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(54) **NON-ORIENTED ELECTRICAL STEEL SHEET AND METHOD FOR MANUFACTURING SAME**

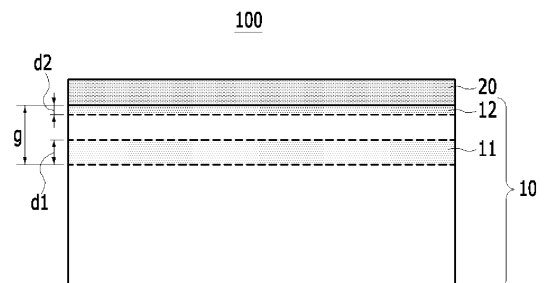
(57) According to an exemplary embodiment of the present invention, a non-oriented electrical steel sheet includes, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, and the balance of Fe and inevitable impurities, satisfies the following Equation 1, has an inner oxide layer formed inside a base steel sheet and having a thickness of 0.2 to 5 μm , and further includes at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb.

[Equation 1]

$$-2.5 \leq [P] / [Cr] - [Mg] \times 100 \leq 6.5$$

(In Equation 1, [P], [Cr] and [Mg] represent contents (wt%) of P, Cr and Mg, respectively.)

FIG. 1



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Description**[Technical Field]**

[0001] The present invention relates to a non-oriented electrical steel sheet and a method for manufacturing the same. Specifically, the present invention relates to a non-oriented electrical steel sheet and a method for manufacturing the same with excellent insulating properties, workability and magnetic properties at the same time by adding an appropriate amount of P, Cr, and Mg elements to a steel sheet, adding Sn and Sb, and forming an inner oxide layer inside the steel sheet.

[Background Art]

[0002] Efficient use of electric energy is becoming a big issue to improve the global environment, such as saving energy, reducing the generation of fine dust and reducing greenhouse gases. Since 50% or more of the total electric energy that is currently generated is consumed by an electric motor, it is necessary to require the high efficiency of the electric motor for efficient use of electricity.

[0003] Recently, as the field of eco-friendly vehicles (hybrid, plug-in hybrid, electric, and fuel cell vehicles) has rapidly developed, interest in high-efficiency driving motors is increasing rapidly. In addition, as high-efficiency motors for home appliances and super-premium motors for heavy electric appliances continue to be recognized in high efficiency and regulated by the government, the demand for efficient use of electric energy is higher than ever.

[0004] On the other hand, electrical steel sheets used as materials for motors are manufactured by stacking thin steel sheets in several layers to reduce eddy current loss, and at this time, each steel sheet needs to be in a state where insulation is maintained and no current flows. To this end, an insulation coating is applied to the surface of the electrical steel sheet.

[0005] Generally, the insulation coating consists of organic and inorganic composite materials. Since the insulation coating reduces eddy current loss by maintaining the insulation between the stacked upper and lower steel sheets, the insulation coating is thickly applied to completely insulate the steel sheets, so that there is an advantage of further improving the motor efficiency. However, when the thickness of an insulation coating layer increases, the motor efficiency decreases due to a decrease in space factor, and damage to a mold occurs due to the formation of foreign substances such as dust during punching, and as a result, there is a problem that producibility is reduced. Therefore, there is a need to secure insulating properties while reducing the thickness of the coating layer by applying the insulation coating to a minimum.

[0006] In the related art, there have been proposed some techniques for forming an oxide layer inside a base steel sheet. However, since P, Cr, and Mg are not added in an appropriate amount, there was a limitation in not sufficiently securing desired insulating properties and magnetic properties.

[Disclosure]

[0007] The present invention has been made in an effort to provide a non-oriented electrical steel sheet and a method for manufacturing the same. Specifically, the present invention has been made in an effort to provide a non-oriented electrical steel sheet and a method for manufacturing the same with excellent insulating properties, workability and magnetic properties at the same time by adding an appropriate amount of P, Cr, and Mg elements to a steel sheet and forming an inner oxide layer inside the steel sheet, and with excellent magnetic properties by further adding Sn and Sb.

[0008] According to an exemplary embodiment of the present invention, a non-oriented electrical steel sheet includes, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, and the balance of Fe and inevitable impurities, satisfies the following Equation 1, has an inner oxide layer formed inside a base steel sheet and having a thickness of 0.2 to 5 μm , and further includes at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb.

