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(54) STEEL SHEET FOR ENAMELING, AND MANUFACTURING METHOD THEREFOR

(57) An enamel steel sheet according to an embodiment of the present invention comprises, in weight %, 0.01 to 0.05% of C, 0.10 to 0.80% of Mn, 0.001 to 0.03% of Si, 0.01 to 0.08% of Al, 0.001 to 0.02% of P, 0.001 to 0.02% of S, 0.005% or less of N (excluding 0%), and 0.003% or less of O (excluding 0%), with the balance being Fe and unavoidable impurities, and satisfies the following Formula 1.

[Formula 1]

$$CVF[50\mu m] / CVF[center] \leq 0.5$$

(In Formula 1, CVF[50 μm] represents the area fraction of cementite (%) at a position 50 μm inside the steel sheet in the thickness direction from the steel sheet surface, and CVF[center] represents the area fraction of cementite (%) at the 1/2 thickness position of the steel sheet).

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Description

[Technical Field]

[0001] An embodiment of the present invention relates to an enamel steel sheet and a manufacturing method thereof. More specifically, an embodiment of the present invention relates to a steel sheet for enameling with excellent fishscale resistance and a manufacturing method thereof.

[Background Art]

[0002] Enamel steel sheets are used as various industrial materials, such as kitchenware, home appliances, boilers, tanks, agricultural silos, and construction panels. For products where formability and surface appearance are important, such as household kitchen sinks or ovens, ultra-low carbon steel is utilized; for applications where mechanical strength or thermal stability is important, such as boilers, high-strength enamel steel sheets are required.

[0003] The enameled steel sheet is produced by a vitreous coating strongly bonding to the surface of a cold-rolled steel sheet, whereby hardness, scratch resistance, acid corrosion resistance, high-temperature resistance, a high-gloss appearance, and color may be imparted. In the enameling firing process (firing) that forms the vitreous material on the surface, the molten vitreous coating forms an alloy layer at the rough interface of the steel sheet and bonds strongly thereto.

[0004] In addition to excellent adhesion between the vitreous material and the steel sheet, the enamel steel sheet must have a high hydrogen occlusion capacity. Fish scale (fishscale) defects, which are surface defects that cause the enamel layer to detach in a fish-scale shape as hydrogen is picked up during the enameling firing process, significantly degrade the value of the enamel product, causing issues such as concentrated rust (rust) in the surrounding area, and thus it is necessary to prevent their occurrence. The origin of hydrogen in fishscale defects is water molecules contained in the enamel glaze. Water reacts with the steel surface to form hydrogen ions, which dissolve into the steel during the firing process. The fishscale defect occurs because the hydrogen solubility of austenite is higher than the hydrogen solubility in ferrite, and because the hydrogen solubility in ferrite is extremely low at low temperatures. The high diffusivity of hydrogen causes it to diffuse to the vitreous/steel sheet interface and form H_2 bubbles even at low temperatures such as room temperature. As these bubbles burst, they form fish-scale-shaped defects.

[0005] To prevent the fishscale defect, it is necessary to form a large number of sites inside the steel that may trap the solute hydrogen in the steel. Accordingly, in order to prevent the fishscale defect that degrades the enameling property and to secure workability, the open coil annealing (OCA, Open Coil Annealing) method, which is a type of batch annealing (BAF, Batch Annealing Furnace) method, is sometimes applied. However, in this case, the heat treatment process takes several days, which leads to problems such as decreased productivity due to prolonged heat treatment, increased manufacturing costs, and significant quality deviations within the coil.

[0006] However, the use of the continuous annealing process, which is the latest technology, overcomes these problems of productivity disadvantages and manufacturing cost increases. Enamel steel produced by the continuous annealing method is based on ultra-low carbon steel and mainly utilizes precipitates, such as titanium (Ti), or inclusions formed by a non-deoxidation method as a hydrogen occlusion source. However, even in this case, various problems occur, such as an increase in cost and a decrease in sheet passability due to the addition of a large amount of carbonitride forming elements, or an increase in the occurrence rate of surface defects caused by precipitates and non-deoxidation products.

[0007] In particular, when titanium-based precipitates are used as a hydrogen occlusion source, problems such as nozzle clogging due to titanium nitride and inclusions can occur. In addition, TiN incorporated into the molten steel exists at an upper portion of the steel sheet, causing blister defects, which are representative bubble defects. Furthermore, a large amount of added titanium forms a titanium-based oxide layer, which acts as a factor hindering the adhesion between the steel sheet and the enamel layer.

[0008] On the other hand, as a representative method, a high oxygen enamel steel sheet is produced by a method of improving fishscale resistance, which comprises increasing the dissolved oxygen content within the steel sheet and occluding hydrogen by utilizing inclusions such as oxides in the steel.

[0009] However, the high oxygen enamel steel sheet also suffers from fundamental problems, such as severe refractory erosion due to high oxygen content, which not only significantly reduces continuous casting productivity in the steelmaking process but also leads to frequent surface defects.

