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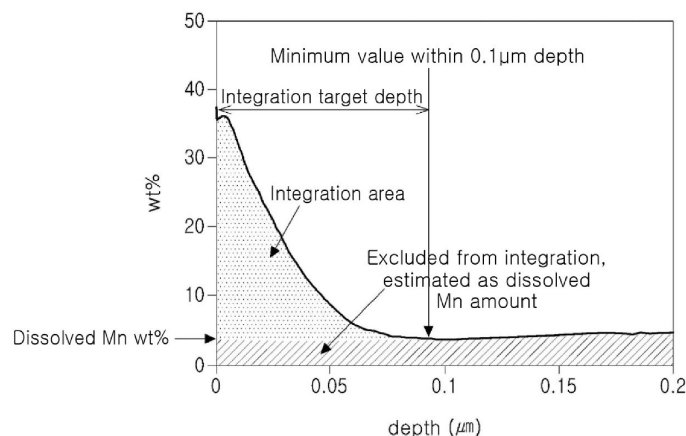
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(54) **COLD-ROLLED STEEL SHEET AND METHOD FOR MANUFACTURING SAME**

(57) The present invention relates to a cold-rolled steel sheet and a method for manufacturing same and, more specifically, to a cold-rolled steel sheet having

excellent surface quality and a method for manufacturing same.

[FIG. 1]



Description

Technical Field

- 5 **[0001]** The present invention relates to a cold-rolled steel sheet and a method for manufacturing the same, and more particularly, to a cold-rolled steel sheet with excellent surface quality and a method for manufacturing the same.

BACKGROUND ART

- 10 **[0002]** Recently, technological development for automotive steel materials has been focused on weight reduction through high-strengthening. For the high-strengthening of steel, various alloying elements are added to utilize precipitation strengthening and solid-solution strengthening, and the development of AHSS (Advanced High Strength Steel), which induces phase transformation during an annealing process, is actively underway.
- 15 **[0003]** Representative elements that can be added for the high-strengthening of steel include Mn, Si, Cr, and B. However, because they have a high tendency to oxidize, they diffuse to the surface to combine with oxygen in the atmosphere during annealing, thereby forming surface oxides. These surface oxides can lower the surface reactivity of the steel sheet, which may cause a deterioration in phosphatability or plateability.
- 20 **[0004]** In addition, as steel materials have become higher in strength, there is a problem of cracks occurring in the heat-affected zone during spot welding due to LME (Liquid Metal Embrittlement). While this was mainly an issue for hot-dip plated steel sheets, with the recent increase in strength, a problem has also arisen for cold-rolled steel sheets. When performing dissimilar welding where a cold-rolled steel sheet is overlapped with a hot-dip plated steel sheet, the plating layer of the hot-dip plated steel sheet comes into contact with the cold-rolled steel sheet in a liquid state, causing LME to occur.
- 25 **[0005]** A representative method for reducing LME is to form a soft decarburized layer on the surface layer of the base steel sheet. This is due to the effect of the decarburized layer on the surface suppressing the occurrence of cracks caused by tensile stress that appears during spot welding.
- 30 **[0006]** Various technologies have been proposed to suppress surface oxides formed on the surface of a steel sheet during annealing. Patent Document 1 discloses oxidizing a steel sheet in a direct flame furnace with an oxidizing atmosphere by controlling the air-fuel ratio of air and fuel to 0.80-0.95 during the annealing process to form iron oxides, including single or composite oxides of Si, Mn, or Al, up to a certain depth inside the steel sheet. Subsequently, the iron oxides are reduced and annealed in a reducing atmosphere, followed by hot-dip galvanizing to provide a hot-dip galvanized or galvanized steel sheet with excellent plating quality.
- 35 **[0007]** However, in the case of steel grades to which a certain amount or more of Si is added, during the reduction process, Si becomes concentrated directly beneath the iron oxide to form band-shaped Si oxides, which then become a starting point for delamination from the surface layer. That is, delamination occurs at the interface between the reduced iron and the base iron, which can make it difficult to secure sealer adhesion and plating layer adhesion.
- 40 **[0008]** Patent Document 2 discloses a method for improving plateability by maintaining a high dew point in an annealing furnace to internally oxidize easily oxidizable alloying elements such as Mn, Si, and Al within the steel, thereby reducing the amount of oxides that are externally oxidized on the steel sheet surface after annealing.
- 45 **[0009]** While the method of Patent Document 2 can solve the plateability problem caused by the external oxidation of Si, which is easily internally oxidized, its effect may be insignificant when a large amount of Mn, which is relatively difficult to internally oxidize, is added. Furthermore, there is a limit to the effect of reducing surface oxidation of Si, Mn, etc., and the formation of a decarburized layer that can be achieved by a single internal oxidation application.
- [0010]** (Patent Document 1) Korean Patent Laid-Open Publication No. 10-2010-0030627 (Published on Mar. 18, 2010)
- [0011]** (Patent Document 2) Korean Patent Laid-Open Publication No. 10-2009-0006881 (Published on Jan. 15, 2009)

Disclosure of Invention

Technical Problem

- 50 **[0012]** An embodiment of the present invention is to provide a cold-rolled steel sheet and a method for manufacturing the same.
- 55 **[0013]** An embodiment of the present invention is to provide a cold-rolled steel sheet with excellent surface quality and a method for manufacturing the same.
- [0014]** The problems of the present invention are not limited to the above-mentioned contents. A person skilled in the art will have no difficulty in understanding additional problems of the present invention from the overall contents of

this specification.

Solution to Problem

- 5 **[0015]** According to an embodiment of the present invention, a cold-rolled steel sheet may include, by weight%, C: 0.10-0.25%, Mn: 1.5-5.0%, Si: 0.5-2.5%, Cr: 1.5% or less, Al: 0.005-0.100%, P: 0.10% or less, S: 0.020% or less, B: 0.0050% or less, with the remainder being Fe and other unavoidable impurities, and have a Si surface enrichment of 0.0100 or less.
- 10 **[0016]** The cold-rolled steel sheet may further include, by weight%, 1.2% or less of one or more selected from Ti, Mo, and Nb.
- [0017]** In the cold-rolled steel sheet, the depth of an internal oxidation layer composed of oxides of one or more of Mn, Si, Cr, and B may be 3 to 15 μm from the surface of the steel sheet toward the center in the thickness direction.
- [0018]** In the cold-rolled steel sheet, the depth of a decarburized layer may be 20 to 150 μm from the surface of the steel sheet toward the center in the thickness direction.
- 15 **[0019]** The cold-rolled steel sheet may have a phosphate coating coverage of 80% or more after being immersed in a phosphate treatment solution at 35°C for 40 seconds.
- [0020]** The cold-rolled steel sheet may have a maximum LME crack length of 10 μm or less.
- [0021]** According to an embodiment of the present invention, a method for manufacturing a cold-rolled steel sheet may include: preparing a cold-rolled steel sheet including, by weight%, C: 0.10-0.25%, Mn: 1.5-5.0%, Si: 0.5-2.5%, Cr: 20 1.5% or less, Al: 0.005-0.100%, P: 0.10% or less, S: 0.020% or less, B: 0.0050% or less, with the remainder being Fe and other unavoidable impurities;
- performing a first annealing on the cold-rolled steel sheet at a temperature in the range of 600-900°C and a dew point temperature of -10 to 30°C;
- 25 performing a first pickling on the first-annealed cold-rolled steel sheet;
- performing a second annealing on the first-pickled cold-rolled steel sheet at a temperature in the range of 700-900°C;
- and performing a second pickling on the second-annealed cold-rolled steel sheet.
- 30 **[0022]** The cold-rolled steel sheet may further include, by weight%, 1.2% or less of one or more selected from Ti, Mo, and Nb.
- [0023]** The first annealing step may be maintained for 50 to 600 seconds, and the second annealing step may be performed at a dew point temperature of -60 to 30°C.
- [0024]** The first annealing step and the second annealing step may be performed in a nitrogen gas atmosphere
- 35 containing 1-80 vol% of hydrogen.
- [0025]** The method may further include a step of metal plating after either the first pickling step or the second pickling step.
- [0026]** The metal plating step may be Fe or Ni plating.