[Equation 1]

$$-2.5 \leq [P] / [Cr] - [Mg] \times 100 \leq 6.5$$

[0009] (In Equation 1, [P], [Cr] and [Mg] represent contents (wt%) of P, Cr and Mg, respectively.)

[0010] The total content of Sn and Sb may be 0.005 to 0.1 wt%.

[0011] 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb may be included.

[0012] The inner oxide layer may be formed in a range of 5 μm or less from the surface of the base steel sheet to an

inner direction of the base steel sheet.

[0013] The inner oxide layer may include at least one kind of oxide of Cr_2O_3 or MgO .

[0014] The average roughness of an interface between the inner oxide layer and the base steel sheet may be 1 to 5 μm .

[0015] The non-oriented electrical steel sheet may further include a surface oxide layer formed in the inner direction of the base steel sheet by coming into contact with the surface of the base steel sheet.

[0016] The inner oxide layer and the surface oxide layer may include 0.05 wt% or more of oxygen.

[0017] The thickness of the inner oxide layer may be greater than the thickness of the surface oxide layer.

[0018] The specific resistance of the non-oriented electrical steel sheet may be 45 $\mu\Omega\cdot\text{cm}$ or higher.

[0019] The non-oriented electrical steel sheet may further include at least one kind of C, S, N, Ti, Nb and V in an amount of 0.004 wt% or less, respectively.

[0020] According to an exemplary embodiment of the present invention, a method for manufacturing a non-oriented electrical steel sheet includes the steps of: preparing a slab including, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, and the balance of Fe and inevitable impurities, satisfying the following Equation 1, and further including at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb; heating the slab; preparing a hot-rolled sheet by hot-rolling the slab; preparing a cold-rolled sheet by cold-rolling the hot-rolled sheet; and finally annealing the cold-rolled sheet.

[0021] The final annealing step may include a rapid heating step of heating at a heating rate of 15°C/sec or more, a general heating step, and a cracking step, and the rapid heating step may be performed at a dew point temperature of -10 to 60°C.

[0022] The slab may include the total content of Sn and Sb of 0.005 to 0.1 wt%.

[0023] The slab may include 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb.

[0024] The rapid heating step may be performed by heating the cold-rolled sheet to 450 to 600°C.

[0025] The general heating step may be performed at a heating rate of 1 to 15°C/sec and a dew point temperature of -50 to -20°C.

[0026] The cracking temperature of the cracking step may be 850 to 1050°C.

[0027] According to the exemplary embodiment of the present invention, it is possible to obtain a non-oriented electrical steel sheet with excellent insulating properties, workability and magnetic properties at the same time by adding an appropriate amount of P, Cr, and Mg elements to a steel sheet and forming an inner oxide layer inside the steel sheet.

[0028] Accordingly, it is possible to minimize the thickness of the insulating layer, thereby increasing a space factor and increasing the efficiency of the motor manufactured from the non-oriented electrical steel sheet.

[0029] Ultimately, it is possible to manufacture eco-friendly motors for automobiles, motors for high-efficiency home appliances, and super premium motors.

[0030] In addition, the non-oriented electrical steel sheet may improve magnetic properties by adding Sn and Sb elements to the steel sheet.

[Description of the Drawings]

[0031]

FIG. 1 is a schematically lateral cross-sectional view of a non-oriented electrical steel sheet according to an exemplary embodiment of the present invention.

FIG. 2 is a photograph of a cross section of a non-oriented electrical steel sheet manufactured in a steel grade 3 taken with a scanning electron microscope (SEM).

[Mode for Invention]

[0032] 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 only used to distinguish any one part, component, region, layer or section from another part, component, region, layer or section. Accordingly, a first part, component, region, layer or section to be described below may be referred to as a second part, component, region, layer or section without departing from the scope of the present invention.

[0033] The terms used herein are for the purpose of only describing specific exemplary embodiments and are not intended to limit the present invention. The singular forms used herein include plural forms as well unless otherwise the phrases clearly have the opposite meaning. The "comprising" used herein means that a specific feature, region, integer, step, operation, element and/or component is embodied and presence or addition of other specific features, regions, integers, steps, operations, elements, and/or components is not excluded.

[0034] When a part is referred to as being "above" or "on" the other part, the part may be directly above or on the other part, or other parts may be involved therebetween. In contrast, when a part is referred to as being "directly above"

the other part, no other part is interposed therebetween.

[0035] Unless defined otherwise, all terms including technical and scientific terms used herein have the same meaning as commonly understood by those skilled in the art to which the present invention belongs. Commonly used predefined terms are further interpreted as having a meaning consistent with the relevant technical literature and the present disclosure, and are not to be construed as ideal or very formal meanings unless defined otherwise.