[Disclosure]

[**Technical Problem**]

[0010] One embodiment of the present invention provides an enamel steel sheet and a manufacturing method thereof. More specifically, one embodiment of the present invention provides a steel sheet for enameling with excellent fishscale resistance and a manufacturing method thereof.

[**Technical Solution**]

[0011] An enamel steel sheet according to an embodiment of the present invention comprises, in weight %, C: 0.01 to 0.05%, Mn: 0.10 to 0.80%, Si: 0.001 to 0.03%, Al: 0.01 to 0.08%, P: 0.001 to 0.02%, S: 0.001 to 0.02%, N: 0.005% or less (excluding 0%), and O: 0.003% or less (excluding 0%), and a balance of Fe and unavoidable impurities, and satisfies Formula 1 below.

[Formula 1]

$$CVF[50\ \mu m]/CVF[center] \leq 0.5$$

(In Formula 1, CVF[50 μm] represents an area fraction of cementite (%) at a position 50 μm from the steel sheet surface in a thickness direction, and CVF[center] represents an area fraction of cementite (%) at a 1/2 thickness position of the steel sheet.)

[0012] The enamel steel sheet according to an embodiment of the present invention may satisfy Formula 2 below.

[Formula 2]

$$Hv[50\ \mu m]/Hv[center] \leq 0.75$$

(In Formula 2, Hv[50 μm] represents the hardness at a position 50 μm inside the steel sheet in the thickness direction from the steel sheet surface, and Hv[center] represents the hardness at the 1/2 position of the steel sheet thickness.)

[0013] The enamel steel sheet according to an embodiment of the present invention may further comprise one or more of Cu: 0.1 weight % or less, Ti: 0.003 weight % or less, Co: 0.005 weight % or less, Nb: 0.003 weight % or less, Ni: 0.01 weight % or less, V: 0.003 weight % or less, and Mo: 0.01 weight % or less.

[0014] The enamel steel sheet according to an embodiment of the present invention may have a hydrogen permeation ratio of 650 seconds/mm^2 or more.

[0015] A manufacturing method of an enamel steel sheet according to an embodiment of the present invention comprises the steps of: manufacturing a hot-rolled steel sheet by hot rolling a slab comprising, in weight %, C: 0.01 to 0.05%, Mn: 0.10 to 0.80%, Si: 0.001 to 0.03%, Al: 0.01 to 0.08%, P: 0.001 to 0.02%, S: 0.001 to 0.02%, N: 0.005% or less (excluding 0%), and O: 0.003% or less (excluding 0%); manufacturing a cold-rolled steel sheet by cold rolling the hot-rolled steel sheet; and annealing the cold-rolled steel sheet.

[0016] The annealing step comprises a heating step and a soaking step, wherein the heating step includes heating the steel sheet from 100°C to a soaking temperature, and the heating step is performed at a dew point temperature of 10 to 23°C, and the soaking step is performed at a dew point temperature of 0 to 13°C.

[0017] In the step of manufacturing the hot-rolled steel sheet, a finish hot rolling temperature may be 800 to 1000°C.

[0018] In the step of manufacturing the hot-rolled steel sheet, a coiling temperature may be 450 to 700°C.

[0019] In the step of manufacturing the cold-rolled steel sheet, a reduction ratio may be 60 to 90%.

[0020] The soaking temperature may be 700 to 850°C.

[0021] The heating step and the soaking step may be performed in an atmosphere of 3 to 20 vol% of hydrogen and the balance of nitrogen.

[0022] A dew point temperature difference of the atmosphere in the heating step and the soaking step may be 3 to 15°C.

[0023] After the annealing step, the method may further comprise a step of skin pass rolling the steel sheet at a reduction ratio of 0.5 to 3%.

[**Advantageous Effects**]

[0024] The steel sheet for enameling with excellent fishscale resistance according to an embodiment of the present

invention may be used as various industrial materials such as kitchenware, home appliances, boilers, tanks, agricultural silos, and construction panels.

[**Mode for Invention**]

[0025] In the present specification, terms such as first, second, and third are used to describe various parts, components, regions, layers, and/or sections, but are not limited thereto. These terms are used only to distinguish one part, component, region, layer, or section from another part, component, region, layer, or section. Accordingly, a first part, component, region, layer, or section described below may be referred to as a second part, component, region, layer, or section without departing from the scope of the present invention.

[0026] In the present specification, when a part is said to "comprise" a certain element, it means that it may further include other elements rather than excluding other elements, unless specifically stated otherwise.

[0027] In the present specification, the terminology used is only for referring to specific embodiments and is not intended to limit the present invention. Singular forms used herein include plural forms as well, unless the phrases clearly indicate the opposite meaning. The meaning of "comprising" used in the specification specifies a specific characteristic, region, integer, step, operation, element, and/or component, and does not exclude the presence or addition of other characteristics, regions, integers, steps, operations, elements, and/or components.

