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(54) HIGH-STRENGTH STEEL PLATE AND METHOD FOR PRODUCING HIGH-STRENGTH STEEL PLATE

(57) Provided are a high-strength steel sheet that has excellent chemical conversion treatability and corrosion resistance after electrodeposition coating even when the content of Si or Mn is high and a method for manufacturing the high-strength steel sheet. When a steel sheet containing, by mass%, 0.03% to 0.35% C, 0.01% to 0.50% Si, 3.6% to 8.0% Mn, 0.01% to 1.0% Al, 0.10% or less P, and 0.010% or less S, the remainder being Fe and inevitable impurities is continuously annealed, the steel sheet is heated at a heating rate of 7 °C/s or more in a temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where 500 ≤ A ≤ 600), the maximum end-point temperature of the steel sheet in an annealing furnace is 600°C to 700°C, the transit time of the steel sheet in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 30 seconds to 10 minutes, and the concentration of hydrogen in an atmosphere is 20% by volume or more in a heating step.

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Description

Technical Field

[0001] The present invention relates to a high-strength steel sheet that has excellent chemical conversion treatability and corrosion resistance after electrodeposition coating even when the content of Si or Mn is high. The present invention also relates to a method for manufacturing the high-strength steel sheet.

Background Art

[0002] In recent years, from the viewpoint of improving the fuel efficiency of automobiles and the viewpoint of enhancing the crash safety of automobiles, there have been growing demands that automobile bodies are lightened and strengthened in such a manner that automobile body materials are strengthened and are thereby gauged down. Therefore, the application of high-strength steel sheets to automobiles is promoted.

[0003] In usual, steel sheets for automobiles are used after being coated. The steel sheets are subjected to a chemical conversion treatment, called a phosphate treatment, as a pretreatment for coating. The chemical conversion treatment of a steel sheet is one of important treatments for ensuring corrosion resistance after coating.

[0004] The addition of Si and Mn is effective in increasing the strength and ductility of a steel sheet. However, even in the case where the steel sheet is annealed in a reducing N_2 + H_2 gas atmosphere in which Fe is not oxidized (Fe oxides are reduced), Si and Mn are oxidized during continuous annealing to form surface oxides (such as SiO_2 and MnO, hereinafter referred to as selective surface oxides) selectively containing Si or Mn in the outermost surface layer of the steel sheet. Since the selective surface oxides inhibit the formation reaction of a chemical conversion coating during a chemical conversion treatment, a fine region (hereinafter referred to as a lack of hiding in some cases) where no chemical conversion coating is produced is formed, leading to a reduction in chemical conversion treatability.

[0005] Patent Literature 1 discloses a method for forming a 20-1,500 mg/m^2 iron coating layer on a steel sheet by an electroplating process as a conventional technique for improving the chemical conversion treatability of a steel sheet containing Si and Mn. However, this method has a problem that an electroplating line is necessary and therefore the increase in number of steps causes an increase in cost.

[0006] Phosphate treatability is enhanced by regulating the Mn/Si ratio as described in Patent Literature 2 or by adding Ni as described in Patent Literature 3. However, the effect depends on the content of Si or Mn in a steel sheet; hence, further improvements are probably necessary for steel sheets with a high Si or Mn content.

[0007] Patent Literature 4 discloses a method in which an internal oxidation layer made of an Si-containing oxide is formed within a depth of 1 μm from the surface of an underlayer of a steel sheet by controlling the dew point at -25°C to 0°C during annealing such that the proportion of the Si-containing oxide in a length of 10 μm in a surface of the steel sheet is 80% or less. However, in the method disclosed in Patent Literature 4, the control of the dew point is difficult and stable operation is also difficult because an area where the dew point is controlled is based on the whole inside of a furnace. In the case where annealing is performed by the unstable control of the dew point, the distribution of internal oxides formed in a steel sheet is uneven and unevenness in chemical conversion treatability (a lack of hiding in the whole or a portion) may possibly be caused in a longitudinal or transverse direction of the steel sheet. Alternatively, in the case of enhanced chemical conversion treatability, there is a problem in that corrosion resistance after electrodeposition coating is poor because the Si-containing oxide is present directly under a chemical conversion coating.

[0008] Patent Literature 5 discloses a method in which an oxide film is formed on a surface of a steel sheet in an oxidizing atmosphere by increasing the temperature of the steel sheet to 350°C to 650°C and the steel sheet is heated to a recrystallization temperature in a reducing atmosphere and is then cooled. However, in this method, the thickness of the oxide film formed on the steel sheet surface is uneven depending on an oxidation process, oxidation does not occur sufficiently, or the oxide film is too thick so that the oxide film remains or peels off during the subsequent annealing in the reducing atmosphere and therefore surface properties are poor in some cases. In an example, a technique for performing oxidation in air is described. However, oxidation in air has a problem that, for example, thick oxides are produced and subsequent reduction is difficult or a reducing atmosphere with a high hydrogen concentration is necessary.

[0009] Patent Literature 6 discloses a method in which an oxide film is formed on a surface of a cold-rolled steel sheet containing 0.1% or more Si and/or 1.0% or more Mn on a mass basis at a steel sheet temperature of 400°C or higher in an atmosphere oxidizing iron, followed by reducing the oxide film on the steel sheet surface in an atmosphere reducing iron. In particular, Fe in the steel sheet surface is oxidized at 400°C or higher using a direct fired burner with an air ratio of 0.93 to 1.10 and the steel sheet is then annealed in an N_2 + H_2 gas atmosphere reducing Fe oxides, whereby selective surface oxidation which deteriorates chemical conversion treatability is suppressed and an Fe oxidation layer is formed on the outermost surface. Patent Literature 6 does not particularly describe the heating temperature of the direct fired burner. When a large amount (about 0.6% or more) of Si is contained, the amount of oxidized Si, which is more likely to be oxidized than Fe, is large; hence, the oxidation of Fe is suppressed or is slight. As a result, the formation of a surface Fe reduction layer after reduction is insufficient or a lack of hiding is caused in a chemical conversion coating in some cases because SiO_2 is present on the steel sheet surface after reduction.

Citation List

Patent Literature

[0010]

PTL 1: Japanese Unexamined Patent Application Publication No. 5-320952

PTL 2: Japanese Unexamined Patent Application Publication No. 2004-323969

PTL 3: Japanese Unexamined Patent Application Publication No. 6-10096

PTL 4: Japanese Unexamined Patent Application Publication No. 2003-113441

PTL 5: Japanese Unexamined Patent Application Publication No. 55-145122

PTL 6: Japanese Unexamined Patent Application Publication No. 2006-45615

Summary of Invention

Technical Problem

[0011] The present invention has been made in view of the above circumstances. It is an object of the present invention to provide a high-strength steel sheet that has excellent chemical conversion treatability and corrosion resistance after electrodeposition coating even when the content of Si or Mn is high. It is an object of the present invention to provide a method for manufacturing the high-strength steel sheet.