[0036] In addition, unless otherwise specified, % means wt%, and 1 ppm is 0.0001 wt%.

[0037] In an exemplary embodiment of the present invention, the meaning of further including an additional element means that the balance of iron (Fe) is replaced by an additional amount of the additional element.

[0038] Hereinafter, an exemplary embodiment of the present invention will be described in detail to be easily implemented by those skilled in the art to which the present invention belongs. As those skilled in the art would realize, the described embodiments may be modified in various different ways, all without departing from the spirit or scope of the present invention.

[0039] In an exemplary embodiment of the present invention, a composition in a non-oriented electrical steel sheet, in particular, a range of P, Cr, and Mg, which are major additives, is optimized, and an inner oxide layer is formed inside the steel sheet to improve insulating properties and workability. At the same time, an appropriate amount of Sn and Sb is added to improve magnetic properties.

[0040] A non-oriented electrical steel sheet according to an exemplary embodiment of the present invention includes, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb and the balance of Fe and inevitable impurities.

[0041] First, the reasons for limiting the components of the non-oriented electrical steel sheet will be described.

Si: 2.5 to 6.0 wt%

[0042] Silicon (Si) serves to lower iron loss by increasing the specific resistance of a material, and if Si is too little added, an effect of improving high-frequency iron loss may be insufficient. On the contrary, if Si is too much added, the hardness of the material increases, and a cold-rolling property is extremely deteriorated, thereby reducing producibility and punchability. Therefore, Si may be added in the above-described range. More specifically, Si may be contained in an amount of 2.6 to 4.5 wt%.

Al: 0.2 to 3.5 wt%

[0043] Aluminum (Al) serves to lowering the iron loss by increasing the specific resistance of the material. If Al is too little added, Al has no effect on reducing high-frequency iron loss, and nitrides are finely formed, thereby reducing magnetic properties. On the contrary, if Al is too much added, Al causes problems in all processes such as steel making and continuous casting, thereby greatly reducing producibility. Accordingly, Al may be added in the above-described range. More specifically, Al may be contained in an amount of 0.4 to 3.3 wt%.

Mn: 0.2 to 4.5 wt%

[0044] Manganese (Mn) serves to improve iron loss by increasing the specific resistance of the material and to form sulfides. If Mn is too little added, MnS may be finely precipitated, thereby reducing magnetic properties. On the contrary, if Mn is too much added, a magnetic flux density may decrease by encouraging the formation of a {111} aggregate structure that is disadvantageous to the magnetic properties. Accordingly, Mn may be added in the above-described range.

[0045] More specifically, Mn may be contained in an amount of 0.3 to 3.5 wt%.

Specific resistance 45 $\mu\Omega\cdot\text{cm}$ or higher

[0046] The specific resistance is a value calculated from $13.25 + 11.3 \times ([\text{Si}] + [\text{Al}] + [\text{Mn}] / 2)$. At this time, [Si], [Al], and [Mn] represent contents (wt%) of Si, Al, and Mn, respectively. The higher the specific resistance, the lower the iron loss. If the specific resistance is too low, the iron loss is deteriorated, thereby making it difficult to be used as a high-efficiency motor. More specifically, the specific resistance may be 50 to 80 $\mu\Omega\cdot\text{cm}$.

Cr: 0.01 to 0.2 wt%

[0047] Chromium (Cr) is a corrosion-resistant element and is concentrated in a surface layer to improve corrosion resistance and suppress the formation of an oxide layer. When Cr is too little contained, oxidation proceeds rapidly, thereby making it difficult to control the formation of the inner oxide layer. When Cr is too much contained, on the contrary,

oxidation is suppressed, thereby making it difficult to form the inner oxide layer. More specifically, Cr may be contained in an amount of 0.015 to 0.15 wt%.

P: 0.005 to 0.08 wt%

[0048] Phosphorus (P) is concentrated on the surface and serves to control the fraction of the inner oxide layer. If the added amount of P is too small, it may be difficult to form a uniform inner oxide layer. If the added amount of P is too large, a melting point of Si-based oxide fluctuates, and the inner oxide layer may be rapidly formed. Accordingly, the content of P may be controlled within the above-described range. More specifically, P may be contained in an amount of 0.005 to 0.07 wt%.