[0028] In the present specification, the term "combination thereof" in a Markush-type expression refers to a mixture or combination of one or more selected from the group consisting of the components described in the Markush-type expression, and signifies the inclusion of one or more selected from the group consisting of the components.

[0029] In the present specification, when a part is referred to as being "on" or "above" another part, it may be directly on or above the other part, or an intervening part may be present therebetween. In contrast, when a part is referred to as being "directly on" or "directly above" another part, no intervening part is present therebetween.

[0030] Unless defined otherwise, all terms, including technical and scientific terms, used herein have the same meaning as commonly understood by a person of ordinary skill in the art to which this invention belongs. Terms defined in commonly used dictionaries are interpreted as having meanings consistent with the related technical literature and the content disclosed herein, and such terms are not to be interpreted in an ideal or overly formal sense unless explicitly defined as such.

[0031] In addition, unless specifically mentioned, % means weight %, and 1 ppm is 0.0001 weight %.

[0032] In an embodiment of the present invention, 'further including an additional element' means that the balance Fe is replaced by an amount of the additional element equivalent to the added amount thereof.

[0033] Hereinafter, embodiments of the present invention will be described in detail so that those skilled in the art to which the present invention pertains may easily implement them. However, the present invention may be implemented in various different forms and is not limited to the embodiments described herein.

[0034] An enamel steel sheet according to an embodiment of the present invention comprises, in weight %, 0.01 to 0.05% of C, 0.10 to 0.80% of Mn, 0.001 to 0.03% of Si, 0.01 to 0.08% of Al, 0.001 to 0.02% of P, 0.001 to 0.02% of S, 0.005% or less of N (excluding 0%), and 0.003% or less of O (excluding 0%), and a balance of Fe and unavoidable impurities.

[0035] First, the reason for limiting the components of the steel sheet will be explained.

C: 0.010 to 0.050 weight %

[0036] If carbon (C) is added in an excessive amount, the amount of solute carbon in the steel increases, increasing the strength, but it hinders texture development during annealing, thereby deteriorating formability and potentially causing bubble defects due to bubbling of the enamel layer. On the other hand, if C is added in an insufficient amount, the structure grows, making it impossible to secure the target yield strength after firing, and the fraction of precipitates acting as a hydrogen occlusion source decreases, making the steel vulnerable to fishscale defects. More specifically, C may be included in an amount of 0.013 to 0.045 weight %.

Mn: 0.100 to 0.800 weight %

[0037] Manganese (Mn) is a representative solid solution strengthening element, which prevents hot shortness and promotes the precipitation of carbides by precipitating sulfur dissolved in the steel in the form of manganese sulfide (MnS). If Mn is added in an insufficient amount, it is difficult to sufficiently obtain the aforementioned effects. On the other hand, if the Mn content is excessive, a center segregation part in the thickness direction is significantly developed during the casting of a steel slab in a continuous casting process, which may worsen formability and lower the Ar3 transformation temperature, causing a problem where transformation occurs during enameling firing, leading to deformation. More specifically, Mn may be included in an amount of 0.150 to 0.770 weight %.

Si: 0.001 to 0.030 weight %

[0038] Silicon (Si) is an element that promotes the formation of carbides that act as a hydrogen occlusion source. If an insufficient amount of Si is added, it is difficult to sufficiently obtain the aforementioned effects. On the other hand, if an excessive amount of Si is added, an oxide film may be formed on the steel sheet surface, which may cause a problem of reducing enamel adhesion. More specifically, Si may be included in an amount of 0.002 to 0.025 weight %.

Al: 0.010 to 0.0800 weight %

[0039] Aluminum (Al) is an element added for the deoxidation of molten steel. If too little Al is added, it is difficult to manufacture killed steel in a stable state. Conversely, if too much Al is added, while advantageous for increasing strength through grain refinement, it not only causes a problem of nozzle clogging due to the excessive formation of inclusions during steelmaking and continuous casting, but may also cause a problem of bubble defects, such as blisters, in the enameling process. More specifically, it may be included in an amount of 0.011 to 0.060 weight %.

P: 0.001 to 0.020 weight %

[0040] Phosphorus (P) is a substitutional element having the most excellent solid solution strengthening effect, and is the most effective element for ensuring yield strength without significantly reducing ductility. If P is added in an excessively small amount, it is difficult to sufficiently obtain the aforementioned effects. On the other hand, if P is added in an excessively large amount, the possibility of brittle fracture occurrence significantly increases, which may increase the possibility of slab fracture during hot rolling and worsen the pickling property of the steel, thereby potentially adversely affecting enamel adhesion. More specifically, P may be included in an amount of 0.005 to 0.018 weight %.

S: 0.001 to 0.020 % by weight

[0041] Sulfur (S) is an impurity element inevitably contained in steel, which combines with Mn or the like to form non-metallic inclusions and thus significantly lowers the toughness of the steel. If S is added in an excessively small amount, a problem of deteriorating weldability may occur. If S is added in an excessively large amount, ductility is significantly lowered, deteriorating workability, and manganese sulfide is excessively precipitated, which may adversely affect the fish-scaling resistance of the product. More specifically, S may be included in an amount of 0.003 to 0.015 weight %.