Solution to Problem

[0012] Hitherto, an inner portion of a steel sheet containing oxidizable elements such as Si and Mn has been willingly oxidized for the purpose of improving the chemical conversion treatability thereof. However, this causes chemical conversion treatment unevenness or a lack of hiding on a surface because of the oxidation of the inner portion or deteriorates corrosion resistance after electrodeposition coating. Therefore, the inventors have investigated a method for solving this problem by a novel technique without being bound to conventional ideas. As a result, the inventors have found that the formation of internal oxides in a surface portion of a steel sheet is suppressed and excellent chemical conversion treatability and high corrosion resistance after electrodeposition coating are achieved in such a manner that the heating rate, atmosphere, and temperature in a heating step during continuous annealing are appropriately controlled. During continuous annealing, the steel sheet is annealed in such a manner that the steel sheet is heated at a heating rate of 7 °C/s or more in a temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$), the maximum end-point temperature of the steel sheet in an annealing furnace is controlled to be 600°C to 700°C, the transit time of the steel sheet in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C is controlled to be 30 seconds to 10 minutes, and the concentration of hydrogen in an atmosphere is controlled to be 20% by volume or more in the heating step. Subsequently, a chemical conversion treatment is performed. Since the heating rate in the temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$) is 7 °C/s or more, the maximum end-point temperature of the steel sheet in the annealing furnace is 600°C to 700°C, and the concentration of hydrogen in the atmosphere in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 20% by volume or more in the heating step, the potential of oxygen at the interface between the steel sheet and the atmosphere is reduced, internal oxidation hardly occurs, and the selective surface diffusion and oxidation (hereinafter referred to as surface oxidation) of Si, Mn, and the like are suppressed.

[0013] No internal oxide is formed and surface oxidation is minimized by controlling the heating rate of such a limited region only and the concentration of hydrogen in an atmosphere, whereby a high-strength steel sheet which is free from a lack of hiding and unevenness and which has excellent chemical conversion treatability and corrosion resistance after electrodeposition coating is obtained. The term "excellent chemical conversion treatability" refers to having an appearance free from a lack of hiding and unevenness after a chemical conversion treatment.

[0014] A high-strength steel sheet obtained by the above method includes a surface portion within 100 μm from a surface of the steel sheet. In the surface portion, the formation of the following oxide is suppressed: an oxide of one or more selected from among Fe, Si, Mn, Al, P, and further B, Nb, Ti, Cr, Mo, Cu, Ni, Sn, Sb, Ta, W, and V. The amount of the formed oxide per side is limited to less than 0.030 g/m^2 in total. This leads to excellence in chemical conversion treatability and a significant increase in corrosion resistance after electrodeposition coating.

[0015] The present invention is based on the above finding and is featured as described below.

(1) A method for manufacturing a high-strength steel sheet includes continuously annealing a steel sheet containing, by mass%, 0.03% to 0.35% C, 0.01% to 0.50% Si, 3.6% to 8.0% Mn, 0.01% to 1.0% Al, 0.10% or less P, and 0.010% or less S, the remainder being Fe and inevitable impurities. In a heating step, the steel sheet is heated at a heating rate of 7 °C/s or more in a temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$), the maximum end-point temperature of the steel sheet in an annealing furnace is 600°C to 700°C, the transit time of the steel sheet in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 30 seconds to 10 minutes, and the concentration of hydrogen in an atmosphere is 20% by volume or more.

(2) In the method for manufacturing the high-strength steel sheet specified in Item (1) above, the steel sheet further contains, by mass%, one or more selected from among 0.001% to 0.005% B, 0.005% to 0.05% Nb, 0.005% to 0.05% Ti, 0.001% to 1.0% Cr, 0.05% to 1.0% Mo, 0.05% to 1.0% Cu, 0.05% to 1.0% Ni, 0.001% to 0.20% Sn, 0.001% to 0.20% Sb, 0.001% to 0.10% Ta, 0.001% to 0.10% W, and 0.001% to 0.10% V as a component composition.

(3) The method for manufacturing the high-strength steel sheet specified in Item (1) or (2) above further includes performing electrolytic pickling in an aqueous solution containing sulfuric acid after the continuous annealing is performed.

(4) A high-strength steel sheet is manufactured by the method specified in any one of Items (1) to (3) above. The amount of an oxide of one or more selected from among Fe, Si, Mn, Al, P, B, Nb, Ti, Cr, Mo, Cu, Ni, Sn, Sb, Ta, W, and V per side is less than 0.030 g/m^2 in total, the oxide being formed in a surface portion of the steel sheet that is within 100 μm from a surface of the steel sheet.

[0016] A high-strength steel sheet according to the present invention has a tensile strength TS of 590 MPa or more. The term "high-strength steel sheet" as used herein includes both a cold-rolled steel sheet and a hot-rolled steel sheet.
Advantageous Effects of Invention

[0017] According to the present invention, a high-strength steel sheet that has excellent chemical conversion treatability and corrosion resistance after electrodeposition coating is obtained even when the content of Si or Mn is high.

Description of Embodiments

[0018] The present invention is described below in detail. In descriptions below, the unit of the content of each element in the steel composition is "mass percent" and is simply denoted by "%" unless otherwise specified.

[0019] First, annealing conditions which are the most important requirements for the present invention and which determine the surface structure of a steel sheet are described. In order to allow a high-strength steel sheet made from steel containing large amounts of Si and Mn to have satisfied corrosion resistance, the internal oxidation of a steel sheet surface layer that may possibly be the origin of corrosion needs to be minimized. Chemical conversion treatability can be enhanced by promoting the internal oxidation of Si and Mn. However, this causes the deterioration of corrosion resistance as described above. Therefore, it is necessary that good chemical conversion treatability is maintained by a method other than promoting the internal oxidation of Si and Mn and corrosion resistance is enhanced by suppressing internal oxidation. As a result of intensive investigations, in the present invention, the potential of oxygen is reduced in an annealing step for the purpose of ensuring chemical conversion treatability and the activity of Si, Mn, and the like, which are oxidizable elements, in a base metal surface portion is reduced. This suppresses the external oxidation of these elements, resulting in improving chemical conversion treatability. Furthermore, the formation of internal oxides in a steel sheet surface portion is suppressed and therefore corrosion resistance after electrodeposition coating is improved.

[0020] Such an effect is obtained in such a manner that when annealing is performed in a continuous annealing line, the heating rate in a temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$) is controlled to be 7 °C/s or more, the maximum end-point temperature of a steel sheet in an annealing furnace is controlled to be 600°C to 700°C, the transit time of the steel sheet in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C is controlled to be 30 seconds to 10 minutes, and the concentration of hydrogen in an atmosphere is controlled to be 20% by volume or more in a heating step. Since heating is performed in such a manner that the heating rate in the temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$) is controlled to be 7 °C/s or more, the formation of surface oxides is minimized. Since the concentration of hydrogen in the atmosphere is controlled to be 20% by volume or more in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C, the potential of oxygen at the interface between the steel sheet and the atmosphere is reduced and the selective surface diffusion and surface oxidation of Si, Mn, and the like is suppressed without forming internal oxides. As a result, excellent chemical conversion treatability free from a lack of hiding and unevenness and high corrosion resistance after electrodeposition coating are achieved.