Mg: 0.0005 to 0.05 wt%

[0049] Magnesium (Mg) serves to promote the surface concentration of Cr and P in an oxidizing atmosphere. When Mg is too little contained, the above-described role may not be properly performed. If Mg is too much contained, the inner oxide layer is formed thick due to excessive surface concentration of Cr and P, resulting in magnetic deterioration. Accordingly, the content of Mg may be controlled within the above-described range. More specifically, Mg may be contained in an amount of 0.001 to 0.03 wt%.

[0050] The non-oriented electrical steel sheet according to an exemplary embodiment of the present invention satisfies the following Equation 1.

[Equation 1]

$$-2.5 \leq [P] / [Cr] - [Mg] \times 100 \leq 6.5$$

[0051] (In Equation 1, [P], [Cr] and [Mg] represent contents (wt%) of P, Cr and Mg, respectively.)

[0052] When the value of $[P] / [Cr] - [Mg] \times 100$ is less than -2.5, the formation of the inner oxide layer hardly occurs. On the other hand, when the value exceeds 6.5, the inner oxide layer is excessively formed and needs to be controlled within an appropriate range. More specifically, the value of $[P] / [Cr] - [Mg] \times 100$ may be -1.5 to 1.0.

At least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb

[0053] Tin (Sn) is segregated on the surface and grain boundaries of the steel sheet to suppress surface oxidation during annealing and improve the texture. If Sn is too little added, the effect may not be sufficient. If Sn is too much added, it is not preferred in that Sn is segregated on the grain boundaries to lower toughness, thereby reducing producibility compared to improvement of magnetic properties. More specifically, Sn may be contained in an amount of 0.02 to 0.07 wt%.

[0054] Antimony (Sb) is segregated on the surface and grain boundaries of the steel sheet to suppress surface oxidation during annealing and improve aggregates. If Sb is too little added, there is no effect, and if Sb exceeds 0.05%, it is not preferred in that Sb is segregated on the grain boundaries to lower the toughness of the material, thereby lowering producibility compared to improvement of magnetic properties. More specifically, Sb may be contained in an amount of 0.01 to 0.03 wt%.

[0055] Sn and Sb may be contained in at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb. That is, Sn may be contained in an amount of 0.01 to 0.08 wt% or Sb may be contained in an amount of 0.005 to 0.05 wt%, or Sn may be contained in an amount 0.01 to 0.08 wt% and Sb may be contained in an amount of 0.005 to 0.05 wt% at the same time. It is best in terms of magnetic properties that Sn is contained in an amount 0.01 to 0.08 wt% and Sb is contained in an amount of 0.005 to 0.05 wt% at the same time.

[0056] The total content of Sn and Sb may be 0.005 to 0.1 wt%. This is because the formation of the oxide layer and improvement of magnetic properties are most effective in the above-described range. If the total content of Sn and Sb is too small, the effect of improving magnetic properties may not be sufficient. If the total content of Sn and Sb is too large, the thickness of the oxide layer becomes thin, thereby deteriorating the insulating properties, and fine inclusions are formed, thereby deteriorating the magnetic properties. More specifically, the total content of Sn and Sb may be 0.015 to 0.09 wt%.

Other impurities

[0057] In addition to the above-described elements, inevitably mixed impurities such as carbon (C), sulfur (S), nitrogen

(N), titanium (Ti), niobium (Nb), and vanadium (V) may be included.

[0058] N is combined with Ti, Nb, and V to form nitrides, and serves to reduce crystal-grain growth properties.

[0059] C reacts with N, Ti, Nb, V, etc. to form fine carbides and serves to interfere with the crystal-grain growth properties and magnetic domain movement.

[0060] S forms sulfides to deteriorate the crystal-grain growth properties.

[0061] When the impurity elements are further included as described above, at least one kind of C, S, N, Ti, Nb, and V may be included in an amount of 0.004 wt% or less.

[0062] The non-oriented electrical steel sheet according to an exemplary embodiment of the present invention has the inner oxide layer formed therein, thereby obtaining excellent effects of insulating properties, workability, and magnetic properties at the same time. Referring to FIG. 1, a structure of the non-oriented electrical steel sheet according to an exemplary embodiment of the present invention will be described. The non-oriented electrical steel sheet of FIG. 1 is only illustrative of the present invention, and the present invention is not limited thereto. Therefore, the structure of the non-oriented electrical steel sheet may be variously modified.