N: 0.0050 weight % or less

[0042] Nitrogen (N) contributes to the strength of the steel material but is difficult to control; in the case of solute nitrogen, it interacts with dislocations, which can lead to frequent aging defects, degraded formability, and bubble defects during the enameling process. More specifically, it may be included in an amount of 0.0010 to 0.0040 weight %.

O: 0.0030 weight % or less

[0043] Oxygen (O) is an essential element in forming oxides, and such oxides not only cause refractory erosion in the steelmaking stage but also act as a factor causing surface defects due to oxides on the surface during steel sheet manufacturing. Therefore, O may be included in an amount of 0.0030 weight % or less. More specifically, it may be included in an amount of 0.0003 to 0.0025 weight %.

[0044] In addition to the above components, the present invention comprises Fe and unavoidable impurities. The addition of effective components other than the above components is not excluded. Examples of the unavoidable impurities include Cu, Ti, Co, Nb, Ni, V, Mo, and the like. In one embodiment of the present invention, Cu, Ti, Co, Nb, Ni, V, Mo, and the like are not intentionally added, and the present invention may further comprise one or more selected from the group consisting of Cu: 0.1 weight % or less, Ti: 0.003 weight % or less, Co: 0.005 weight % or less, Nb: 0.003 weight % or less, Ni: 0.01 weight % or less, V: 0.003 weight % or less, and Mo: 0.01 weight % or less.

[0045] An enamel steel sheet according to an embodiment of the present invention satisfies Formula 1 below.

[Formula 1]

$$CVF[50\ \mu m]/CVF[center] \leq 0.50$$

(In Formula 1, CVF[50 μm] represents the area fraction of cementite (%) at a position 50 μm inside the steel sheet in the thickness direction from the surface of the steel sheet, and CVF[center] represents the area fraction of cementite (%) at the 1/2 thickness position of the steel sheet.)

[0046] When the ratio of the area fraction of cementite within a depth of 50 μm from the surface of the enamel steel sheet to the area fraction of cementite at the center of the steel sheet is too high, it means that a large number of cementite particles have been generated on the steel sheet surface, which may lead to a problem where the hydrogen occlusion capacity is reduced because decarburization of the surface layer is not sufficiently performed. More specifically, the value on the left side of Formula 1 may be in the range of 0.10 to 0.45.

[0047] The cementite fraction may be obtained as a cementite fraction relative to the total field of view area using an image analyzer after obtaining images with an optical microscope for a plane parallel to the rolled surface of the steel sheet (ND plane) by polishing the steel sheet to a depth of 50 μm from the steel sheet surface or to the center portion (1/2 thickness position). In an embodiment of the present invention, the rest of the microstructure other than cementite may consist of ferrite.

[0048] The enamel steel sheet according to an embodiment of the present invention may satisfy Formula 2 below.

[Formula 2]

$$Hv[50\ \mu m]/Hv[center] \leq 0.75$$

(In Formula 2, Hv[50 μm] denotes the hardness at a position 50 μm inside the steel sheet in the thickness direction from the steel sheet surface, and Hv[center] represents the hardness at a position 1/2 of the thickness of the steel sheet.)

[0049] In an embodiment of the present invention, when the hardness at the surface is higher than at the center, a problem occurs in that the hydrogen occlusion capacity is reduced, so fishscale resistance may be inferior. More specifically, the value on the left side of Formula 2 may be 0.40 to 0.73.

[0050] An enamel steel sheet according to an embodiment of the present invention may have a hydrogen permeation ratio of 650 seconds/mm^2 or more. The hydrogen permeation ratio is a representative index for evaluating fishscale resistance, which indicates resistance to fishscale defects-a fatal defect when applying an enamel steel manufactured using a cold-rolled steel sheet according to an embodiment of the present invention-and evaluates the ability to trap hydrogen within the steel sheet by a method listed in the European standard (EN10209-2013). The hydrogen permeation ratio is a value expressed as t_s/t^2 (unit: seconds/mm^2), calculated by measuring the time (t_s, unit: seconds) taken for hydrogen to be generated on one side of the steel sheet and permeate through to the opposite side of the steel sheet, and dividing this value by the square of the material thickness (t, unit: mm). If the hydrogen permeation ratio is too low, when fishscale resistance is evaluated by accelerated heat treatment at 200°C for 24 hours after enameling, a defect rate of 50% or more occurs, which causes problems in using the steel sheet as a stable enamel product. Therefore, to secure a steel sheet with excellent fishscale resistance, it is necessary to manage the hydrogen permeation ratio at 650 seconds/mm^2 or more. Further specifically, the hydrogen permeation ratio may be 690 seconds/mm^2 or more. The upper limit of the hydrogen permeation ratio is not particularly limited, but may be, for example, 1700 seconds/mm^2.