40 ADVANTAGEOUS EFFECTS OF INVENTION

- [0027]** According to an embodiment of the present invention, a cold-rolled steel sheet and a method for manufacturing the same can be provided.
- 45 **[0028]** According to an embodiment of the present invention, a cold-rolled steel sheet with excellent surface quality and a method for manufacturing the same can be provided.
- [0029]** According to an embodiment of the present invention, a cold-rolled steel sheet with excellent phosphatability that can be used for automotive steel materials and a method for manufacturing the same can be provided.
- [0030]** According to an embodiment of the present invention, a cold-rolled steel sheet with excellent resistance to LME that occurs during welding with a plated steel sheet and a method for manufacturing the same can be provided.
- 50 **[0031]** The various and beneficial advantages and effects of the present invention are not limited to the above-mentioned contents and will be more easily understood in the process of describing specific embodiments of the present invention.

BRIEF DESCRIPTION OF DRAWINGS

- 55 **[0032]**

FIG. 1 illustrates a method for calculating the Mn surface enrichment of a steel sheet according to an embodiment

of the present invention.

FIG. 2 is a cross-sectional SEM image of Inventive Example 1 according to an embodiment of the present invention, illustrating a method for measuring the depth of the internal oxidation layer.

FIG. 3 illustrates a method for obtaining the depth of the decarburized layer of a steel sheet according to an embodiment of the present invention, and is a graph showing the carbon concentration according to the depth of the steel sheet during GDS (Glow Discharge Spectrometer) analysis.

FIG. 4 is a cross-sectional SEM image of a steel sheet according to an embodiment of the present invention, illustrating a method for obtaining the depth of the decarburized layer of a nital-etched steel sheet.

Best Mode for the Invention

[0033] Hereinafter, preferred embodiments of the present invention will be described. The embodiments of the present invention may be modified in various forms, and the scope of the present invention should not be construed as being limited to the embodiments described below. These embodiments are provided to explain the present invention in more detail to those of ordinary skill in the art to which the present invention pertains.

[0034] Hereinafter, the present invention will be described in detail.

[0035] Hereinafter, the steel composition of the present invention will be described in detail.

[0036] Unless otherwise specified in the present invention, the percentage indicating the content of each element is based on weight.

[0037] A cold-rolled steel sheet according to an embodiment of the present invention may include, by weight%, C: 0.10-0.25%, Mn: 1.5-5.0%, Si: 0.5-2.5%, Cr: 1.5% or less, Al: 0.005-0.100%, P: 0.10% or less, S: 0.020% or less, and B: 0.0050% or less.

Carbon (C): 0.10-0.25%

[0038] Carbon (C) is an important element that can be added to stabilize retained austenite, and to secure this effect, it can be added at 0.10% or more. According to an embodiment of the present invention, carbon (C) can be added at 0.15% or more. On the other hand, if the carbon (C) content exceeds 0.25%, a problem of poor weldability may occur. According to an embodiment of the present invention, it may be 0.23% or less.

Manganese (Mn): 1.5-5.0%

[0039] Manganese (Mn) is an essential element in transformation-induced plasticity steels as it exhibits the effect of suppressing ferrite transformation during cooling, in addition to forming and stabilizing retained austenite. Furthermore, to secure sufficient austenite to ensure strength and ductility, manganese (Mn) can be included at 1.5% or more. According to an embodiment of the present invention, it may be 2.0% or more. On the other hand, if the content exceeds 5.0%, band formation due to segregation induced during slab heating and hot rolling processes may become excessive, leading to a problem of deteriorating physical properties. Therefore, according to an embodiment of the present invention, the upper limit of the manganese (Mn) content can be limited to 5.0%. According to an embodiment of the present invention, it may be 3.0% or less.

Silicon (Si): 0.5-2.5%

[0040] Silicon (Si) is an element that suppresses the precipitation of carbides in ferrite and promotes the diffusion of carbon in ferrite into austenite, thereby contributing to the stabilization of retained austenite. To obtain the above effects, silicon (Si) can be added at 0.5% or more. According to an embodiment of the present invention, it may be 0.7% or more. However, if added excessively, surface reactivity may be lowered, so the upper limit of the silicon (Si) content can be limited to 2.5%. According to an embodiment of the present invention, it may be 2.0% or less.

Chromium (Cr): 1.5% or less

[0041] Chromium (Cr) is a hardenability-increasing element and serves to suppress the formation of ferrite. Therefore, a small amount can be added as needed to secure an appropriate amount of retained austenite. According to an embodiment of the present invention, the chromium (Cr) content may be 0%. However, if the content is excessive, the amount of ferroalloy input may become excessive, causing an increase in cost. Therefore, the upper limit of the chromium (Cr) content can be limited to 1.5%. According to an embodiment of the present invention, it may be 1.0% or less.

Aluminum (Al): 0.005-0.100%

[0042] Aluminum (Al) is an element that contributes to the stabilization of retained austenite by suppressing the formation of carbides in ferrite, and to obtain this effect, it can be added at 0.005% or more. According to an embodiment of the present invention, it may be 0.010% or more. However, if the content exceeds 0.100%, it may be difficult to produce a sound slab due to its reaction with mold flux during casting. In addition, since it can form surface oxides and impair hot-dip galvanizing properties, the upper limit of the aluminum (Al) content can be limited to 0.100%. According to an embodiment of the present invention, it may be 0.080% or less.

Phosphorus (P): 0.10% or less

[0043] Phosphorus (P) is a solid-solution strengthening element, but if its content exceeds 0.10%, weldability deteriorates and the risk of steel embrittlement increases, so its upper limit can be limited to 0.10%.

Sulfur (S): 0.020% or less

[0044] Sulfur (S) is an impurity element that impairs the ductility and weldability of the steel sheet. Therefore, as the sulfur (S) content increases, the possibility of impairing the ductility and weldability of the steel sheet increases, so considering this, its upper limit can be limited to 0.020%.

Boron (B): 0.0050% or less

[0045] Boron (B) is an element that can be added to secure strength. However, if the content of boron (B) exceeds 0.0050%, it can become concentrated on the surface of the annealed material and significantly deteriorate the surface quality, so its content can be limited to 0.0050% or less.

[0046] The steel material of the present invention may include the remainder iron (Fe) and unavoidable impurities in addition to the above-described composition. Unavoidable impurities cannot be excluded as they may be unintentionally incorporated in a normal manufacturing process. Since these impurities are known to any person skilled in the art of ordinary steel manufacturing, all of their contents are not particularly mentioned in this specification.

[0047] A cold-rolled steel sheet according to an embodiment of the present invention may further include, by weight%, 1.2% or less of one or more selected from Ti, Mo, and Nb.

One or more of Titanium (Ti), Molybdenum (Mo), and Niobium (Nb): 1.2% or less

[0048] Titanium (Ti) can form nitrides to reduce the concentration of N in the steel. On the other hand, if excessively included, a decrease in the carbon concentration of martensite and a decrease in strength may occur due to carbide precipitation.

[0049] Molybdenum (Mo) can contribute to an improvement in strength. In particular, it has the effect of securing strength without deteriorating the wettability of molten metals such as zinc.