[0021] The reason why the temperature range in which the heating rate is controlled is 450°C or higher is as described below. In a temperature range lower than 450°C, surface oxidation and internal oxidation do not occur to such an extent that the occurrence of a lack of hiding and unevenness, the deterioration of corrosion resistance, and the like are problematic. Thus, the temperature range, in which an effect of the present invention is exhibited, is 450°C or higher.

[0022] The reason why the temperature range is A°C (where $500 \leq A \leq 600$) or lower is as described below. In a temperature range lower than 500°C, the time for which the heating rate is controlled to be 7 °C/s or more is short and therefore an effect of the present invention is small. The effect of suppressing surface oxidation is insufficient. Therefore, A is 500 or more. The case of higher than 600°C is disadvantageous from the viewpoints of the deterioration of annealing furnace internals (rolls and the like) and an increase in cost, although there is no problem for an effect of the present invention. Thus, A is 600 or less.

[0023] The reason why the heating rate is 7 °C/s or more is as described below. The effect of suppressing surface oxidation is recognized when the heating rate is 7 °C/s or more. The upper limit of the heating rate is not particularly limited. When the heating rate is 500 °C/s or more, the above effect is saturated, which is disadvantageous in terms of cost. Therefore, the heating rate is preferably 500 °C/s or less. The heating rate can be adjusted to 7 °C/s or more in such a manner that, for example, an induction heater is placed in an annealing furnace in which the temperature of the steel sheet is 450°C to A°C.

[0024] The reason why the maximum end-point temperature of the steel sheet in the annealing furnace is 600°C to 700°C is as described below. When the maximum end-point temperature of the steel sheet is lower than 600°C, good material quality is not obtained. Therefore, a temperature range in which an effect of the present invention is exhibited is 600°C or higher. However, in a temperature range higher than 700°C, surface oxidation is significant and the deterioration of chemical conversion treatability is serious. Furthermore, in the temperature range higher than 700°C, the effect of balancing between strength and ductility is saturated from the viewpoint of material quality. From the above, the maximum end-point temperature of the steel sheet is 600°C to 700°C.

[0025] The reason why the transit time of the steel sheet in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 30 seconds to 10 minutes is as described below. When the transit time of the steel sheet in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C is less than 30 seconds, target material quality (TS, El) is not obtained. When the transit time of the steel sheet in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C is more than 10 minutes, the effect of balancing between strength and ductility is saturated.

[0026] The reason why the concentration of hydrogen in the atmosphere in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 20% by volume or more is as described below. The effect of suppressing surface oxidation begins to be recognized when the concentration of hydrogen is 20% by volume. The upper limit of the concentration of hydrogen is not particularly limited. When the concentration of hydrogen is more than 80% by volume, the above effect is saturated, which is disadvantageous in terms of cost. Therefore, the concentration of hydrogen is preferably 80% by volume or less.

[0027] The composition of the steel sheet of the high-strength steel sheet of the present invention are described below.

C: 0.03% to 0.35%

[0028] C forms martensite and the like as a steel microstructure to enhance workability. Therefore, the content of C needs to be 0.03% or more. However, when the content of C is more than 0.35%, strength increases extremely and elongation decreases, resulting in the deterioration of workability. Thus, the content of C is 0.03% to 0.35%.

Si: 0.01% to 0.50%

[0029] Although Si is an element that is effective in strengthening steel to obtain good material quality, Si is an oxidizable element and therefore is disadvantageous for chemical conversion treatability. Si is an element that should be avoided being added as much as possible. However, about 0.01% of Si is inevitably contained in steel. Reducing the content of Si to 0.01% or less leads to an increase in cost. From the above, the lower limit is 0.01%. On the other hand, when the content of Si is more than 0.50%, the effect of increasing the strength and elongation of steel is saturated and chemical conversion treatability is deteriorated. Thus, the content of Si is 0.01% to 0.50%.

Mn: 3.6% to 8.0%

[0030] Mn is an element effective in increasing the strength of steel. In order to ensure mechanical properties and strength, 3.6% or more Mn needs to be contained. However, when more than 8.0% Mn is contained, it is difficult to ensure chemical conversion treatability and the balance between strength and ductility. Furthermore, there is a cost disadvantage. Thus, the content of Mn is 3.6% to 8.0%.

Al: 0.01% to 1.0%

[0031] Al is added for the purpose of deoxidizing molten steel. When the content of Al is less than 0.01%, the purpose of deoxidizing molten steel is not achieved. The effect of deoxidizing molten steel is achieved when the content of Al is 0.01% or more. However, when the content of Al is more than 1.0%, an increase in cost is caused. Furthermore, the surface oxidation of Al is increased and it is difficult to improve chemical conversion treatability. Thus, the content of Al is 0.01% to 1.0%.

P $\leq$ 0.10%

[0032] P is one of inevitably contained elements. In order to adjust the content of P to less than 0.005%, an increase in cost may possibly be caused. Therefore, the content of P is preferably 0.005% or more. However, when more than 0.10% of P is contained, weldability is deteriorated. Furthermore, the deterioration of chemical conversion treatability is significant and it is difficult to enhance chemical conversion treatability even by the present invention. Thus, the content of P is 0.10% or less and the lower limit is preferably 0.005%.

S $\leq$ 0.010%

[0033] S is one of the inevitably contained elements. The lower limit is not particularly limited. When a large amount of S is contained, weldability and corrosion resistance are deteriorated. Therefore, the content of S is 0.010% or less.

[0034] In order to improve surface quality and to further improve the balance between strength and ductility, the following element may be added where appropriate: an element that is one or more selected from among 0.001% to 0.005% B, 0.005% to 0.05% Nb, 0.005% to 0.05% Ti, 0.001% to 1.0% Cr, 0.05% to 1.0% Mo, 0.05% to 1.0% Cu, 0.05% to 1.0% Ni, 0.001% to 0.20% Sn, 0.001% to 0.20% Sb, 0.001% to 0.10% Ta, 0.001% to 0.10% W, and 0.001% to 0.10% V.

[0035] In the case where these elements are added, the reason for limiting the appropriate amount of each added element is as described below.

B: 0.001% to 0.005%

[0036] When the content of B is less than 0.001%, the effect of accelerating hardening is unlikely to be obtained. However, when the content of B is more than 0.005%, chemical conversion treatability is deteriorated. Thus, when B is contained, the content of B is 0.001% to 0.005%. Incidentally, in the case where the addition of B is judged to be unnecessary to improve mechanical properties, B need not be added.

Nb: 0.005% to 0.05%

[0037] When the content of Nb is less than 0.005%, the effect of adjusting strength is unlikely to be obtained. However, when the content of Nb is more than 0.05%, an increase in cost is caused. Thus, when Nb is contained, the content of Nb is 0.005% to 0.05%.

Ti: 0.005% to 0.05%

[0038] When the content of Ti is less than 0.005%, the effect of adjusting strength is unlikely to be obtained. However, when the content of Ti is more than 0.05%, the deterioration of chemical conversion treatability is caused. Thus, when Ti is contained, the content of Ti is 0.005% to 0.05%.

Cr: 0.001% to 1.0%

[0039] When the content of Cr is less than 0.001%, a hardening effect is unlikely to be obtained. However, when the content of Cr is more than 1.0%, Cr is surface-oxidized and therefore weldability is deteriorated. Thus, when Cr is contained, the content of Cr is 0.001% to 1.0%.