[0051] A manufacturing method for an enamel steel sheet according to an embodiment of the present invention comprises the steps of: manufacturing a hot-rolled steel sheet by hot rolling a slab comprising, in weight %, 0.01 to 0.05% of C, 0.10 to 0.80% of Mn, 0.001 to 0.03% of Si, 0.01 to 0.08% of Al, 0.001 to 0.02% of P, 0.001 to 0.02% of S, 0.005% or less of N (excluding 0%), and 0.003% or less of O (excluding 0%); manufacturing a cold-rolled steel sheet by cold rolling the hot-rolled steel sheet; and annealing the cold-rolled steel sheet.

[0052] First, a slab satisfying the aforementioned composition is prepared. Molten steel whose components are adjusted to the aforementioned composition in the steelmaking stage may be manufactured into a slab through continuous casting. The alloy composition of the slab is substantially the same as that of the aforementioned enamel steel sheet. Since the alloy composition has been described above, redundant explanation will be omitted.

[0053] Before hot rolling the slab, the manufactured slab may be heated. By heating, the subsequent hot rolling process may be smoothly performed, and the slab may be homogenized. More specifically, heating may refer to reheating.

[0054] At this time, the slab heating temperature may be 1100 to 1300°C. If the slab heating temperature is too low,

the rolling load rapidly increases in the subsequent hot rolling process, and in particular, inclusions inside the slab are not sufficiently re-dissolved, which may cause surface defects after hot rolling. On the other hand, if the slab heating temperature is too high, austenite undergoes abnormal grain growth, and as the final microstructure coarsens, strength may decrease. More specifically, it may be 1150 to 1250°C.

[0055] Thereafter, the heated slab is hot rolled to manufacture a hot-rolled steel sheet.

[0056] At this time, the finish hot rolling temperature may be 800 to 1000°C. If the finish hot rolling temperature is too low, there is a concern that the rolling load may increase significantly, and elongated grains may develop due to a recrystallization delay, and cold rollability may become inferior. On the other hand, if the finish hot rolling temperature is too high, the structure of the steel sheet may coarsen, causing the steel material to become brittle, the scale may become thick, and there is a concern that surface quality, such as high-temperature rolling scale defects, may be significantly degraded. More specifically, the finish hot rolling temperature may be 830 to 900°C.

[0057] Thereafter, the hot-rolled steel sheet manufactured by hot rolling undergoes a coiling process. More specifically, the coiling process may be a hot-rolled coiling process.

[0058] At this time, the coiling temperature may be 450 to 700°C. If the hot rolling coiling temperature is too low, grains may coarsen, which may cause a problem of reduced cold rollability. On the other hand, if the coiling temperature is too high, solute carbon and nitrogen may not be sufficiently precipitated and may remain, which may worsen workability and cause cold rollability to deteriorate. More specifically, the coiling temperature may be 590 to 710°C.

[0059] The method may further comprise a step of pickling the coiled hot-rolled steel sheet before cold rolling.

[0060] Thereafter, the coiled hot-rolled steel sheet is manufactured into a cold-rolled steel sheet through cold rolling.

[0061] At this time, the cold reduction ratio may be 50 to 90%. If the cold reduction ratio is too low, the amount of nucleation for annealing recrystallization is small, and thus grains may grow too large during annealing, degrading strength and workability. On the other hand, if the cold reduction ratio is too high, the amount of nucleation is too large, and thus the annealing recrystallized grain may rather be too fine, degrading ductility. More specifically, the cold reduction ratio may be 75 to 85%.

[0062] Thereafter, the cold-rolled steel sheet may be manufactured into an annealed steel sheet by an annealing treatment, and in this case, the annealing treatment may refer to a continuous annealing treatment.

[0063] In an embodiment of the present invention, the annealing step comprises a heating step and a soaking step of heating the steel sheet from 100°C to a soaking temperature. In the heating step, the steel sheet may be heated to a temperature higher than the soaking temperature, and subsequently cooled to a soaking temperature for soaking.

[0064] The heating step is performed at a dew point temperature of 10 to 23°C. If the dew point temperature is too low in the heating step, decarburization does not occur sufficiently in localized areas, resulting in the formation of a large amount of cementite on the surface, and the properties of a predetermined cold-rolled steel sheet for enameling may not be secured. If the dew point temperature is too high, grain growth occurs due to the decarburization reaction, causing deterioration of surface physical properties, and due to the generation of oxides, problems of deterioration of workability due to material nonuniformity and deterioration of fish-scaling resistance may occur. More specifically, the heating step may be performed at a dew point temperature of 13 to 20°C.

[0065] The soaking step is performed at a dew point temperature of 0 to 13°C. If the dew point temperature is too low in the soaking step, decarburization does not sufficiently occur locally, such that a large number of cementite particles are generated on the surface, and the properties of the predetermined cold-rolled steel sheet for enameling may not be secured. If the dew point temperature is too high, problems of deterioration of surface physical properties and deterioration of fish-scaling resistance may occur due to the generation of oxides caused by surface oxidation. More specifically, the soaking step may be performed at a dew point temperature of 3 to 10°C.