[0050] Niobium (Nb) can segregate in the form of carbides at austenite grain boundaries, suppressing the coarsening of austenite crystal grains during annealing heat treatment to increase strength, but an excessive input amount can cause an increase in cost.

[0051] Considering this, one or more of titanium (Ti), molybdenum (Mo), and niobium (Nb) can be included at 1.2% or less.

[0052] Hereinafter, the steel microstructure of the present invention will be described in detail.

[0053] In a cold-rolled steel sheet according to an embodiment of the present invention, the depth of an internal oxidation layer composed of oxides of one or more of Mn, Si, Cr, and B may be 3 to 15 μm from the surface of the steel sheet toward the center in the thickness direction.

[0054] Internal oxidation occurs simultaneously with an internal oxidation layer formed along grain boundaries and an internal oxidation layer formed within grains, but the depth of the internal oxidation layer according to an embodiment of the present invention can be based on the grain boundary internal oxidation layer.

[0055] If the depth of the internal oxidation layer is less than 3 μm , the amount of internal oxidation is insufficient, and the amount of surface oxides formed by diffusion to the surface is relatively large, which may lead to an insufficient effect of improving surface quality. According to an embodiment of the present invention, the depth of the internal oxidation layer may be 4 μm or more. According to an embodiment of the present invention, the depth of the internal oxidation layer may be 5 μm or more. On the other hand, if the depth of the internal oxidation layer exceeds 15 μm , the heat treatment time to form a deep internal oxidation layer becomes excessively long, which may lead to a problem of poor economic feasibility.

[0056] In a cold-rolled steel sheet according to an embodiment of the present invention, the depth of a decarburized layer may be 20 to 150 μm from the surface of the steel sheet toward the center in the thickness direction.

[0057] If the depth of the decarburized layer is less than 20 μm , the thickness of the soft layer may be insufficient, leading to an inadequate LME improvement effect. According to an embodiment of the present invention, it may be 30 μm or more. According to an embodiment of the present invention, it may be 35 μm or more. According to an embodiment of the present invention, it may be 40 μm or more. According to an embodiment of the present invention, it may be 50 μm or more. On the other hand, if the depth of the decarburized layer exceeds 150 μm , there may be a problem of a decrease in tensile strength due to an unnecessarily thick soft layer.

[0058] A cold-rolled steel sheet according to an embodiment of the present invention may have a Si surface enrichment of 0.0100 or less.

[0059] According to an embodiment of the present invention, the Si surface enrichment of the steel sheet may refer to the amount of surface Si oxides formed by the diffusion of Si from the inside of the steel to the surface and its combination with oxygen. In addition, according to an embodiment of the present invention, the Si surface enrichment may refer to the maximum Si enrichment in the region up to 0.1 μm from the surface of the steel sheet toward the center in the thickness direction.

[0060] If the Si surface enrichment exceeds 0.0100, the exposed Fe area on the steel sheet surface where the phosphate solution can react with the steel sheet is insufficient, making it difficult to secure excellent phosphate coverage. According to an embodiment of the present invention, the Si enrichment may be 0.0070 or less.

[0061] A cold-rolled steel sheet according to an embodiment of the present invention may have a phosphate coating coverage of 80% or more and a maximum LME crack length of 10 μm or less after being immersed in a phosphate treatment solution at 35°C for 40 seconds.

[0062] According to an embodiment of the present invention, the maximum LME crack length was evaluated in accordance with the SEP 1220-2 standard. The cold-rolled steel sheet of the present invention and a hot-dip galvanized steel sheet without a decarburized layer were overlapped and spot-welded. Subsequently, the welded cold-rolled steel sheet was sheared in the 0°, 45°, and 90° directions per specimen and observed with an OM (Optical Microscopy) to measure the LME crack length. At this time, only B-type cracks in the heat-affected zone were measured, and the maximum crack length was presented.

[0063] Hereinafter, the method for manufacturing the steel of the present invention will be described in detail.

[0064] A cold-rolled steel sheet according to an embodiment of the present invention can be manufactured by subjecting a cold-rolled steel sheet satisfying the above-mentioned alloy composition to a first annealing, a first pickling, a second annealing, and a second pickling.

Preparation of Cold-Rolled Steel Sheet

[0065] A cold-rolled steel sheet satisfying the alloy composition according to an embodiment of the present invention can be prepared. The method for manufacturing the cold-rolled steel sheet according to an embodiment of the present invention is not particularly limited and may be a conventional condition applicable in the same technical field.

First Annealing

[0066] The cold-rolled steel sheet can be subjected to a first annealing, which is maintained for 50 to 600 seconds at a temperature in the range of 600-900°C and a dew point temperature of -10 to 30°C.

[0067] According to an embodiment of the present invention, an internal oxidation layer and a decarburized layer can be effectively formed by performing the first annealing. During the first annealing, an internal oxidation layer composed of oxides of Si, Mn, Cr, B, etc., is formed to a certain depth or more from the steel sheet surface, thereby depleting the Si, Mn, Cr, B, etc., dissolved in the surface layer of the steel sheet.

[0068] During the first annealing, Si has a very high tendency to oxidize, so it can be oxidized internally, and the formation of surface oxides can be prevented. On the other hand, Mn, which has a relatively lower tendency to oxidize compared to Si, can form a large amount of surface oxides on the surface. These surface oxides caused by Mn can be removed through the first pickling performed after the first annealing.

[0069] Through the first annealing, an internal oxidation layer is formed, reducing Si oxides on the surface, and subsequently, by removing Mn oxides through pickling, the surface can be in a clean state. When the second annealing is performed on such a clean surface, the exposed Fe area on the surface increases during phosphate treatment, which can promote the phosphate reaction.

[0070] In addition, due to the cleaned surface after the first annealing, during the second annealing, the adsorption of oxygen in the atmosphere onto the steel sheet surface becomes easier, and the decarburization reaction, in which carbon in the steel diffuses to the surface and combines with the adsorbed oxygen, can be promoted. Through this, high phosphatability can be secured, and by forming a sufficient decarburized layer, LME (Liquid Metal Embrittlement)

can be reduced during welding.

[0071] During the first annealing, if the annealing temperature is less than 600°C, the diffusion of alloying elements such as Si and Mn to the grain boundaries of the surface layer to form an internal oxidation layer is not easy, and the diffusion of carbon to the surface for surface decarburization may also not be smooth. On the other hand, if the annealing temperature exceeds 900°C, internal oxidation and decarburization may occur, but at an excessively high temperature, the energy consumption for maintaining the high temperature is large, which is an uneconomical problem.

[0072] During the first annealing, if the dew point temperature is less than -10°C, the partial pressure of oxygen in the atmosphere is insufficient, which may make it difficult for oxygen to penetrate into the steel sheet. According to an embodiment of the present invention, it may be 0°C or higher. On the other hand, if the dew point temperature exceeds 30°C, there is a concern that the atmosphere may become one in which even iron is oxidized. According to an embodiment of the present invention, the dew point temperature can be limited to 20°C or less in order to more effectively internally oxidize Si without oxidizing iron.

[0073] During the first annealing, if the holding time is less than 50 seconds, it may be insufficient for the formation of the internal oxidation layer and the decarburized layer. On the other hand, if the holding time exceeds 600 seconds, the diffusible alloying elements in the surface layer have already completed their reaction, making it difficult to expect additional effects, and it may also be disadvantageous from an economic point of view.

[0074] According to an embodiment of the present invention, during the first annealing, the annealing atmosphere gas may be a nitrogen gas atmosphere containing 1-80 vol% of hydrogen. If the hydrogen content is less than 1 vol%, the steel sheet, which is iron, may be oxidized. On the other hand, if the hydrogen content exceeds 80 vol%, there is a risk of explosion in the event of a gas leak, and costs may increase.