Mo: 0.05% to 1.0%

[0040] When the content of Mo is less than 0.05%, the effect of adjusting strength is unlikely to be obtained. However, when the content of Mo is more than 1.0%, an increase in cost is caused. Thus, when Mo is contained, the content of Mo is 0.05% to 1.0%.

Cu: 0.05% to 1.0%

[0041] When the content of Cu is less than 0.05%, the effect of accelerating the formation of a retained γ-phase is unlikely to be obtained. However, when the content of Cu is more than 1.0%, an increase in cost is caused. Thus, when Cu is contained, the content of Cu is 0.05% to 1.0%.

Ni: 0.05% to 1.0%

[0042] When the content of Ni is less than 0.05%, the effect of accelerating the formation of the retained γ-phase is unlikely to be obtained. However, when the content of Ni is more than 1.0%, an increase in cost is caused. Thus, when Ni is contained, the content of Ni is 0.05% to 1.0%.

Sn: 0.001% to 0.20%, Sb: 0.001% to 0.20%

[0043] Sn and Sb may be contained from the viewpoint of suppressing the nitriding or oxidation of a surface of the steel sheet or the decarburization of a region of tens of micrometers in the steel sheet surface, the decarburization being due to oxidation. Suppressing the nitriding or oxidation thereof prevents the amount of martensite produced in the steel sheet surface from being reduced, thereby improving fatigue properties and surface quality. From the above viewpoint, when Sn and/or Sb is contained, the content of each of Sn and Sb is 0.001% or more. When the content of either of Sn and Sb is more than 0.20%, the deterioration of toughness is caused. Therefore, the content of each of Sn and Sb is preferably 0.20% or less.

Ta: 0.001% to 0.10%

[0044] Ta forms a carbide and a carbonitride with C and N to contribute to increasing strength and also contributes to increasing yield ratio (YR). Ta has the property of refining the microstructure of a hot-rolled steel sheet. This property reduces the diameter of ferrite grains after cold rolling and annealing. Thus, the amount of C segregated along grain boundaries increases with the increase in area of the grain boundaries and a high bake hardening value (BH value) can be obtained. From this viewpoint, 0.001% or more Ta may be contained. However, containing more than 0.10% Ta causes an increase in material cost and may possibly interfere with the formation of martensite in the course of cooling after annealing. Furthermore, TaC precipitated in the hot-rolled steel sheet increases deformation resistance during cold rolling to make stable actual manufacture difficult in some cases. Thus, when Ta is contained, the content of Ta is 0.10% or less.

W: 0.001% to 0.10%, V: 0.001% to 0.10%

[0045] W and V are elements which form a carbonitride and which have the property of increasing the strength of steel by a precipitation effect and may be added as required. In the case where W and/or V is added, this property is exhibited when the content of each of W and V is 0.001% or more. However, when more than 0.10% W and/or V is contained, strength is extremely increased and ductility is deteriorated. From the above, when W and/or V is contained, the content of each of W and V is 0.001% to 0.10%.

[0046] The remainder other than the above elements are Fe and inevitable impurities. If an element other than the above elements is contained, the present invention is not adversely affected. The upper limit of the element other than the above elements is 0.10%.

[0047] A method for manufacturing the high-strength steel sheet according to the present invention and the reason for limiting the method are described below.

[0048] Steel containing the above chemical components is hot-rolled, followed by cold rolling, whereby a steel sheet is obtained. The steel sheet is annealed in a continuous annealing line. Furthermore, the steel sheet is preferably electrolytically pickled in an aqueous solution containing sulfuric acid. The steel sheet is then subjected to a chemical conversion treatment. In the present invention, when the steel sheet is annealed, the heating rate in a temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \le A \le 600$) is 7 °C/s or more, the maximum end-point temperature of the steel sheet in an annealing furnace is 600°C to 700°C, the transit time of the steel sheet in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 30 seconds to 10 minutes, and the concentration of hydrogen in an atmosphere is 20% by volume or more in a heating step. This is the most important requirement in the present invention. In the above, hot rolling is directly followed by annealing without performing cold rolling in some cases.

Hot rolling

[0049] Hot rolling can be performed under conditions usually used.

Pickling

[0050] Pickling is preferably performed after hot rolling. Mill scales formed on a surface are removed in a pickling step, followed by cold rolling. Pickling conditions are not particularly limited.

Cold rolling

[0051] Cold rolling is preferably performed with a rolling reduction of 40% to 80%. When the rolling reduction is less than 40%, the recrystallization temperature is reduced and therefore mechanical properties are likely to be deteriorated. However, when the rolling reduction is more than 80%, not only rolling costs increase because of the high-strength steel sheet but also chemical conversion treatability is deteriorated because surface oxidation increases during annealing in some cases.

[0052] The cold-rolled or hot-rolled steel sheet is annealed and is then subjected to the chemical conversion treatment.

[0053] In the annealing furnace, the heating step is performed such that the steel sheet is heated to a predetermined temperature in an upstream heating zone and a soaking step is performed such that the steel sheet is held at a predetermined temperature for a predetermined time in a downstream soaking zone.

[0054] In the heating step, the heating rate in the temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$) is 7 °C/s or more, the maximum end-point temperature of the steel sheet in an annealing furnace is 600°C to 700°C, the transit time of the steel sheet in the temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 30 seconds to 10 minutes, and the concentration of hydrogen in the atmosphere is controlled to be 20% by volume or more as described above.

[0055] Gaseous components in the annealing furnace are nitrogen, hydrogen, and inevitable impurities. If no effect of the present invention is impaired, another gaseous component may be contained.

[0056] The concentration of hydrogen in a temperature range other than the temperature range corresponding to a steel sheet temperature of 600°C to 700°C, that is, a temperature range lower than 600°C or higher than 700°C, is not particularly limited. When the concentration of hydrogen therein is less than 1% by volume, no activation effect due to reduction is obtained and chemical conversion treatability is deteriorated in some cases. The upper limit is not particularly limited. When the upper limit is more than 50% by volume, an increase in cost is caused and an effect is saturated. Thus, the concentration of hydrogen therein is preferably 1% to 50% by volume and more preferably 5% to 30% by volume. The remainder are N_2 and inevitable impurity gases. If no effect of the present invention is impaired, a gaseous component such as H_2O, CO_2, or CO may be contained.

[0057] After cooling from the temperature range of 600°C to 700°C, quenching or tempering may be performed as required. Conditions are not particularly limited. Tempering is preferably performed at a temperature of 150°C to 400°C. This is because elongation tends to be deteriorated when the temperature is lower than 150°C and hardness tends to be reduced when the temperature is higher than 400°C.

[0058] In the present invention, even if electrolytic pickling is not performed, good chemical conversion treatability can be ensured. However, after continuous annealing is performed, electrolytic pickling is preferably performed in an aqueous solution containing sulfuric acid for the purpose of removing slight amounts of surface oxides inevitably formed during annealing to ensure better chemical conversion treatability.