[0066] A dew point temperature difference of the atmosphere in the heating step and the soaking step may be 3 to 15°C. If the difference is too small or too large, decarburization may not sufficiently occur or occur excessively, which may be a problem. The dew point temperature difference of the atmosphere in the heating step and the soaking step may be 5 to 10°C.

[0067] The soaking temperature may be 700 to 850°C. If the soaking temperature is too low, the decarburization reaction rate is low, a large amount of cementite is generated on the surface due to the low carbon solubility of ferrite, and recrystallization is not completed, so the formability may become insufficient. If the soaking temperature is too high, shape defects due to sagging may occur during the annealing process. More specifically, the soaking temperature may be 700 to 850°C.

[0068] The heating step and the soaking step may be performed in an atmosphere comprising 3 to 20 vol% of hydrogen and the balance of nitrogen. If the amount of hydrogen is too low, the oxygen partial pressure at the surface layer increases, leading to excessive decarburization and an excessive oxidation atmosphere, which may cause problems. If the amount of hydrogen is too high, the hydrogen partial pressure at the surface layer becomes high, which may hinder the decarburization reaction between the surface and oxygen. More specifically, the atmosphere may comprise 5 to 15 vol% of hydrogen.

[0069] Annealing is preferably performed by a continuous annealing method, and the soaking time is preferably

maintained such that recrystallization is completed, and it may be performed in the range of 10 seconds to 30 minutes.

[0070] After the annealing step, the method may further comprise a step of skin pass rolling the steel sheet at a reduction ratio of 0.5 to 3%.

[0071] The shape of the material may be controlled through skin pass rolling. If the reduction ratio is too small, shape correction may not be sufficient. If the reduction ratio is too high, the deformation is excessive, which may lead to a decrease in ductility. More specifically, the reduction ratio of skin pass rolling may be 1.0 to 2.5%.

[0072] Furthermore, the method may further comprise a step of enameling firing to dry the enameled glaze after the annealing step of the cold-rolled steel sheet. Through the enameling firing process, various characteristics suitable for applications such as chemical resistance and heat resistance of enamel products may be obtained by applying an enamel layer on the steel sheet surface through heating to a high temperature and cooling to room temperature. However, if the firing temperature is too low, there is a problem in that the adhesion properties of the enamel layer cannot be secured, while if the firing temperature is too high, it acts as a cost increase factor due to the increase in energy source usage; therefore, the firing temperature may be applied at 780 to 850°C. More specifically, the firing temperature may be 790 to 840°C.

[0073] 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 and describing the present invention in more detail and are not intended to limit the scope of the rights of the present invention. This is because the scope of the rights of the present invention is determined by the matters described in the claims and matters reasonably inferred therefrom.

Example

[0074] Slabs were manufactured with an alloy composition comprising the components shown in Table 1, with the balance being Fe and unavoidable impurities in wt%. The slab was maintained at 1200°C for 2 hours, followed by hot rolling. At this time, the final thickness of the hot-rolled steel sheet was adjusted to 4.0 mm. After the oxide film on the surface was removed through pickling treatment, the hot-rolled specimens were subjected to cold rolling at various reduction ratios. Thereafter, the specimens were annealed for 3 minutes under the conditions summarized in Table 2 below. The atmosphere was an atmosphere containing 10 vol% hydrogen and the balance nitrogen.

[0075] The cementite fraction was determined by obtaining images with an optical microscope at a depth of 50 μm from the steel sheet surface and at the center portion, and then calculating the ratio of the cementite area to the total field of view area using an image analyzer.

[0076] Hardness was measured at a depth of 50 μm from the steel sheet surface and at the center portion using Vickers hardness. A load of 100 g was applied, and 5 points were measured at 1 mm intervals to obtain an average value.

[0077] The hydrogen permeation ratio is one of the indices for evaluating the resistance to fish scale, which is a fatal defect of enamel. In accordance with the experimental method specified in the European standard (EN10209-2013), the time (ts, unit: seconds) required for hydrogen generated at one side of a steel sheet to permeate through to the opposite side is measured and divided by the square of the material thickness (d, unit: mm), and the result is expressed as ts/d^2 (unit: s/mm^2).

[0078] The microstructural characteristics and the like of the material secured through the above process are shown in Table 3 below.