[0075] According to an embodiment of the present invention, during the first annealing, a two-stage or more cooling process can be performed after holding to obtain the desired microstructure. During the first annealing, the cooling rate is not particularly limited and may be a condition applicable in the same technical field. According to an embodiment of the present invention, during the first annealing, cooling can be performed at a cooling rate of 1-100°C/s.

[0076] If the cooling rate is not high, gas cooling using a nitrogen gas containing a certain amount of hydrogen can be performed, and to increase the cooling rate, mist cooling, water quenching, or water jet cooling using water can be performed. When wet cooling with a large amount of water is performed, the steel sheet comes into direct contact with water, and the dew point temperature due to steam can rise rapidly, so an iron oxide film can be formed on the surface. In this case, the iron oxide film needs to be removed through pickling after cooling is completed.

[0077] Meanwhile, during cooling, the atmosphere may be a nitrogen gas atmosphere containing 1-80 vol% of hydrogen.

[0078] In addition, according to an embodiment of the present invention, during the first annealing, the heating rate may be 1-50°C/s.

First Pickling

[0079] The first-annealed cold-rolled steel sheet can be subjected to a first pickling.

[0080] According to an embodiment of the present invention, oxides formed on the surface of the steel sheet during the first annealing can be removed through the first pickling.

[0081] During the first pickling, the type of acid is not particularly limited, but according to an embodiment of the present invention, an acid solution of 3-20 wt% at 30-80°C can be used. According to an embodiment of the present invention, pickling can be performed using 5 wt% hydrochloric acid at 50-60°C. According to an embodiment of the present invention, when applying strong acid pickling, 18 wt% hydrochloric acid at 80°C can be used.

[0082] According to an embodiment of the present invention, metal plating can be additionally performed after the first pickling. According to an embodiment of the present invention, Fe, Ni, etc., can be plated by metal plating. By additionally performing the metal plating process, it can help prevent Si, Mn, etc., from diffusing to the surface during the second annealing. The metal plating conditions are not particularly limited and may be conditions applicable in the same technical field. According to an embodiment of the present invention, during Fe plating, the coating weight may be 0.1-3 g/m². According to an embodiment of the present invention, during Ni plating, the coating weight may be 5-700 mg/m². According to an embodiment of the present invention, during metal plating, a device on the exit side of the annealing line can be used.

Second Annealing

[0083] The first-pickled cold-rolled steel sheet can be subjected to a second annealing at a temperature in the range of 700-900°C and a dew point temperature of -60 to 30°C.

[0084] According to an embodiment of the present invention, the desired tensile properties can be secured by

performing the second annealing. During the second annealing, due to the internal oxidation layer formed during the first annealing process, the annealing can proceed in a state where a depleted layer, in which the solid solution state of Si, Mn, Cr, B, etc., is greatly reduced to a certain depth from the steel sheet surface, is formed. Due to this depleted layer, the surface oxides of Si, Mn, Cr, and B formed by diffusion to the steel sheet surface during the second annealing can be greatly suppressed.

[0085] That is, by performing the first annealing and the first pickling before the second annealing, the steel sheet after the second annealing can have a cleaner surface state. A clean steel sheet surface has a large exposed Fe area, which improves surface reactivity, thereby having the effect of improving phosphatability. The phosphatability improves as there are fewer oxides on the surface of the annealed steel sheet, because the phosphate solution can easily react with the Fe of the steel sheet. Although there are various surface oxides that adversely affect phosphatability, such as Mn, Si, Cr, and B, Mn and Si can be representative among them.

[0086] During the second annealing, if the annealing temperature is less than 700°C, it may be insufficient to obtain the desired microstructure. On the other hand, if the annealing temperature exceeds 900°C, the economic feasibility may decrease due to energy consumption.

[0087] During the second annealing, if the dew point temperature is less than -60°C, it is a very difficult problem in reality, considering the ability to maintain the atmosphere in large-scale production facilities. According to an embodiment of the present invention, the lower limit can be limited to -10°C in order to form a deeper internal oxidation layer and decarburized layer in addition to securing physical properties. According to an embodiment of the present invention, it may be 0°C or higher. On the other hand, if the dew point temperature exceeds 30°C, iron may be oxidized, and it may be difficult to secure an additional decarburized layer. According to an embodiment of the present invention, it may be 20°C or less.

[0088] According to an embodiment of the present invention, during the second annealing, the holding time may be 30 to 300 seconds.

[0089] According to an embodiment of the present invention, during the second annealing, the annealing atmosphere gas may be a nitrogen gas atmosphere containing 1-80 vol% of hydrogen. If the hydrogen content is less than 1 vol%, the steel sheet, which is iron, may be oxidized. On the other hand, if the hydrogen content exceeds 80 vol%, there is a risk of explosion in the event of a gas leak, and costs may increase.

[0090] During the second annealing, the cooling conditions are not particularly limited. According to an embodiment of the present invention, during the second annealing, slow cooling is performed down to 650°C after holding, and then rapid cooling can be performed according to the target physical properties. According to an embodiment of the present invention, the conditions during cooling are not particularly limited, but the conditions can be varied to achieve the target physical properties. In addition, since the formation of surface oxides, the internal oxidation layer, and the decarburized layer mostly occurs in a relatively high-temperature region, the cooling conditions are not particularly limited in the present invention.

[0091] Meanwhile, according to an embodiment of the present invention, during the second annealing, after holding, gas cooling and wet cooling using water can be performed in the same manner as during the first annealing.

[0092] According to an embodiment of the present invention, during cooling, a reducing atmosphere can be applied to at least the iron in order to prevent oxidation of the iron. To maintain the reducing atmosphere, a nitrogen gas atmosphere containing 1-80 vol% of hydrogen, the same as the atmosphere gas during the second annealing, can be applied.

[0093] Furthermore, according to an embodiment of the present invention, the rapidly cooled steel sheet can be reheated to a certain temperature for tempering and then cooled to room temperature, as needed.

Second Pickling

[0094] The second-annealed cold-rolled steel sheet can be subjected to a second pickling.

[0095] According to an embodiment of the present invention, surface oxides formed during the second annealing can be removed through the second pickling. According to an embodiment of the present invention, during the second pickling, pickling can be performed in the same manner as the first pickling.

[0096] During the second pickling, the type of acid is not particularly limited, but according to an embodiment of the present invention, an acid solution of 3-20 wt% at 30-80°C can be used. According to an embodiment of the present invention, pickling can be performed using 5 wt% hydrochloric acid at 50-60°C. According to an embodiment of the present invention, when applying strong acid pickling, 18 wt% hydrochloric acid at 80°C can be used.

[0097] According to an embodiment of the present invention, metal plating can be additionally performed after the second pickling. By additionally performing the metal plating process after the second pickling, it can help improve phosphatability by allowing the surface conditioner to be well adsorbed onto the steel sheet surface during the surface conditioning step of the phosphate treatment. After the second pickling, the metal plating conditions can be applied in the same manner as the metal plating process after the first pickling described above.

[0098] Hereinafter, the present invention will be described in more detail through examples. However, it should be noted that the following examples are only for illustrating the present invention in more detail and are not intended to limit the scope of the present invention.

(Example)

[0099] Cold-rolled steel sheets having the compositions shown in Table 1 below were prepared. Two types of steel sheets were subjected to a first annealing and a first pickling under the conditions shown in Table 2 below. During the first annealing, the atmosphere was a reducing atmosphere of nitrogen gas containing 5% hydrogen. In addition, during the first annealing, the temperature was raised to 800°C at a heating rate of 3°C/s and maintained for 150 seconds, and after subsequent cooling, a first pickling was performed by immersing in a 5 vol% hydrochloric acid solution at 50°C for 5 seconds.