[0059] A pickling solution used for electrolytic pickling is not particularly limited. Nitric acid and hydrofluoric acid are highly corrosive to equipment, requires caution in handling, and therefore are not preferable. Hydrochloric acid may possibly generate a chlorine gas from a cathode and therefore is not preferable. Thus, in consideration of corrosiveness and environments, sulfuric acid is preferably used. The concentration of sulfuric acid is preferably 5% to 20% by mass. When the concentration of sulfuric acid is less than 5% by mass, conductivity is low; hence, the voltage of an electrolytic bath rises during electrolysis to increase the load of a power supply in some cases. However, when the concentration of sulfuric acid is more than 20% by mass, the loss due to drag-out is large, which is problematic in terms of cost.

[0060] Conditions for electrolytic pickling are not particularly limited. In order to efficiently remove surface oxides, such as oxides of Si and Mn, formed after annealing and inevitably surface-oxidized, alternating electrolysis is preferably performed at a current density of 1 A/dm^2 or more. The reason for performing alternating electrolysis is as described below. When the steel sheet is being held as a cathode, a pickling effect is small. In contrast, when the steel sheet is being held as an anode, Fe dissolved during electrolysis is accumulated in the pickling solution and therefore the concentration of Fe in the pickling solution is increased; hence, a problem with dry stains or the like occurs if the pickling solution is attached to a surface of the steel sheet.

[0061] The temperature of an electrolytic solution is preferably 40°C to 70°C. The temperature of a bath is increased by heat generated by continuous electrolysis and therefore it is difficult to maintain the electrolytic solution at lower than 40°C in some cases. From the viewpoint of the durability of a lining of an electrolytic cell, it is not preferable that the temperature of the electrolytic solution exceeds 70°C. When the temperature of the electrolytic solution is lower than 40°C, the pickling effect is small. Therefore, the temperature of the electrolytic solution is preferably 40°C or higher.

[0062] The high-strength steel sheet according to the present invention is obtained as described above. The surface structure of the steel sheet is featured as described below.

[0063] In a surface portion of the steel sheet that is within 100 μm from a surface of the steel sheet, the amount of the following oxide per side is limited to less than 0.030 g/m^2 in total: an oxide of one or more selected from among Fe, Si, Mn, Al, P, B, Nb, Ti, Cr, Mo, Cu, Ni, Sn, Sb, Ta, W, and V.

[0064] In the steel sheet, which is made from steel containing large amounts of Si and Mn, it is required that the internal oxidation of a surface layer of a base steel sheet is minimized, chemical conversion treatment unevenness and a lack of hiding are suppressed, and corrosion and cracking during heavy machining are also suppressed. Therefore, in the present invention, the potential of oxygen is reduced in the annealing step for the purpose of ensuring good chemical conversion treatability, whereby the activity of Si, Mn, and the like, which are oxidizable elements, in a base metal surface portion is reduced. Furthermore, the external oxidation of these elements is suppressed and the formation of internal oxides in the base metal surface portion is also suppressed. As a result, not only good chemical conversion treatability is ensured but also workability and corrosion resistance after electrodeposition coating are enhanced. Such an effect is obtained in such a manner that in a surface portion of the steel sheet that is within 100 μm from a surface of the base steel sheet, the amount of the following oxide is limited to less than 0.030 g/m^2 in total: an oxide of at least one selected from among Fe, Si, Mn, Al, P, B, Nb, Ti, Cr, Mo, Cu, Ni, Sn, Sb, Ta, W, and V. When the sum (hereinafter referred to as the internal oxidation amount) of the amounts of formed oxides is 0.030 g/m^2 or more, not only corrosion resistance and workability are deteriorated but also chemical conversion treatment unevenness and a lack of hiding are caused. Even if the internal oxidation amount is limited to less than 0.0001 g/m^2, the effect of improving corrosion resistance and the effect of enhancing workability are saturated. Therefore, the lower limit of the internal oxidation amount is preferably 0.0001 g/m^2.

EXAMPLES

[0065] The present invention is described below in detail with reference to examples.

[0066] Hot-rolled steel sheets with a steel composition shown in Table 1 were pickled, whereby mill scales were removed. Thereafter, the hot-rolled steel sheets were cold-rolled under conditions shown in Tables 2 and 3, whereby cold-rolled steel sheets with a thickness of 1.0 mm were obtained. Incidentally, after the mill scales were removed, some of the hot-rolled steel sheets (a thickness of 2.0 mm) were used without being cold-rolled.

[Table 1]

(mass percent)

Steel symbol	C	Si	Mn	Al	P	S	Cr	Mo	B	Nb	Cu	Ni	Ti	Sn	Sb	Ta	W	V
A	0.11	0.02	4.4	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
B	0.02	0.02	4.5	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
C	0.35	0.02	4.8	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
D	0.13	0.11	4.6	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
E	0.12	0.31	4.7	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
F	0.11	0.49	4.5	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
G	0.12	0.02	3.7	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
H	0.11	0.03	6.2	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
I	0.11	0.02	8.0	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
J	0.12	0.02	4.6	0.29	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
K	0.11	0.03	4.5	0.99	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
L	0.12	0.02	4.6	0.02	0.04	0.003	-	-	-	-	-	-	-	-	-	-	-	-
M	0.11	0.03	4.4	0.03	0.09	0.003	-	-	-	-	-	-	-	-	-	-	-	-
N	0.12	0.03	4.6	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
O	0.12	0.02	4.7	0.02	0.01	0.003	0.7	-	-	-	-	-	-	-	-	-	-	-
P	0.11	0.03	4.6	0.02	0.01	0.003	-	0.2	-	-	-	-	-	-	-	-	-	-
Q	0.12	0.02	4.6	0.03	0.01	0.003	-	-	0.002	-	-	-	-	-	-	-	-	-
R	0.11	0.03	4.5	0.04	0.01	0.003	-	-	0.002	0.02	-	-	-	-	-	-	-	-
S	0.12	0.02	4.6	0.02	0.01	0.003	-	0.2	-	-	0.2	0.1	-	-	-	-	-	-
T	0.12	0.03	4.7	0.03	0.01	0.003	-	-	0.002	-	-	-	0.01	-	-	-	-	-
U	0.11	0.02	4.7	0.04	0.01	0.003	-	-	-	-	-	-	0.04	-	-	-	-	-
U1	0.12	0.02	4.5	0.02	0.01	0.003	-	-	-	-	-	-	-	0.04	-	-	-	-
U2	0.11	0.03	4.6	0.03	0.01	0.003	-	-	-	-	-	-	-	-	0.03	-	-	-
U3	0.12	0.03	4.5	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	0.02	-	-
U4	0.11	0.03	4.6	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	0.02	-
U5	0.12	0.03	4.7	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	0.02
XA	0.02	0.03	4.5	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
XB	0.36	0.02	4.6	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
XC	0.11	0.59	4.5	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
XD	0.12	0.02	3.5	0.03	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
XE	0.12	0.02	4.5	1.10	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-
XF	0.11	0.03	4.6	0.03	0.11	0.003	-	-	-	-	-	-	-	-	-	-	-	-
XG	0.12	0.02	4.6	0.02	0.01	0.020	-	-	-	-	-	-	-	-	-	-	-	-
XH	0.11	0.02	8.1	0.02	0.01	0.003	-	-	-	-	-	-	-	-	-	-	-	-

Underlined items are outside the scope of the present invention.