[0063] As illustrated in FIG. 1, in a non-oriented electrical steel sheet 100 according to an exemplary embodiment of the present invention, an inner oxide layer 11 is formed in a base steel sheet 10. Since the inner oxide layer 11 is formed as described above, even if an insulating layer 20 is formed thin, it is possible to secure appropriate insulating properties.

[0064] The inner oxide layer 11 is formed inside the base steel sheet 10 and is distinguished from the insulating layer 20 formed outside the base steel sheet 10. More specifically, the inner oxide layer 11 may be formed in a range of 5 μm or less from the surface of the base steel sheet 10 to an inner direction of the base steel sheet 10. The range of 5 μm or less in the inner direction of the base steel sheet 10 is indicated by g in FIG. 1. That is, a distance from the surface of the base steel sheet 10 to the innermost surface of the inner oxide layer 11 may be 5 μm or less. If the inner oxide layer 11 is formed on the inside of the base steel sheet 10 too much, that is, if g in FIG. 1 is too large, a desired insulating property may not be obtained, but a problem of deteriorating magnetic properties may occur. A minimum value of g in FIG. 1 becomes a thickness of the inner oxide layer 11, and when g in FIG. 1 is the same as a thickness d1 of the inner oxide layer 11, it is meant that the inner oxide layer 11 is formed in contact with the surface of the steel sheet.

[0065] The thickness d1 of the inner oxide layer 11 may be 0.2 to 5 μm . If the thickness d1 of the inner oxide layer 11 is too thin, desired insulating properties may not be properly secured. If the thickness d1 of the inner oxide layer 11 is too thick, a problem of deteriorating the magnetic properties of the steel sheet may occur. More specifically, the thickness of the inner oxide layer 11 may be 1 to 3 μm .

[0066] The inner oxide layer 11 has the same alloy component as the base steel sheet 10, but is distinguished from the base steel sheet 10 containing a trace of oxygen in that 0.05 wt% or more of oxygen is contained. As described above, since the base steel sheet 10 contains Cr and Mg, oxygen in the inner oxide layer 11 reacts with Cr and Mg to form at least one kind of oxide of Cr_2O_3 or MgO . More specifically, the inner oxide layer 11 may contain 0.1 wt% or more of oxygen.

[0067] In FIG. 1, an interface between the inner oxide layer 11 and the base steel sheet 10 is flatly expressed, but is substantially roughly formed as illustrated in FIG. 2. This is because oxygen is rapidly introduced into the base steel sheet 10 during the manufacturing process, and base iron is generated while oxidizing, and it is advantageous for insulation that the interface is roughly formed. More specifically, the average roughness of the interface between the inner oxide layer 11 and the base steel sheet 10 may be 1 to 5 μm . In this case, the interface means both an upper surface and a lower surface of the inner oxide layer 11. As such, since the roughness exists on the surface of the inner oxide layer 11, the thickness d1 of the inner oxide layer 11 may vary according to a measurement position in an exemplary embodiment of the present invention, and the thickness d1 of the inner oxide layer 11 means the average thickness of the entire steel sheet.

[0068] As illustrated in FIG. 1, the non-oriented electrical steel sheet 100 according to an exemplary embodiment of the present invention further includes a surface oxide layer 12 formed in the inner direction of the base steel sheet 10 by coming into contact with the surface of the base steel sheet 10. The surface oxide layer 12 is distinguished from the base steel sheet 10 in that the surface oxide layer 12 has the same alloy component as the base steel sheet 10, but contains 0.05 wt% or more of oxygen. In addition, the surface oxide layer 12 is also distinguished from the inner oxide layer 11 in that the surface oxide layer 12 is formed on the surface side of the base steel sheet 10 rather than the inner oxide layer 11.

[0069] The surface oxide layer 12 may be formed very thin in contact with the surface of the base steel sheet 10, and the thickness d1 of the inner oxide layer 11 may be greater than a thickness d2 of the surface oxide layer 12. When the thickness d1 of the inner oxide layer 11 is formed to be thick, it is possible to secure appropriate insulating properties and magnetic properties. More specifically, the inner oxide layer 11 may be twice or more thicker than the thickness d2 of the surface oxide layer 12.

[0070] As illustrated in FIG. 1, a gap may be formed between the inner oxide layer 11 and the surface oxide layer 12. More specifically, the gap g-d1-d2 may be 0.5 to 3 μm . An appropriate gap is formed between the inner oxide layer 11 and the surface oxide layer 12 to further secure insulating properties and magnetic properties. When the gap is formed,

as illustrated in FIG. 1, the base steel sheet 10, the inner oxide layer 11, the base steel sheet 10, and the surface oxide layer 12 are sequentially formed. Such a gap is formed because Cr, P, and Mg having high oxidation properties are concentrated in a specific region near the surface.