[Table 1]

Steel Type	Alloy Composition (wt%)								
	C	Mn	Si	Cr	Al	P	S	Ti	B
A	0.20	2.4	1.0	-	0.030	0.01	0.002	0.02	0.0018
B	0.19	2.7	1.6	0.5	0.040	0.01	0.001	0.02	0.0020

[0100] In addition, Table 2 below shows the measured Si and Mn surface enrichments before and after the first pickling, following the first annealing, and also presents the analysis of the depths of the internal oxidation layer and the decarburized layer. The Si and Mn surface enrichments before and after pickling can be estimated as the amount of Si and Mn oxides remaining on the steel sheet surface. The Si and Mn surface enrichment is due to diffusion to the surface during annealing and combination with oxygen in the atmosphere, enriching the surface, and can be considered as the amount of oxidation.

[0101] Specific Si and Mn surface enrichments can be calculated by performing GDS analysis. In the GDS data, the main components of each steel element, Fe, Mn, Si, Cr, and B, are retained, and the data is processed so that the sum of the weight percentages of the main components becomes 100%. Here, Fe is included as it is the main component of the steel sheet, and oxygen is not included. In addition, components contained in the steel sheet other than the above components can be added and processed, but the components that are enriched on the surface during annealing are limited, and their amount is extremely small, so they were omitted.

[0102] FIG. 1 illustrates a method for calculating the Mn surface enrichment of a steel sheet according to an embodiment of the present invention. The Si surface enrichment can also be calculated by the same method described below. As shown in FIG. 1, a graph is drawn with the depth of the processed data on the x-axis and the weight% of each component on the y-axis. For each component, the depth is limited to 0.1 μm , and then the minimum point of the weight% of each component within 0.1 μm is found, and that value is estimated as the amount of the dissolved component. Once the amount of the dissolved component is found, the data at deeper depths is deleted based on that position. The amount of the dissolved component is subtracted from the weight% of each component from the surface to the position of the dissolved component amount. This process is to calculate by excluding the dissolved Mn or Si values in order to sort out only the oxides from the GDS data. After that, the integrated value from the surface to the position of the dissolved component value can be estimated as the enrichment amount using the data from which the dissolved component value has been subtracted. If the minimum weight% value of each component occurs at the outermost surface between depths of 0 and 0.01 μm , it can be interpreted that there is almost no surface enrichment of that component.

[0103] In addition, the depth of the internal oxidation layer in Table 2 was recorded by observing the cross-section of the annealed steel sheet at a magnification of 3000x with an SEM and recording the grain boundary internal oxidation depth. FIG. 2 is a cross-sectional SEM image of Inventive Example 1 according to an embodiment of the present invention, illustrating a method for measuring the depth of the internal oxidation layer. As shown in FIG. 2, an average value can be derived by randomly measuring three points in a 3000x magnification image.

[0104] The specific depth of the decarburized layer can be derived by analyzing the carbon content by depth using a GDS (Glow Discharge Spectrometer). There are two methods. The first is when a section where the carbon content graph appears horizontal is visible within the GDS measurable depth, which is the case when GDS analysis is possible beyond the depth of the decarburized layer to the bulk structure. The depth of the decarburized layer at this time is obtained as shown in FIG. 3. FIG. 3 illustrates a method for obtaining the depth of the decarburized layer of a steel sheet according to an embodiment of the present invention, and is a graph showing the carbon concentration according to the depth of the steel sheet during GDS (Glow Discharge Spectrometer) analysis. A graph is drawn with

the carbon content, and the average of the 10 carbon content data values at the deepest depth in the carbon content graph is calculated. This average value of the 10 carbon content data at the deepest depth is called the core value. Then, the depth indicating the first carbon content that drops by 5% or more from the core value among the carbon content data in the direction from the deepest position to the surface is found. This point is the deepest depth of the decarburized layer. The total depth of the decarburized layer of the cold-rolled steel sheet is from the surface to the deepest decarburization depth.

[0105] The second is when the depth of the decarburized layer is very deep and exceeds the GDS measurable range. In this case as well, the analysis is performed based on the 10 carbon content values at the deepest depth, just like the first case. Whether the carbon content at the deepest depth of the GDS data has reached the core value can be predicted by the OES (Optical Emission Spectrometry) analysis value. That is, if the analysis is performed to the deepest depth measurable by GDS, an analysis value of at least 50 μm depth or more is obtained. If the carbon content at the deepest depth is lower than the OES carbon content, it means that the core has not yet been reached, so it can be estimated that the depth of the decarburized layer is at least 50 μm or more. To know the approximate depth of the decarburized layer, cross-sectional microstructure observation is performed through nital etching (ethanol or methanol containing 2-5 vol% nitric acid). FIG. 4 is a cross-sectional SEM image of a steel sheet according to an embodiment of the present invention, illustrating a method for obtaining the depth of the decarburized layer of a nital-etched steel sheet. As shown in FIG. 4, it can be observed with an SEM, and the magnification can be from 1000x to 3000x. The decarburized structure of the surface layer shows coarse grains mainly of ferrite, and the core (Bulk) structure shows a fine microstructure including austenite. The depth composed mainly of the coarse decarburized structure can be regarded as the depth of the decarburized layer.

[Table 2]

Specimen No.	Steel Type	1st Annealing	after 1st Annealing		after 1st Annealing & 1st Pickling			
		Dew Point Temp. ($^{\circ}\text{C}$)	Si Surface Enrichment	Mn Surface Enrichment	Si Surface Enrichment	Mn Surface Enrichment	Internal Oxidation Layer Depth (μm)	Decarburized Layer Depth (μm)
1	A	-40	0.208	0.339	0.0672	0.0082	0	7
2	A	5	0.016	0.212	0.0052	0.0048	4.4	14
3	B	-40	0.211	0.422	0.0698	0.0095	0	4
4	B	5	0.013	0.255	0.0044	0.0052	3.8	17

[0106] Specimen Nos. 1 and 3 in Table 2 are cases where the dew point temperature is -40°C , which does not satisfy the conditions of the present invention, while Specimen Nos. 2 and 4 are cases where the dew point temperature satisfies the conditions of the present invention. It can be confirmed that the Si and Mn surface enrichments of Specimen Nos. 2 and 4 are significantly reduced compared to Specimen Nos. 1 and 3.

[0107] Meanwhile, looking at the results after pickling, it can be confirmed that the Si surface enrichment of Specimen Nos. 1 and 3 is lower than before pickling. However, in the case of Specimen Nos. 2 and 4, since a small amount was enriched due to internal oxidation even before pickling, it can be confirmed that the value is much lower after pickling compared to Specimen Nos. 1 and 3.

[0108] The surface enrichment of Mn also decreased, but its reduction ratio is smaller than that of the Si surface enrichment. The surface enrichment of Mn after pickling was significantly reduced in all cases compared to before pickling. This is because Mn oxides are easily dissolved by pickling. Before pickling, in the case of Specimen Nos. 2 and 4, where the dew point temperature satisfied the conditions of the present invention, the Mn surface enrichment was lower than that of Specimen Nos. 1 and 3 because an internal oxidation layer was formed, and this tendency is shown to be the same even after pickling.

[0109] In the case of Specimen Nos. 1 and 3, an internal oxidation layer was not formed, and it can be confirmed that a decarburized layer was also hardly formed, being 7 μm or less.