[0067] Next, each of the hot-rolled steel sheets and cold-rolled steel sheets obtained as described above was charged into a continuous annealing line. In the continuous annealing line, as shown in Tables 2 and 3, each steel sheet was processed and annealed by controlling the heating rate in a temperature range corresponding to a steel sheet temperature of 450°C to A°C (where 500 ≤ A ≤ 600) in an annealing furnace, the concentration of hydrogen in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C in the annealing furnace, the transit time of the steel sheet, and the maximum end-point temperature of the steel sheet, followed by water quenching and then tempering at

300°C for 140 seconds. Subsequently, the steel sheet was pickled in such a manner that the steel sheet was immersed in a 40°C aqueous solution containing 5% by mass sulfuric acid. Some of the steel sheets were electrolytically pickled under current density conditions shown in Tables 2 and 3 by alternating electrolysis in such a manner that a specimen was held as an anode and a cathode in that order for 3 seconds, whereby specimens were obtained. The concentration of hydrogen in the annealing furnace other than a region where the concentration of hydrogen was controlled as described above was basically 10% by volume. Gaseous components in an atmosphere were a nitrogen gas, a hydrogen gas, and inevitable impurity gases. The dew point of the atmosphere was controlled by absorbing or removing moisture in the atmosphere. The dew point of the atmosphere was -35°C.

[0068] The specimens obtained as described above were measured for TS and El. Furthermore, the specimens were investigated for chemical conversion treatability and corrosion resistance after electrodeposition coating. The amount (internal oxidation amount) of oxides present in a surface portion of each steel sheet, the surface portion being located directly under a surface layer of the steel sheet and being within 100 μm from the surface layer, was measured. Measurement methods and evaluation standards are as described below.

Chemical conversion treatability

[0069] A chemical conversion solution used was a chemical conversion solution (PALBOND® L3080) produced by Nihon Parkerizing Co., Ltd. Each specimen was subjected to a chemical conversion treatment by a method below. The specimen was degreased with a degreasing solution, FINECLEANER®, produced by Nihon Parkerizing Co., Ltd.; was washed with water; was surface-modified with a surface modifier, PREPALENE® Z, produced by Nihon Parkerizing Co., Ltd. for 30 seconds; was immersed in the chemical conversion solution (PALBOND® L3080) at 43°C for 120 seconds; was washed with water; and was then dried with hot air. Randomly selected five fields of view of the specimen subjected to the chemical conversion treatment were observed with a scanning electron microscope (SEM) at 500x magnification. The area fraction of a lack of hiding in a chemical conversion coating was measured by image processing. The specimen was evaluated depending on the area fraction of a lack of hiding as described below. "A" is an acceptable level.

A: 10% or less
B: more than 10%

Corrosion resistance after electrodeposition coating

[0070] A test piece with a size of 70 mm × 150 mm was cut out of each specimen, obtained by the above method, subjected to the chemical conversion treatment, followed by cationic electrodeposition coating (baking conditions: 170°C for 20 minutes, a thickness of 25 μm) using PN-150G® manufactured by Nippon Paint Co., Ltd. Thereafter, end portions and a surface not evaluated were sealed with an Al tape and cross cuts (a cross angle of 60°) were made with a cutter knife so as to reach a base metal, whereby a specimen was prepared. Next, the specimen was immersed in a 5% aqueous solution of NaCl (55°C) for 240 hours, was taken out, was washed with water, and was then dried, followed by peeling the tape from a cross cut portion. The separation width was measured and was evaluated as described below. "A" is an acceptable level.

A: a separation width of less than 2.5 mm per side
B: a separation width of 2.5 mm or more per side

Workability

[0071] A JIS #5 tensile test piece was taken from each sample in a 90° direction with respect to a rolling direction and was measured for workability in such a manner that tensile testing was performed at a constant cross head speed of 10 mm/min in accordance with JIS Z 2241 and the tensile strength (TS/MPa) and elongation (El/%) were determined. A test piece satisfying the inequality $TS \times El \geq 18{,}000$ was rated good. A test piece satisfying the inequality $TS \times El < 18{,}000$ was rated poor.

Internal oxidation amount in region within 100 μm from surface layer of steel sheet

[0072] The internal oxidation amount was measured by "impulse furnace fusion-infrared absorption spectrometry". Incidentally, the amount of oxygen contained in steel (that is, an unannealed high-strength steel sheet) needs to be subtracted. Therefore, in the present invention, surface portions of both sides of each continuously annealed high-strength steel sheet were polished by 100 μm or more, the concentration of oxygen in steel was measured, and the measurement was defined as the oxygen amount OH in steel. Furthermore, the concentration of oxygen in steel was measured over the continuously annealed high-strength steel sheet in a thickness direction and the measurement was defined as the oxygen amount OI after internal oxidation. The difference between OI and OH (= OI - OH) was calculated using the oxygen amount OI of the high-strength steel sheet, obtained as described above, after internal oxidation and the oxygen amount OH in steel. Furthermore, a value (g/m^2) converted into an amount per unit area (that is, 1 m^2) per side was defined as the internal oxidation amount.

[0073] Results obtained as described above are shown in Tables 2 and 3 together with manufacturing conditions.

[Table 2]