[0071] As illustrated in FIG. 1, the insulating layer 20 may be further formed on the base steel sheet 10. The insulating layer 20 is formed on the surface of the base steel sheet 10, that is, outside the base steel sheet 10, and is distinguished from the inner oxide layer 11 and the surface oxide layer 12 described above. In an exemplary embodiment of the present invention, since the inner oxide layer 11 is properly formed, even if the thickness of the insulating layer 20 is formed to be thin, sufficient insulating properties may be secured. By forming the thickness of the insulating layer 20 to be thin, a space factor is increased, and damage to a mold during punching is reduced. Specifically, the thickness of the insulating layer 20 may be 0.7 to 1.0 μm . Since the insulating layer 20 is widely known in the technical field of the non-oriented electrical steel sheet, a detailed description will be omitted.

[0072] As described above, the non-oriented electrical steel sheet according to an exemplary embodiment of the present invention may simultaneously secure insulating properties and magnetic properties. The insulating properties may be 5.0 Ωcm^2 or more based on the thickness of 1 μm of the insulating layer 20. Specifically, the insulating properties may be 6.0 Ωcm^2 or more. In addition, a magnetic flux density B50 induced in a magnetic field of 5000 A/m may be 1.64 T or more. More specifically, the magnetic flux density B50 may be 1.65 T or more. Based on a thickness of 0.25 mm, iron loss W10/400 when the magnetic flux density of 1.0 T is induced at a frequency of 400 Hz may be 15.0 W/kg or less. More specifically, the iron loss W10/400 may be 14.7 W/kg or less.

[0073] A method for manufacturing a non-oriented electrical steel sheet according to an exemplary embodiment of the present invention includes the steps of: preparing a slab including, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, and the balance of Fe and inevitable impurities, satisfying the following Equation 1, and further including at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb; heating the slab; preparing a hot-rolled sheet by hot-rolling the slab; preparing a cold-rolled sheet by cold-rolling the hot-rolled sheet; and finally annealing the cold-rolled sheet.

[0074] Hereinafter, each step will be described in detail.

[0075] First, the slab is prepared. Since the reason for limiting an addition ratio of each composition in the slab is the same as the reason for limiting the composition of the non-oriented electrical steel sheet described above, a repeated description will be omitted. Since the composition of the slab is not substantially changed during the manufacturing process of hot rolling, hot-rolled sheet annealing, cold rolling, final annealing, etc., which will be described below, the composition of the slab and the composition of the non-oriented electrical steel sheet are substantially the same as each other.

[0076] Next, the slab is heated. Specifically, the slab is charged to a heating furnace and heated to 1100 to 1250°C. When the slab is heated at a temperature of more than 1250°C, a precipitate may be re-dissolved and finely precipitated after hot rolling.

[0077] The heated slab is hot-rolled to 2 to 2.3 mm to form a hot-rolled sheet. In the step of preparing the hot-rolled sheet, the final rolling temperature may be 800 to 1000°C.

[0078] After preparing the hot-rolled sheet, the annealing of the hot-rolled sheet may be further included. In this case, the annealing temperature of the hot-rolled sheet may be 850 to 1150°C. If the annealing temperature of the hot-rolled sheet is less than 850°C, the structure does not grow or grows finely, so that there is little effect of increasing the magnetic flux density. If the annealing temperature exceeds 1150°C, magnetic properties are rather deteriorated, and rolling workability may deteriorate due to deformation of the sheet shape. More specifically, the temperature range may be 950 to 1125°C. More specifically, the annealing temperature of the hot-rolled sheet is 900 to 1100°C. The annealing of the hot-rolled sheet is performed in order to increase the orientation advantageous for magnetic properties as necessary, and may be omitted.

[0079] Next, the hot-rolled sheet is pickled and cold-rolled to have a predetermined sheet thickness. Although applied differently depending on the thickness of the hot-rolled sheet, the hot-rolled sheet may be cold-rolled so that the final thickness is 0.2 to 0.65 mm by applying a reduction ratio of 70 to 95%.

[0080] The final cold-rolled sheet is subjected to final annealing. At this time, in order to form an appropriate inner oxide layer, the final annealing step includes a rapid heating step, a general heating step, and a cracking step.