[0110] In the case of Specimen Nos. 2 and 4, Si, which has a high tendency to oxidize, could not diffuse to the surface and instead combined with oxygen that penetrated into the steel sheet due to the high dew point temperature in the high-temperature atmosphere, forming an internal oxidation layer. Therefore, it can be confirmed that the Si surface enrichment is higher in the case of Specimen Nos. 1 and 3 than in Specimen Nos. 2 and 4.

[0111] In the case of Specimen Nos. 1 and 3, if Si and Mn do not form an internal oxidation layer and diffuse to the

surface to form surface oxides, it is difficult to remove the Si surface oxides even if pickling is performed later. It can be confirmed that Mn, which is easily dissolved in hydrochloric acid compared to Si, is removed after pickling. However, if the second annealing is performed with a large amount of Si oxides formed on the surface, the Si surface oxides will hinder the adsorption of oxygen from the atmosphere onto the steel sheet and its diffusion into the interior, and it will also be disadvantageous for the decarburization reaction in which carbon inside the steel sheet diffuses to the surface and combines with the adsorbed oxygen.

[0112] In addition, using the cold-rolled steel sheets having the compositions of Table 1, a first annealing, a first pickling, a second annealing, and a second pickling were performed under the conditions shown in Table 3 below. At this time, during the first annealing, the atmosphere was a reducing atmosphere of nitrogen gas containing 5% hydrogen. In addition, during the first annealing, the temperature was raised to 800°C at a heating rate of 3°C/s and maintained for 150 seconds, and after subsequent cooling, a first pickling was performed by immersing in a 5 vol% hydrochloric acid solution at 50°C for 5 seconds. Subsequently, during the second annealing, the atmosphere was a reducing atmosphere of nitrogen gas containing 5% hydrogen, and during the second annealing, the temperature was raised to 810°C at a heating rate of 3.2°C/s, maintained for 50 seconds, and then cooled. During cooling, a first cooling was performed at 3.1°C/s down to 650°C, followed by a second cooling at 20°C/s down to 350°C. After the second cooling, a final cooling was performed at 2°C/s down to room temperature to produce an annealed steel sheet. The final annealed steel sheet was subjected to a second pickling by immersing it in a 5 vol% hydrochloric acid solution at 50°C for 5 seconds.

[0113] For the manufactured steel sheets, the Si and Mn surface enrichments and the depths of the internal oxidation layer and decarburized layer were measured by the method described above and are shown in Table 3 below.

[0114] In addition, to evaluate the phosphatability, the phosphate coating coverage was measured and is shown in Table 3 below. The steel sheets for which the second pickling was completed underwent the steps of degreasing, surface conditioning, and phosphate treatment in order to carry out the phosphate treatment. Degreasing was performed using an alkaline degreasing agent at 45°C for 120 seconds, and surface conditioning was performed at room temperature for 30 seconds. After that, a coating was formed by immersing in a phosphate treatment solution at 35°C for 40 seconds.

[0115] Meanwhile, the phosphate treatment according to an embodiment of the present invention is a method for relative evaluation between specimens and does not coincide with that used by automobile manufacturers, but the tendency is not significantly different even if evaluated with other solutions and methods.

[0116] The measured values of the phosphate coating coverage in Table 3 below were obtained by performing a phosphate treatment, observing at a magnification of 500x with an SEM, and recording the coverage of the phosphate coating through image analysis. Here, coverage is the area ratio of the phosphate coating covering the surface of the steel sheet.

[0117] In addition, an LME resistance evaluation was performed, and the results are shown in Table 3 below. The LME evaluation was performed in accordance with the SEP 1220-2 standard, and the manufactured cold-rolled steel sheet and a hot-dip galvanized steel sheet without a decarburized layer were overlapped and spot-welded. The LME crack length was measured by shearing the welded cold-rolled steel sheet in the 0°, 45°, and 90° directions per specimen and observing it with an OM (Optical Microscopy). Only B-type cracks in the heat-affected zone were measured, and the results were indicated by ○, △, and × according to the maximum crack length.

- : Maximum LME crack length of 10 μm or less
- △: Maximum LME crack length over 10 μm and 30 μm or less
- ×: Maximum LME crack length over 30 μm

[Table 3]

Specimen No.	Steel Type	1st Annealing		2nd Annealing	after 2nd Annealing & 2nd Pickling				Phosphate Coating Coverage (%)	LME Evaluation	Classification
		Dew Point Temp. (°C)	Dew Point Temp. (°C)		Si Surface Enrichment	Mn Surface Enrichment	Internal Oxidation Layer Depth (μm)	Decarburized Layer Depth (μm)			
1	A	Not performed	-40	-40	0.0586	0.0011	0	5	38	×	Comparative Ex. 1
2	A	Not performed	5	5	0.0107	0.0068	2.6	18	63	Δ	Comparative Ex. 2
3	A	-40	-40	-40	0.0854	0.0072	0	2	< 35	×	Comparative Ex. 3
4	A	-40	5	5	0.0710	0.0066	2.3	16	50	Δ	Comparative Ex. 4
5	A	5	-40	-40	0.0050	0.0032	4.4	25	82	o	Inventive Ex. 1
6	A	5	5	5	0.0013	0.0024	6.2	55	88	o	Inventive Ex. 2
7	B	Not performed	-40	-40	0.0624	0.0007	0	4	< 35	×	Comparative Ex. 5
8	B	Not performed	5	5	0.0118	0.0071	2.8	15	58	Δ	Comparative Ex. 6
9	B	-40	-40	-40	0.1044	0.0097	0	5	< 35	×	Comparative Ex. 7
10	B	-40	5	5	0.0767	0.0058	2.1	14	47	Δ	Comparative Ex. 8
11	B	5	-40	-40	0.0053	0.0073	3.8	48	81	o	Inventive Ex. 3
12	B	5	5	5	0.0020	0.0018	6.7	73	85	o	Inventive Ex. 4

[0118] As shown in Table 3, the inventive examples that satisfy the alloy composition and manufacturing method proposed in the present invention have secured all the desired properties.

[0119] In particular, Inventive Examples 1 and 2 are examples in which internal oxidation was performed during the first annealing while performing two annealing cycles. In Inventive Example 1, although internal oxidation was not performed during the second annealing, an internal oxidation layer was formed to a certain depth or more, and the phosphate coating coverage property was also excellent. This is the result of forming a sufficient level of a depleted layer of Mn and Si by performing internal oxidation during the first annealing, and then performing the second annealing in a clean state where the Mn surface oxides formed on the surface were removed by pickling after annealing. If the surface of the steel sheet after the first annealing is clean, there are almost no oxides on the steel sheet surface during the second annealing. Even if internal oxidation is not performed during the second annealing, the amount of Si and Mn that diffuses to the surface can be limited due to the already existing depleted layer. As a result, the Si surface enrichment of the final surface is at a very low level. Inventive Example 2 shows a cleaner surface state by performing internal oxidation even during the second annealing. This is because a clean steel sheet surface with almost no surface oxides after the first annealing and first pickling allows oxygen to penetrate more easily and deeply into the steel sheet during the second annealing, so there are almost no alloying elements that diffuse to the surface during the second annealing.

[0120] Inventive Examples 3 and 4 also show a similar tendency to Inventive Examples 1 and 2.

[0121] On the other hand, Comparative Examples 1 and 2 are examples in which only the second annealing was performed without performing the first annealing. In Comparative Example 1, no internal oxidation layer was observed, and the phosphate coating coverage was also very poor. The Si surface enrichment is relatively high, which means that a large amount of Si oxides are formed on the surface. In addition, the depth of the decarburized layer was also observed to be shallow. In Comparative Example 2, an internal oxidation layer was formed with a depth of 2.6 μm , so surface oxidation was suppressed to a certain level, and it can be seen that the phosphate coating coverage was also improved. In addition, a decarburized layer was also formed with a thickness of 18 μm , but this is not a sufficient level to expect an LME improvement effect.