No.	Steel				Annealing furnace					Internal oxidation amount (g/m^2)	Electrolytic pickling	Current density (A/dm^2)	Chemical conversion treatability	Corrosion resistance after electrodeposition coating	TS (MPa)	El (%)	TS×El	Workability	Remarks
	Steel symbol	Si (mass percent)	Mn (mass percent)	Cold or hot rolling	Heating rate in temperature range of 450°C to A°C (°C/s)	Concentration of hydrogen in temperature range of 600°C to 700°C (volume percent)	A (°C)	Maximum end-point temperature of steel sheet (°C)	Transit time of steel sheet in temperature range of 600°C to 700°C (minutes)										
1	A	0.02	4.4	Cold rolling	12	5	550	649	1.2	0.096	Not performed	–	B	B	1058	22.0	23276	Good	Comparative example
2	A	0.02	4.4	Cold rolling	12	12	550	651	1.2	0.055	Not performed	–	B	B	1052	21.5	22618	Good	Comparative example
3	A	0.02	4.4	Cold rolling	12	19	550	648	1.2	0.031	Not performed	–	B	A	1051	22.4	23542	Good	Comparative example
4	A	0.02	4.4	Cold rolling	12	20	550	652	1.2	0.029	Not performed	–	A	A	1053	21.6	22745	Good	Inventive example
5	A	0.02	4.4	Cold rolling	12	24	550	649	1.2	0.020	Not performed	–	A	A	1052	21.9	23039	Good	Inventive example
6	A	0.02	4.4	Hot rolling	12	25	550	650	1.2	0.018	Not performed	–	A	A	1055	21.9	23105	Good	Inventive example
7	A	0.02	4.4	Cold rolling	12	36	550	649	1.2	0.011	Not performed	–	A	A	1058	21.1	22324	Good	Inventive example
8	A	0.02	4.4	Cold rolling	12	51	550	647	1.2	0.006	Not performed	–	A	A	1050	20.8	21840	Good	Inventive example
5a	A	0.02	4.4	Cold rolling	12	24	550	649	0.2	0.021	Not performed	–	A	A	941	16.4	15432	Poor	Comparative example
5b	A	0.02	4.4	Cold rolling	12	24	550	649	0.4	0.020	Not performed	–	A	A	991	18.1	17937	Poor	Comparative example
5c	A	0.02	4.4	Cold rolling	12	24	550	649	0.5	0.019	Not performed	–	A	A	1059	21.8	23086	Good	Inventive example
5d	A	0.02	4.4	Cold rolling	12	24	550	649	3.0	0.020	Not performed	–	A	A	1054	22.0	23188	Good	Inventive example
5e	A	0.02	4.4	Cold rolling	12	24	550	649	10.0	0.019	Not performed	–	A	A	1056	22.1	23338	Good	Inventive example
5f	A	0.02	4.4	Cold rolling	12	24	550	598	1.2	0.020	Not performed	–	B	A	1055	21.8	22999	Good	Comparative example
5g	A	0.02	4.4	Cold rolling	12	25	550	600	1.2	0.021	Not performed	–	A	A	1053	21.9	23061	Good	Inventive example
5h	A	0.02	4.4	Cold rolling	12	25	550	700	1.2	0.019	Not performed	–	A	A	1057	21.8	23043	Good	Inventive example
5i	A	0.02	4.4	Cold rolling	12	24	550	703	1.2	0.021	Not performed	–	B	A	1059	21.4	22663	Good	Comparative example
9	A	0.02	4.4	Cold rolling	1	24	550	650	1.2	0.019	Not performed	–	B	B	1060	21.6	22896	Good	Comparative example
10	A	0.02	4.4	Cold rolling	3	25	550	649	1.2	0.017	Not performed	–	B	B	1050	21.5	22575	Good	Comparative example
11	A	0.02	4.4	Cold rolling	5	23	550	651	1.2	0.015	Not performed	–	B	A	1049	21.5	22554	Good	Comparative example
12	A	0.02	4.4	Cold rolling	9	24	550	650	1.2	0.017	Not performed	–	A	A	1051	21.4	22491	Good	Inventive example
13	A	0.02	4.4	Cold rolling	30	25	550	652	1.2	0.019	Not performed	–	A	A	1049	20.7	21714	Good	Inventive example
14	A	0.02	4.4	Cold rolling	100	25	550	651	1.2	0.021	Not performed	–	A	A	1047	21.4	22406	Good	Inventive example
15	A	0.02	4.4	Cold rolling	12	24	495	650	1.2	0.015	Not performed	–	B	B	1050	21.0	22050	Good	Comparative example
16	A	0.02	4.4	Cold rolling	12	25	500	649	1.2	0.016	Not performed	–	A	A	1054	21.4	22556	Good	Inventive example
17	A	0.02	4.4	Cold rolling	12	24	525	648	1.2	0.019	Not performed	–	A	A	1050	21.6	22680	Good	Inventive example
18	A	0.02	4.4	Cold rolling	12	24	575	650	1.2	0.017	Not performed	–	A	A	1051	20.9	21966	Good	Inventive example
19	A	0.02	4.4	Cold rolling	12	25	600	650	1.2	0.018	Not performed	–	A	A	1059	20.8	22027	Good	Inventive example
20	A	0.02	4.4	Cold rolling	12	25	550	651	1.2	0.017	Performed	1	A	A	1051	21.0	22071	Good	Inventive example
21	A	0.02	4.4	Cold rolling	12	24	550	649	1.2	0.018	Performed	3	A	A	1049	21.4	22449	Good	Inventive example
22	A	0.02	4.4	Cold rolling	12	23	550	650	1.2	0.020	Performed	10	A	A	1056	21.2	22387	Good	Inventive example

Underlined items are manufacturing conditions outside the scope of the present invention.

[Table 3]

No.	Steel				Annealing furnace					Internal oxidation amount	Electrolytic pickling	Current density	Chemical conversion treatability	Corrosion resistance after electrodeposition coating	TS	El	TS×El	Workability	Remarks
	Steel symbol	Si (mass percent)	Mn (mass percent)	Cold or hot rolling	Heating rate in temperature range of 450°C to A°C (°C/s)	Concentration of hydrogen in temperature range of 600°C to 700°C (volume percent)	A (°C)	Maximum end-point temperature of steel sheet (°C)	Transit time of steel sheet in temperature range of 600°C to 700°C (minutes)	(g/m^2)		(A/dm^2)			(MPa)	(%)			
23	B	0.02	4.5	Cold rolling	12	25	550	648	1.2	0.017	Not performed	-	A	A	1044	20.9	21820	Good	Inventive example
24	C	0.02	4.8	Cold rolling	12	23	550	652	1.2	0.016	Not performed	-	A	A	1046	21.1	22071	Good	Inventive example
25	D	0.11	4.6	Cold rolling	12	24	550	650	1.2	0.017	Not performed	-	A	A	1041	20.8	21653	Good	Inventive example
26	E	0.31	4.7	Cold rolling	12	25	550	650	1.2	0.019	Not performed	-	A	A	1043	21.1	22007	Good	Inventive example
27	F	0.49	4.5	Cold rolling	12	25	550	649	1.2	0.021	Not performed	-	A	A	1052	21.8	22934	Good	Inventive example
28	G	0.02	3.7	Cold rolling	12	24	550	650	1.2	0.018	Not performed	-	A	A	877	23.0	20171	Good	Inventive example
29	H	0.03	6.2	Cold rolling	12	24	550	651	1.2	0.017	Not performed	-	A	A	1167	17.2	20072	Good	Inventive example
30	I	0.02	8.0	Cold rolling	12	25	550	652	1.2	0.019	Not performed	-	A	A	1205	15.0	18075	Good	Inventive example
31	J	0.02	4.6	Cold rolling	12	24	550	650	1.2	0.020	Not performed	-	A	A	1056	21.8	23021	Good	Inventive example
32	K	0.03	4.5	Cold rolling	12	25	550	649	1.2	0.021	Not performed	-	A	A	1050	21.0	22050	Good	Inventive example
33	L	0.02	4.6	Cold rolling	12	25	550	650	1.2	0.020	Not performed	-	A	A	1052	20.9	21987	Good	Inventive example
34	M	0.03	4.4	Cold rolling	12	23	550	648	1.2	0.019	Not performed	-	A	A	1055	20.7	21839	Good	Inventive example
35	N	0.03	4.6	Cold rolling	12	24	550	650	1.2	0.018	Not performed	-	A	A	1049	21.5	22554	Good	Inventive example
36	O	0.02	4.7	Cold rolling	12	25	550	649	1.2	0.017	Not performed	-	A	A	1050	21.3	22365	Good	Inventive example
37	P	0.03	4.6	Cold rolling	12	23	550	651	1.2	0.019	Not performed	-	A	A	1051	20.7	21756	Good	Inventive example
38	Q	0.02	4.6	Cold rolling	12	24	550	652	1.2	0.018	Not performed	-	A	A	1052	21.0	22092	Good	Inventive example
39	R	0.03	4.5	Cold rolling	12	24	550	650	1.2	0.017	Not performed	-	A	A	1058	21.6	22853	Good	Inventive example
40	S	0.02	4.6	Cold rolling	12	25	550	652	1.2	0.018	Not performed	-	A	A	1056	21.4	22598	Good	Inventive example
41	T	0.03	4.7	Cold rolling	12	24	550	650	1.2	0.021	Not performed	-	A	A	1054	21.6	22766	Good	Inventive example
42	U	0.02	4.7	Cold rolling	12	25	550	650	1.2	0.020	Not performed	-	A	A	1050	20.8	21840	Good	Inventive example
43	U1	0.02	4.5	Cold rolling	12	23	550	651	1.2	0.019	Not performed	-	A	A	1051	20.9	21966	Good	Inventive example
44	U2	0.03	4.6	Cold rolling	12	25	550	649	1.2	0.018	Not performed	-	A	A	1050	21.4	22470	Good	Inventive example
45	U3	0.03	4.5	Cold rolling	12	24	550	650	1.2	0.019	Not performed	-	A	A	1053	21.3	22429	Good	Inventive example
46	U4	0.03	4.6	Cold rolling	12	25	550	650	1.2	0.017	Not performed	-	A	A	1048	21.9	22951	Good	Inventive example
47	U5	0.03	4.7	Cold rolling	12	24	550	649	1.2	0.018	Not performed	-	A	A	1058	20.5	21689	Good	Inventive example
48	XA	0.03	4.5	Cold rolling	12	25	550	651	1.2	0.019	Not performed	-	A	A	1354	12.8	17331	Poor	Comparative example
49	XB	0.02	4.6	Cold rolling	12	24	550	650	1.2	0.020	Not performed	-	A	A	987	14.6	14410	Poor	Comparative example
50	XC	0.59	4.5	Cold rolling	12	23	550	650	1.2	0.026	Not performed	-	B	A	1204	11.5	13846	Poor	Comparative example
51	XD	0.02	3.5	Cold rolling	12	25	550	651	1.2	0.023	Not performed	-	A	A	856	22.9	19602	Poor	Comparative example
52	XE	0.02	4.5	Cold rolling	12	24	550	651	1.2	0.028	Not performed	-	B	B	1164	20.5	23862	Good	Comparative example
53	XF	0.03	4.6	Cold rolling	12	25	550	650	1.2	0.024	Not performed	-	B	A	1196	20.8	24877	Good	Comparative example
54	XG	0.02	4.6	Cold rolling	12	24	550	649	1.2	0.020	Not performed	-	A	B	1113	21.6	24041	Good	Comparative example
55	XH	0.02	8.1	Cold rolling	12	25	550	650	1.2	0.022	Not performed	-	B	B	1211	14.8	17923	Poor	Comparative example