[Table 1]

Steel type	C	Mn	Si	Al	P	S	N	O
Inventive Steel 1	0.027	0.565	0.018	0.025	0.018	0.008	0.0019	0.0016
Inventive Steel 2	0.018	0.751	0.023	0.054	0.012	0.006	0.0038	0.0012
Inventive Steel 3	0.044	0.247	0.002	0.011	0.010	0.005	0.0011	0.0005
Inventive Steel 4	0.013	0.766	0.023	0.037	0.013	0.008	0.0027	0.0005
Inventive Steel 5	0.039	0.182	0.009	0.024	0.006	0.006	0.0025	0.0020
Comparative Steel 1	0.002	0.192	0.003	0.016	0.010	0.007	0.0019	0.0020
Comparative Steel 2	0.005	0.853	0.102	0.043	0.041	0.007	0.0025	0.0013
Comparative Steel 3	0.077	0.899	0.251	0.028	0.018	0.003	0.0035	0.0015

[Table 2]

Classification	Steel type	Hot rolling		Cold rolling	Annealing of cold-rolled sheet		
		Finishing temperature (°C)	Coiling temperature (°C)	Cold reduction ratio	Soaking temperature (°C)	Heating dew point temperature (°C)	Soaking dew point temperature (°C)
Inventive Example 1	Inventive Steel1	890	650	83	750	15	5
Inventive Example 2	Inventive Steel1	890	650	83	800	15	5
Inventive Example 3	Inventive Steel1	890	650	83	800	20	10
Inventive Example 4	Inventive Steel2	880	660	80	810	15	5
Inventive Example 5	Inventive Steel2	880	660	80	830	15	5
Inventive Example 6	Inventive Steel3	840	600	80	800	20	10
Inventive Example 7	Inventive Steel3	840	600	80	800	20	15
Inventive Example 8	Inventive Steel4	890	680	80	750	20	10
Inventive Example 9	Inventive Steel4	890	680	80	780	20	10
Inventive Example 10	Inventive Steel4	890	680	80	800	20	10
Inventive Example 11	Inventive Steel4	890	680	80	820	20	10
Inventive Example 12	Inventive Steel5	890	660	83	800	15	5
Inventive Example 13	Inventive Steel5	890	660	83	830	15	5
Comparative Example1	Inventive Steel1	890	650	83	880	20	10
Comparative Example2	Inventive Steel2	880	660	80	760	5	-5
Comparative Example3	Inventive Steel2	880	660	80	760	25	10
Comparative Example4	Inventive Steel3	840	600	80	800	20	15
Comparative Example5	Inventive Steel3	840	600	80	800	10	-5
Comparative Example8	Inventive Steel3	840	600	80	650	20	10
Comparative Example9	Comparative Steel1	890	660	83	800	15	5
Comparative	Comparative Steel2	890	660	83	800	15	5

(continued)

Classification	Steel type	Hot rolling		Cold rolling	Annealing of cold-rolled sheet		
		Finishing temperature (°C)	Coiling temperature (°C)	Cold reduction ratio	Soaking temperature (°C)	Heating dew point temperature (°C)	Soaking dew point temperature (°C)
Example1 0							
Comparative Example1 1	Comparative Steel3	860	600	83	750	15	5

[Table 3]

Classification	Formula 1	Formula 2	Hydrogen permeation ratio
Inventive Example1	0.34	0.73	693
Inventive Example2	0.27	0.67	778
Inventive Example3	0.16	0.59	864
Inventive Example4	0.42	0.62	797
Inventive Example5	0.39	0.63	726
Inventive Example6	0.21	0.49	1021
Inventive Example7	0.14	0.43	1077
Inventive Example8	0.43	0.69	708
Inventive Example9	0.41	0.66	695
Inventive Example10	0.31	0.51	726
Inventive Example11	0.33	0.53	738
Inventive Example12	0.35	0.55	990
Inventive Example13	0.28	0.52	1056
Comparative Example1	0.87	0.85	657
Comparative Example2	0.63	0.73	678
Comparative Example3	0.80	0.91	585
Comparative Example4	0.76	0.80	541
Comparative Example5	0.75	0.79	504
Comparative Example8	0.73	0.84	607
Comparative Example9	0	0.95	324
Comparative Example10	0	0.94	305
Comparative Example11	0.43	0.69	534

[0079] As shown in Tables 1 to 3, in the case of the Inventive Examples that properly satisfy the alloy composition and manufacturing conditions, it may be confirmed that the cementite ratio of the surface and center of the steel sheet is properly formed and an excellent hydrogen permeation ratio may be secured.

[0080] On the other hand, in Comparative Examples 1 to 6, which satisfied the alloy composition but did not satisfy the manufacturing conditions, it may be confirmed that the cementite ratio of the surface and the center of the steel sheet was not properly formed, resulting in an inferior hydrogen permeation ratio.

[0081] Comparative Examples 7 to 9 did not satisfy the alloy composition. Even in these cases, it may be confirmed that the cementite ratio of the surface and the center was not properly formed, resulting in an inferior hydrogen permeation ratio.

[0082] The present invention is not limited to the above embodiments but may be manufactured in various different

forms, and those of ordinary skill in the art to which the present invention belongs will understand that it may be implemented in other specific forms without changing the technical idea or essential features of the present invention. Therefore, it should be understood that the embodiments described above are illustrative in all respects and not restrictive.