[0122] Comparative Examples 3 and 4 were subjected to first and second annealing, but are examples in which internal oxidation was not performed during the first annealing. In Comparative Example 3, a large amount of surface oxides were formed during the first annealing, and although the Mn surface oxides were removed through pickling, the Si surface oxides remained as they were. As the second annealing proceeded in this state, more surface oxides accumulated, resulting in very poor phosphate coating coverage. In Comparative Example 4, a large amount of surface oxides were formed during the first annealing, and Si surface oxides remained after pickling. However, as internal oxidation occurred during the second annealing, the additional surface oxides from the second annealing were relatively reduced. However, the level of phosphate coating coverage targeted in the present invention was not secured.

[0123] Comparative Example 2, Comparative Example 4, and Inventive Example 1 are all cases where internal oxidation was performed once. Meanwhile, the first annealing of the present invention for causing internal oxidation has a longer holding time than the second annealing, and the formation of the internal oxidation layer and the decarburized layer is dominated by the time maintained at a high temperature. Therefore, the depths of the internal oxidation layer and the decarburized layer of Inventive Example 1, in which internal oxidation was performed in the first annealing, were relatively deeper than those of Comparative Example 2 and Comparative Example 4, in which internal oxidation was performed in the second annealing.

[0124] Comparative Examples 5 to 8 also show a similar tendency to Comparative Examples 1 to 4.

[0125] Although the present invention has been described in detail through the examples above, other forms of embodiments are also possible. Therefore, the technical spirit and scope of the claims described below are not limited to the examples.

Claims

1. A cold-rolled steel sheet, comprising:

by weight%, C: 0.10 to 0.25%, Mn: 1.5 to 5.0%, Si: 0.5 to 2.5%, Cr: 1.5% or less, Al: 0.005 to 0.100%, P: 0.10% or less, S: 0.020% or less, and B: 0.0050% or less, with a remainder being Fe and other unavoidable impurities,
wherein a Si surface enrichment is 0.0100 or less.

2. The cold-rolled steel sheet of claim 1,

wherein the cold-rolled steel sheet further comprises, by weight%, 1.2% or less of one or more selected from the

group consisting of Ti, Mo, and Nb.

3. The cold-rolled steel sheet of claim 1,
wherein a depth of an internal oxidation layer, which is composed of one or more oxides selected from the group
consisting of Mn, Si, Cr, and B, is 3 to 15 μm from a surface of the steel sheet toward a center in a thickness
direction.

4. The cold-rolled steel sheet of claim 1,
wherein a depth of a decarburized layer is 20 to 150 μm from a surface of the steel sheet toward a center in a
thickness direction.

5. The cold-rolled steel sheet of claim 1,
wherein the cold-rolled steel sheet has a phosphate coating coverage of 80% or more after being immersed in a
phosphate treatment solution at 35°C for 40 seconds.

6. The cold-rolled steel sheet of claim 1,
wherein the cold-rolled steel sheet has a maximum LME crack length of 10 μm or less.

7. A method for manufacturing a cold-rolled steel sheet, the method comprising:

preparing a cold-rolled steel sheet comprising, by weight%, C: 0.10 to 0.25%, Mn: 1.5 to 5.0%, Si: 0.5 to
2.5%, Cr: 1.5% or less, Al: 0.005 to 0.100%, P: 0.10% or less, S: 0.020% or less, and B: 0.0050% or less, with
a remainder being Fe and other unavoidable impurities;
performing a first annealing on the cold-rolled steel sheet at a temperature in a range of 600 to 900°C and a
dew point temperature of -10 to 30°C;
performing a first pickling on the first-annealed cold-rolled steel sheet;
performing a second annealing on the first-pickled cold-rolled steel sheet at a temperature in a range of 700 to
900°C; and
performing a second pickling on the second-annealed cold-rolled steel sheet.

8. The method of claim 7,
wherein the cold-rolled steel sheet further comprises, by weight%, 1.2% or less of one or more selected from the
group consisting of Ti, Mo, and Nb.

9. The method of claim 7,

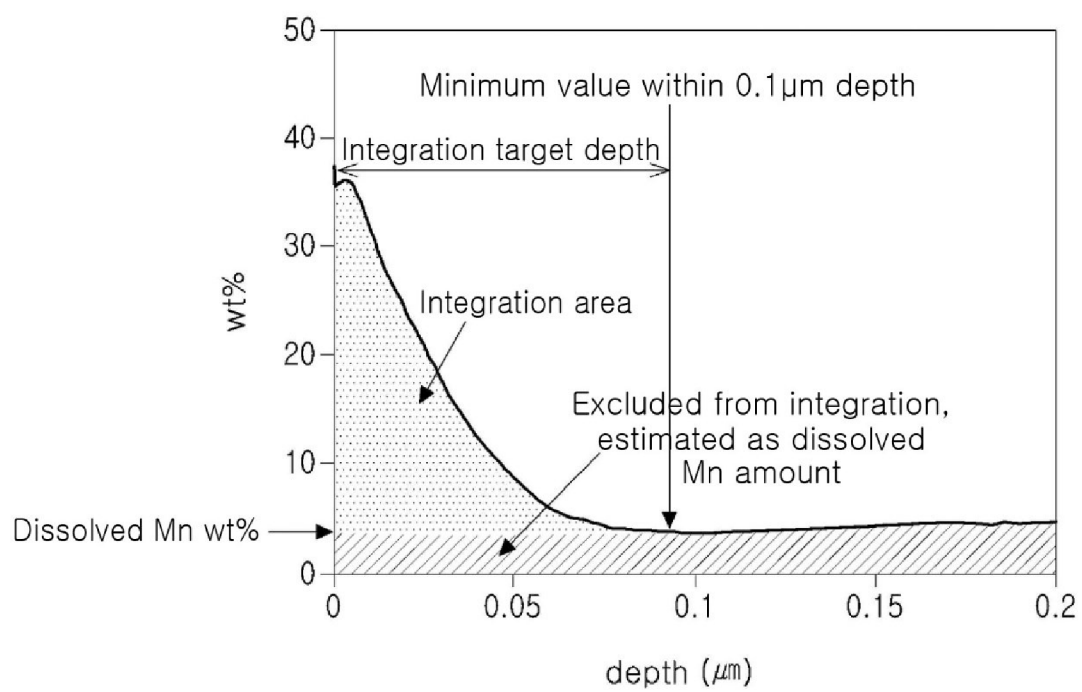
wherein the first annealing step is maintained for 50 to 600 seconds, and
the second annealing step is performed at a dew point temperature of -60 to 30°C.

10. The method of claim 7,
wherein the first annealing step and the second annealing step are performed in a nitrogen gas atmosphere
comprising 1 to 80 vol% of hydrogen.