Underlined items are manufacturing conditions outside the scope of the present invention.

[0074] As is clear from Tables 2 and 3, high-strength steel sheets manufactured by a method according to the present invention has excellent chemical conversion treatability, corrosion resistance after electrodeposition coating, and workability, although the high-strength steel sheets contain large amounts of oxidizable elements such as Si and Mn. However, in comparative examples, one or more of chemical conversion treatability, corrosion resistance after electrodeposition coating, and workability are inferior.

Industrial Applicability

[0075] A high-strength steel sheet according to the present invention has excellent chemical conversion treatability, corrosion resistance, and workability and can be used as a surface-treated steel sheet for lightening and strengthening automobile bodies. The high-strength steel sheet can be used in various fields, such as home appliances and building materials, other than automobiles in the form of a surface-treated steel sheet manufactured by imparting rust resistance to a base steel sheet.

Claims

1. A method for manufacturing a high-strength steel sheet, comprising continuously annealing a steel sheet containing, by mass%, 0.03% to 0.35% C, 0.01% to 0.50% Si, 3.6% to 8.0% Mn, 0.01% to 1.0% Al, 0.10% or less P, and 0.010% or less S, the remainder being Fe and inevitable impurities, wherein in a heating step, the steel sheet is heated at a heating rate of 7 °C/s or more in a temperature range corresponding to an annealing furnace inside temperature of 450°C to A°C (where $500 \leq A \leq 600$), the maximum end-point temperature of the steel sheet in an annealing furnace is 600°C to 700°C, the transit time of the steel sheet in a temperature range corresponding to a steel sheet temperature of 600°C to 700°C is 30 seconds to 10 minutes, and the concentration of hydrogen in an atmosphere is 20% by volume or more.

2. The method for manufacturing the high-strength steel sheet according to Claim 1, wherein the steel sheet further contains, by mass%, one or more selected from among 0.001% to 0.005% B, 0.005% to 0.05% Nb, 0.005% to 0.05% Ti, 0.001% to 1.0% Cr, 0.05% to 1.0% Mo, 0.05% to 1.0% Cu, 0.05% to 1.0% Ni, 0.001% to 0.20% Sn, 0.001% to 0.20% Sb, 0.001% to 0.10% Ta, 0.001% to 0.10% W, and 0.001% to 0.10% V as a component composition.

3. The method for manufacturing the high-strength steel sheet according to Claim 1 or 2, further comprising performing electrolytic pickling in an aqueous solution containing sulfuric acid after the continuous annealing is performed.

4. A high-strength steel sheet manufactured by the method according to any one of Claims 1 to 3, wherein the amount of an oxide of one or more selected from among Fe, Si, Mn, Al, P, B, Nb, Ti, Cr, Mo, Cu, Ni, Sn, Sb, Ta, W, and V per side is less than 0.030 g/m^2 in total, the oxide being formed in a surface portion of the steel sheet that is within 100 μm from a surface of the steel sheet.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/000460

A. CLASSIFICATION OF SUBJECT MATTER
C21D9/46(2006.01)i, *C21D1/76*(2006.01)i, *C22C38/00*(2006.01)i, *C22C38/06*(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)
C21D9/46-48, C21D1/76, C22C38/00-38/60

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 2014-15675 A (JFE Steel Corp.), 30 January 2014 (30.01.2014), claims; paragraph [0044] (Family: none)	1-4
Y	JP 2012-251239 A (JFE Steel Corp.), 20 December 2012 (20.12.2012), paragraphs [0057], [0058]; tables 1, 2 & US 2014/103684 A1 & EP 2708610 A1 & CN 103582714 A & KR 10-2013-140176 A & WO 2012/153471 A1	1-4

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 March 2015 (19.03.15)	21 April 2015 (21.04.15)

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/000460

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-183131 A (JFE Steel Corp.), 13 July 2006 (13.07.2006), fig. 5 & US 2008/118390 A1 & EP 1731626 A1 & CN 100485072 C & KR 1020060134030 A & WO 2005/095663 A1	1-4
A	JP 2007-262463 A (JFE Steel Corp.), 11 October 2007 (11.10.2007), paragraph [0017] (Family: none)	3

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2004323969 A **[0010]**
- JP 6010096 A **[0010]**
- JP 2003113441 A **[0010]**
- JP 55145122 A **[0010]**
- JP 2006045615 A **[0010]**