Claims

1. An enamel steel sheet comprising, in weight %, C: 0.01 to 0.05%, Mn: 0.10 to 0.80%, Si: 0.001 to 0.03%, Al: 0.01 to 0.08%, P: 0.001 to 0.02%, S: 0.001 to 0.02%, N: 0.005% or less (excluding 0%), and O: 0.003% or less (excluding 0%), with the balance being Fe and unavoidable impurities, and

satisfying Formula 1 below.

[Formula 1]

$$CVF[50\ \mu m]/CVF[center] \leq 0.5$$

(In Formula 1, CVF[50 μm] represents the area fraction of cementite (%) at a position 50 μm inside the steel sheet in the thickness direction from the steel sheet surface, and CVF[center] represents the area fraction of cementite (%) at the 1/2 thickness position of the steel sheet).

2. The enamel steel sheet of claim 1,

wherein the enamel steel sheet satisfies Formula 2 below.

[Formula 2]

$$Hv[50\ \mu m]/Hv[center] \leq 0.75$$

(In Formula 2, Hv[50 μm] denotes the hardness at a position 50 μm inside the steel sheet in the thickness direction from the surface of the steel sheet, and Hv[center] represents the hardness at a 1/2 position of the steel sheet thickness).

3. The enamel steel sheet of claim 1,
further comprising one or more selected from the group consisting of Cu: 0.1 weight % or less, Ti: 0.003 weight % or less, Co: 0.005 weight % or less, Nb: 0.003 weight % or less, Ni: 0.01 weight % or less, V: 0.003 weight % or less, and Mo: 0.01 weight % or less.

4. The enamel steel sheet of claim 1,
wherein a hydrogen permeation ratio is 650 seconds/mm^2 or more.

5. A method of manufacturing an enamel steel sheet, comprising:

hot-rolling a slab containing, by weight %, 0.01 to 0.05% of C, 0.10 to 0.80% of Mn, 0.001 to 0.03% of Si, 0.01 to 0.08% of Al, 0.001 to 0.02% of P, 0.001 to 0.02% of S, 0.005% or less of N (excluding 0%), and 0.003% or less of O (excluding 0%), with the balance being Fe and unavoidable impurities,
cold-rolling the hot-rolled steel sheet to manufacture a cold-rolled steel sheet; and
annealing the cold-rolled steel sheet;
wherein the annealing step comprises a heating step of heating the steel sheet from 100°C to a soaking temperature, and a soaking step,
wherein the heating step is performed at a dew point temperature of 10 to 23°C,
wherein the soaking step is performed at 0 to 13°C.

6. The method of manufacturing an enamel steel sheet of claim 5,

wherein in the step of manufacturing the hot-rolled steel sheet,
the finish hot rolling temperature is 800 to 1000°C.

7. The method of manufacturing an enamel steel sheet of claim 5,

wherein in the step of manufacturing the hot-rolled steel sheet,
the coiling temperature is 450 to 700°C.

8. The method of manufacturing an enamel steel sheet of claim 5,
wherein in the step of manufacturing the cold-rolled steel sheet, a reduction ratio is 60 to 90%.

9. The method of manufacturing an enamel steel sheet of claim 5,
wherein the soaking temperature is 700 to 850°C.

10. The method of manufacturing an enamel steel sheet of claim 5,
wherein the heating step and the soaking step are performed in an atmosphere comprising 3 to 20 vol% of hydrogen and the balance of nitrogen.

11. The method of manufacturing an enamel steel sheet of claim 5,
wherein a dew point temperature difference of the atmosphere in the heating step and the soaking step is 3 to 15 °C.

12. The method of manufacturing an enamel steel sheet of claim 5,
further comprising, after the annealing step, a step of skin pass rolling the steel sheet at a reduction ratio of 0.5 to 3%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2024/063301

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/04(2006.01)i; **C22C 38/02**(2006.01)i; **C22C 38/06**(2006.01)i; **C22C 38/00**(2006.01)i; **C22C 38/16**(2006.01)i; **C22C 38/14**(2006.01)i; **C22C 38/10**(2006.01)i; **C22C 38/08**(2006.01)i; **C22C 38/12**(2006.01)i; **C21D 8/02**(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 38/04(2006.01); B21B 1/24(2006.01); C21D 1/76(2006.01); C21D 3/04(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/00(2006.01); C22C 38/02(2006.01); C22C 38/14(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: 법랑(enamel), 피쉬스케일(fishscale), 수소투과(hydrogen permeation), 이슬점(dew point), 시멘타이트(cementite)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	KR 10-2021-0080723 A (POSCO) 01 July 2021 (2021-07-01) See paragraph [0122] and claims 1, 9 and 13.	1-12
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A	JP 06-279864 A (SUMITOMO METAL IND. LTD.) 04 October 1994 (1994-10-04) See paragraph [0035] and claims 1-4.	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
"D" document cited by the applicant in the international application
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"O" document referring to an oral disclosure, use, exhibition or other means
"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	Date of mailing of the international search report
15 April 2025	**15 April 2025**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2024/063301

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