid of two or more thereof.
7. A method of producing a cold-rolled steel sheet according to any one of claims 1 to 6, wherein the pickling is carried out with any of a mixed acid of nitric acid and hydrochloric acid wherein a concentration of nitric acid is more than 50 g/L but not more than 200 g/L and a ratio (HCl/HNO₃) of hydrochloric acid concentration to nitric acid concentration is 0.01-1.0, or a mixed acid of nitric acid and hydrofluoric acid wherein a concentration of nitric acid is more than 50 g/L but not more than 200 g/L and a ratio (HF/HNO₃) of hydrofluoric acid concentration to nitric acid concentration is 0.01-1.0.
8. A method of producing a cold-rolled steel sheet according to any one of claims 1 to 7, wherein the steel sheet comprises 0.5-3.0 mass% of Si.
9. A method of producing a cold-rolled steel sheet according to claim 8, wherein the steel sheet has a chemical composition comprising, in addition to Si, C: 0.01-0.30 mass%, Mn: 1.0-7.5 mass%, P: not more than 0.05 mass%, S: not more than 0.01 mass%, Al: not more than 0.06 mass% and the remainder being Fe and inevitable impurities.
10. A method of producing a cold-rolled steel sheet according to claim 8 or 9, wherein the steel sheet contains, in addition to the chemical composition, one or more selected from Nb: not more than 0.3 mass%, Ti: not more than 0.3 mass%, V: not more than 0.3 mass%, Mo: not more than 0.3 mass%, Cr: not more than 0.5 mass%, B: not more than 0.006 mass% and N: not more than 0.008 mass%.
11. A method of producing a cold-rolled steel sheet according to any one of claims 8 to 10, wherein the steel sheet contains, in addition to the chemical composition, one or more selected from Ni: not more than 2.0 mass%, Cu: not more than 2.0 mass%, Ca: not more than 0.1 mass% and REM: not more than 0.1 mass%.
12. A cold-rolled steel sheet produced by a method as claimed in any one of claims 1 to 11, **characterized in that** a Si-containing oxide layer is removed from the surface of the steel sheet by pickling after continuous annealing and a surface covering ratio of an iron-based oxide existing on the surface of the steel sheet after repickling is not more than 40%.
13. A cold-rolled steel sheet according to claim 12, wherein a maximum thickness of the iron-based oxide existing on the surface of the steel sheet after repickling is not more than 150 nm.
14. A member for automobile **characterized by** using a cold-rolled steel sheet as claimed in claim 12 or 13.