[0081] The rapid heating step is a step of heating the cold-rolled sheet at a high heating rate of 15°C/sec or more. If the heating rate is insufficient, the inner oxide layer may not be formed properly. More specifically, in the rapid heating step, the cold-rolled sheet may be heated at a rate of 15°C/sec to 30°C/sec.

[0082] The rapid heating step is performed at a dew point temperature of -10 to 60°C. The inner oxide layer may be properly formed through such an oxidizing atmosphere. If the dew point temperature is too low, it is difficult to form the inner oxide layer. On the contrary, if the dew point temperature is too high, the inner oxide layer is formed too thick, so that magnetic properties are deteriorated, and dust or the like is generated during punching, and as a result, producibility may be deteriorated.

[0083] The rapid heating step refers to a step of heating the cold-rolled sheet to 450 to 600°C.

[0084] Next, the general heating step is a step of heating the rapidly heated cold-rolled sheet to a cracking temperature. Specifically, a start temperature of the general heating step is 450 to 600°C, and an end temperature thereof is 850 to 1050°C. Since the inner oxide layer was properly formed in the above-described rapid heating step, there is no need to increase the heating rate or control the atmosphere to an oxidizing atmosphere in the general heating step. Specifically,

[0085] Next, the cracking step may be annealed for 30 seconds to 3 minutes at a cracking temperature of 850 to 1050°C. If the cracking temperature is too high, rapid growth of crystal grains may occur, thereby reducing the magnetic flux density and high-frequency iron loss. More specifically, the final annealing may be performed at a cracking temperature of 900 to 1000°C. In the final annealing process, all (i.e., 99% or more) of the processed structure formed in the previous cold-rolling step may be recrystallized.

[0086] Thereafter, the forming of the insulating layer may be further included. Except for forming a thin thickness, the insulating layer may be formed using a general method. Since the method of forming the insulating layer is widely known in the technical field of the non-oriented electrical steel sheet, a detailed description will be omitted.

[0087] Hereinafter, preferred Examples of the present invention and Comparative Examples will be described. However, the following Examples are only a preferred embodiment of the present invention, and the present invention is not limited to the following Examples.

Example 1

[0088] A slab composed as shown in Table 1 below was prepared. In addition to components shown in Table 1, C, S, N, Ti, etc. were all controlled to 0.003 wt%. The slab was heated to 1150°C and hot-finish rolled at 850°C to prepare a hot-rolled sheet having a sheet thickness of 2.0 mm. The hot-rolled sheet was annealed at 1100°C for 4 minutes and then pickled. Then, the hot-rolled sheet was cold-rolled to make a sheet thickness of 0.25 mm, and then final annealing was performed. The heating rate and dew point conditions of the rapid heating step to 500°C were summarized in Table 2 below. Thereafter, the temperature was raised to 1000°C, and maintained at 1000°C for 45 seconds. Then, an insulating layer having a thickness of 1 μm was formed.

[0089] Insulating properties were measured with a Franklin tester, and magnetic properties were determined as average values in a rolling direction and a vertical direction using a single sheet tester, which were summarized in Table 2 below.

[Table 1]

Steel grade	Si (wt %)	Al (wt %)	Mn (wt %)	Specific resistance (μΩ·cm)	Cr (wt %)	P (wt %)	Mg (wt %)	Value of Equation 1	Sn (wt %)	Sb (wt %)
1	2.8	0.5	0.5	53	0.02	0.01	0.001	0.4	0.05	0.01
2	2.8	0.5	0.5	53	0.01	0.075	0.001	7.4	0.05	0.01
3	2.8	0.5	0.5	53	0.02	0.006	0.003	0	0.05	0.01
4	3.1	0.7	1.5	65	0.05	0.03	0.02	-1.4	0.05	0.01
5	3.1	0.7	1.5	65	0.05	0.03	0.02	-1.4	0.05	0.01
6	3.1	0.7	1.5	65	0.05	0.01	0.02	-1.8	0.05	0.01
7	2.7	1.5	2.5	75	0.05	0.01	0.06	-5.8	0.05	0.01
8	2.7	1.5	2.5	75	0.05	0.07	0.005	0.9	0.05	0.01
9	2.7	1.5	2.5	75	0.15	0.07	0.005	-0.03	0.05	0.01
10	2.8	0.8	1.8	64	0.15	0.01	0.002	-0.13	0.05	0.01
11	2.8	0.8	1.8	64	0.15	0.07	0.03	-2.53	0.05	0.01
12	2.8	0.8	1.8	64	0.25	0.01	0.025	-2.46	0.05	0.01
13	3.2	0.5	0.5	58	0.0003	0.0003	0.0003	0.97	0.05	0.01