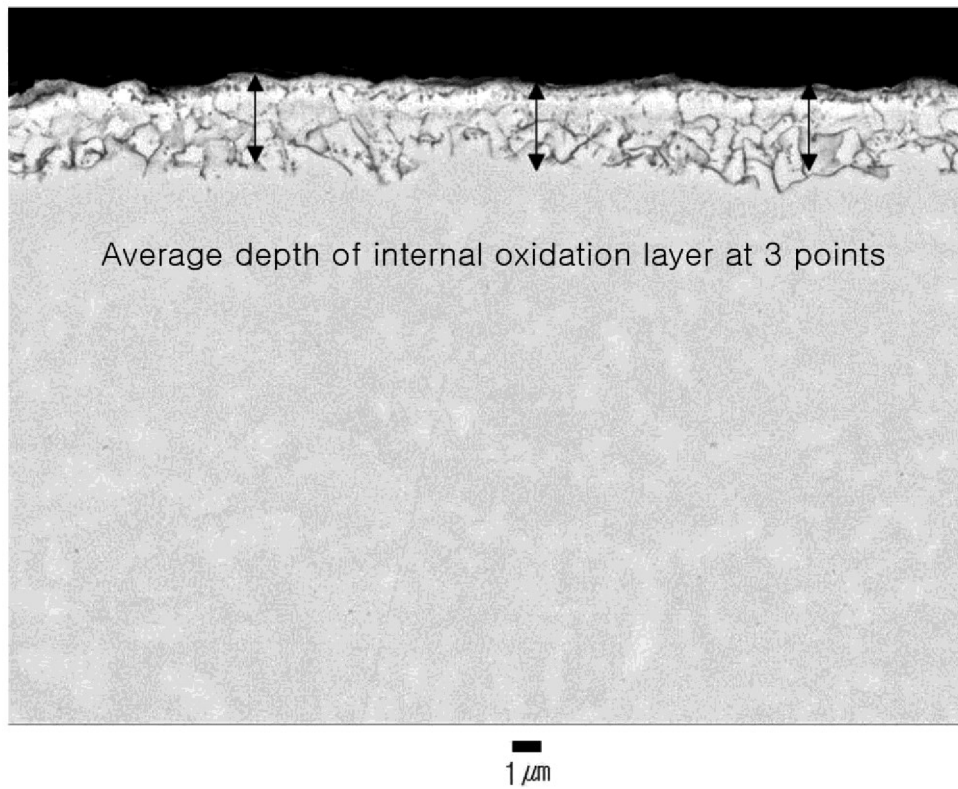
11. The method of claim 7,
further comprising a step of performing metal plating after either the first pickling step or the second pickling step.

12. The method of claim 11,
wherein the metal plating step is Fe plating or Ni plating.

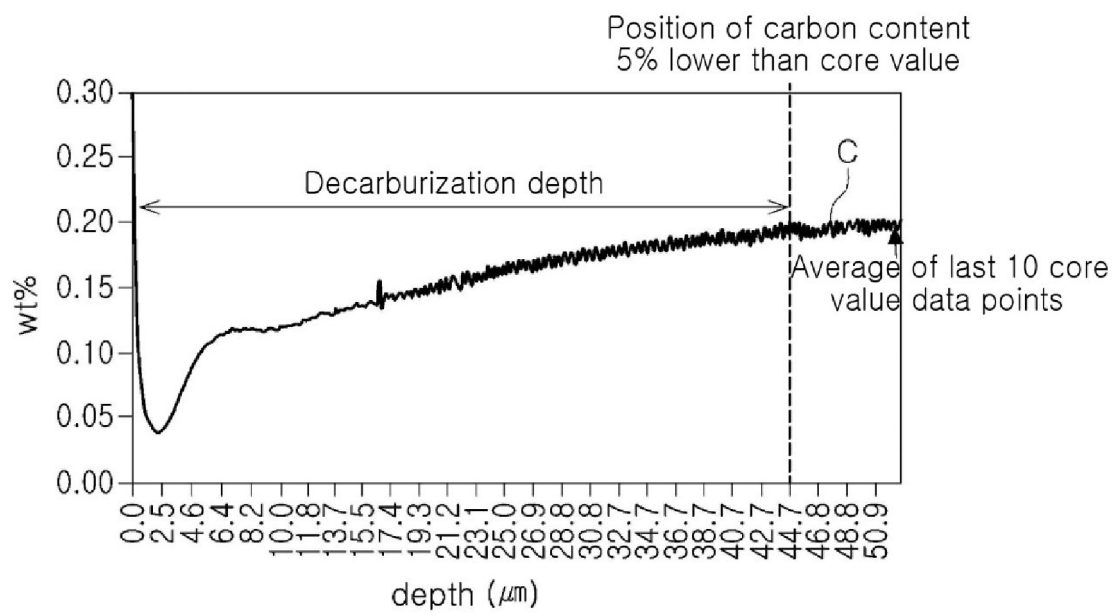
[FIG. 1]



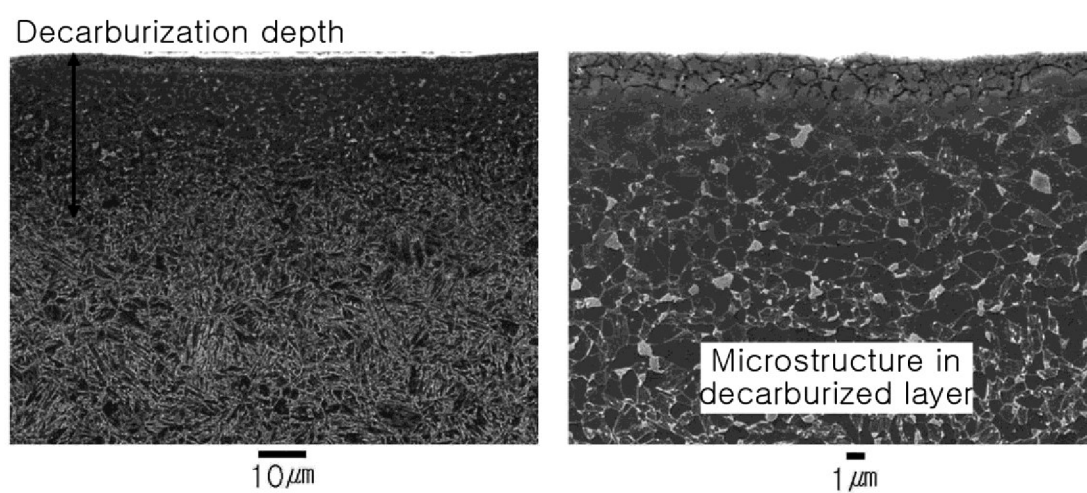
[FIG. 2]



[FIG. 3]



[FIG. 4]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2024/020354

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/38(2006.01)i; C22C 38/34(2006.01)i; C22C 38/06(2006.01)i; C22C 38/32(2006.01)i; C22C 38/28(2006.01)i;
C22C 38/22(2006.01)i; C23C 22/07(2006.01)i; C21D 8/04(2006.01)i; C23G 1/08(2006.01)i; C23C 2/04(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)

C22C 38/38(2006.01); C21D 1/26(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01);
C22C 38/06(2006.01); C22C 38/14(2006.01); C23C 2/28(2006.01); C25D 3/12(2006.01)

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

Korean utility models and applications for utility models: IPC as above

Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & keywords: 탈탄층(decarburized layer), LME(liquid metal embrittlement), Si 농화량(silicon
enrichment), 이슬점 온도(dew point temperature), 소둔(annealing), 산세(pickling), 산화물(oxide), 산화층(oxide layer)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2017-0071658 A (POSCO) 26 June 2017 (2017-06-26) See paragraphs [0067] and [0088]-[0103], claims 1-6 and tables 2 and 3.	1-12
Y	KR 10-2018-0070940 A (POSCO) 27 June 2018 (2018-06-27) See claim 6.	1-12
Y	KR 10-2019-0077987 A (POSCO) 04 July 2019 (2019-07-04) See claim 1.	11-12
A	JP 2019-531408 A (BAOSHAN IRON & STEEL CO., LTD.) 31 October 2019 (2019-10-31) See paragraph [0056] and claims 1 and 7-9.	1-12
A	KR 10-2020-0069328 A (ARCELORMITTAL) 16 June 2020 (2020-06-16) See claims 1-13.	1-12

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

18 March 2025

Date of mailing of the international search report

18 March 2025

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2024/020354

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