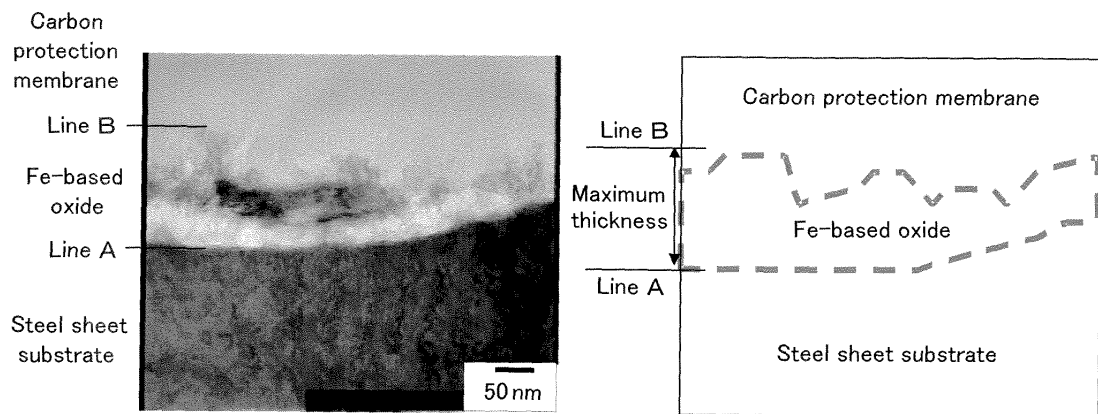
【Figure1】



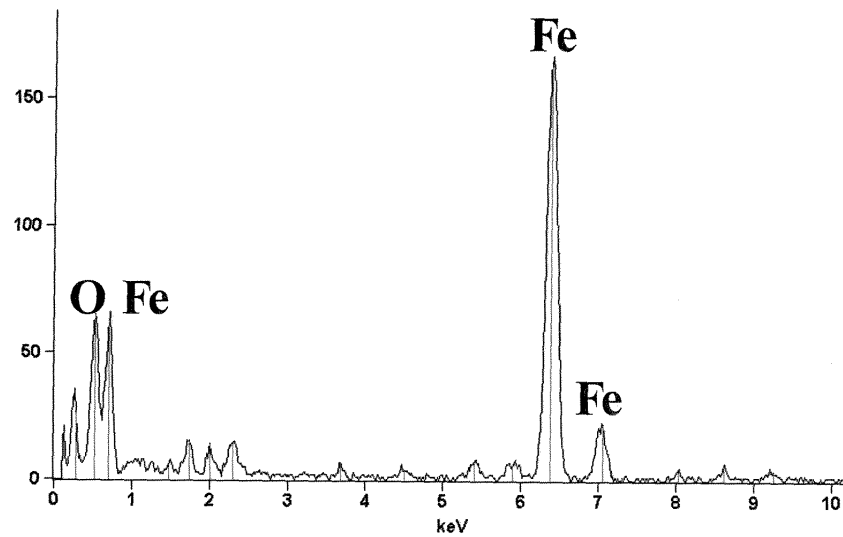
【Figure 2】



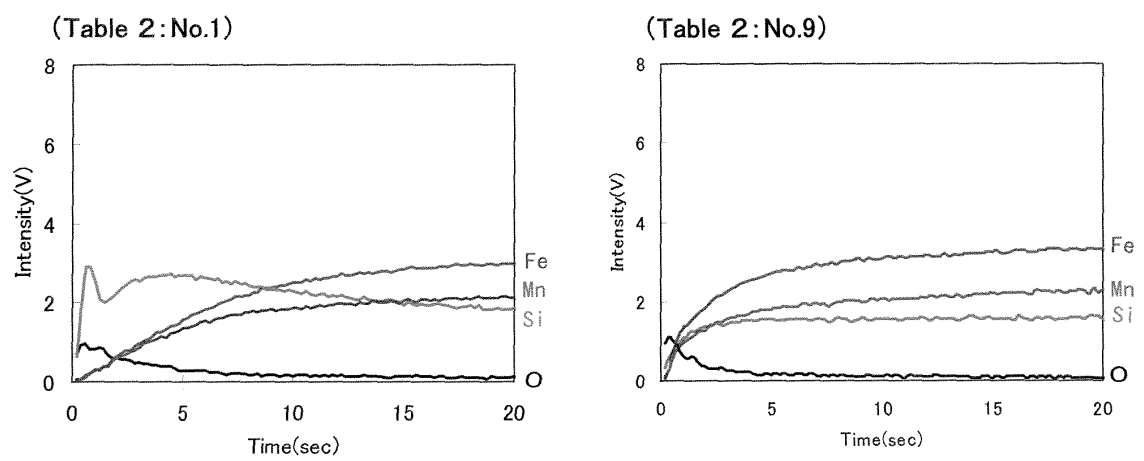
【Figure 3】



【Figure 4】



【Figure 5】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/069193

A. CLASSIFICATION OF SUBJECT MATTER

C23G1/08(2006.01)i, B21B3/02(2006.01)i, C21D9/46(2006.01)i, C22C38/00(2006.01)i, C22C38/02(2006.01)i, C22C38/58(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23G1/08, B21B3/02, C21D9/46, C22C38/00, C22C38/02, C22C38/58

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
<u>X</u> A	JP 2003-119551 A (Kawasaki Steel Corp.), 23 April 2003 (23.04.2003), paragraphs [0007] to [0011], [0026] to [0028]; drawings (Family: none)	<u>1, 5, 12-14</u> 2-4, 6-11
A	JP 2009-221586 A (JFE Steel Corp.), 01 October 2009 (01.10.2009), entire text (Family: none)	1-14

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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Date of the actual completion of the international search
27 September, 2011 (27.09.11)

Date of mailing of the international search report
11 October, 2011 (11.10.11)

Name and mailing address of the ISA/
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Patent documents cited in the description

- JP 2004204350 A [0007]
- JP 2004244698 A [0007]
- JP 2007217743 A [0007]
- JP 2007246951 A [0007]