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[Table 2]

Steel grade	Heating rate (°C/sec)	Dew point (°C)	Thickness of inner oxide layer (μm)	Insulation resistance (Ωcm ²)	W10/400 (W/kg)	B50 (T)	Note
1	15	-5	1.4	7.1	14.4	1.68	Example
2	13	10	3.2	11.0	17.0	1.63	Comparative Example
3	15	20	1.1	5.9	14.1	1.68	Example
4	18	-20	0.1	3.2	15.3	1.63	Comparative Example
5	18	35	1.6	7.7	13.1	1.65	Example
6	8	5	0.14	4.1	14.8	1.63	Comparative Example
7	15	45	4.1	13.7	17.1	1.61	Comparative Example
8	18	50	1.4	5.9	14.0	1.65	Example
9	26	70	5.1	16.7	18.3	1.61	Comparative Example
10	28	30	2.3	9.5	14.3	1.65	Example
11	25	20	0.18	2.3	14.3	1.61	Comparative Example
12	27	10	0.65	3.5	14.9	1.62	Comparative Example
13	15	20	0.06	1.4	15.0	1.62	Comparative Example

[0090] As shown in Tables 1 and 2, it can be seen that in steel grades of Examples and Examples satisfying heating rate and dew point conditions at the time of rapid heating, an appropriate inner oxide layer is formed therein, and both insulation resistance properties and magnetic properties are excellent.

[0091] On the other hand, it can be seen that the magnetic properties of steel grades 2, 7, 11, 12, and 13 that do not contain an appropriate amount of P, Cr, and Mg are poor. In particular, it was confirmed that even if the steel grades 11 and 13 satisfied the heating rate and dew point conditions at the time of rapid heating, the inner oxide layer was not properly formed, and the insulation resistance properties were also poor. Particularly, since the steel grade 13 does not contain P or Mg, it can be confirmed that the inner oxide layer is not properly formed even though Cr is less contained.

[0092] On the other hand, steel grades 4, 6, and 9 contained an appropriate amount of P, Cr, and Mg, but did not satisfy the heating rate and dew point conditions at the time of rapid heating, so that an appropriate inner oxide layer was not formed. The steel grades 4 and 6 in which the inner oxide layer was formed too thin had particularly poor insulation resistance properties, and the steel grade 9 in which the inner oxide layer was formed too thick had very poor magnetic properties.

[0093] FIG. 2 shows a photograph of a cross section of a non-oriented electrical steel sheet manufactured in a steel grade 3 taken with a scanning electron microscope (SEM). As shown in FIG. 2, it can be seen that the inner oxide layer is properly formed.

Example 2

[0094] A slab composed as shown in Table 3 below was prepared. In addition to components shown in Table 3, C, S, N, Ti, etc. were all controlled to 0.003 wt%. The slab was heated to 1150°C and hot-finish rolled at 850°C to prepare a hot-rolled sheet having a sheet thickness of 2.0 mm. The hot-rolled sheet was annealed at 1100°C for 4 minutes and then pickled. Then, the hot-rolled sheet was cold-rolled to make a sheet thickness of 0.25 mm, and then final annealing was performed. The heating rate and dew point conditions of the rapid heating step to 500°C were summarized in Table 2 below. Thereafter, the temperature was raised to 1000°C, and maintained at 1000°C for 45 seconds. Then, an insulating

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layer having a thickness of 1 μm was formed.

[0095] Insulating properties were measured with a Franklin tester, and magnetic properties were determined as average values in a rolling direction and a vertical direction using a single sheet tester, which were summarized in Table 4 below.

[Table 3]

Steel grade	Si (wt %)	Al (wt %)	Mn (wt%)	Specific resistance ($\mu\Omega \cdot \text{cm}$)	Cr (wt %)	P (wt%)	Mg (wt%)	Value of Equation 1	Sn (wt%)	Sb (wt%)
14	2.8	0.7	0.7	57	0.02	0.02	0.001	0.9	0.01	0.01
15	2.8	0.7	0.7	57	0.02	0.02	0.001	0.9	0.09	0.05
16	2.8	0.7	0.7	57	0.02	0.02	0.001	0.9	0.01	-
17	2.8	0.7	0.7	57	0.02	0.02	0.001	0.9	0.05	0.02
18	2.8	0.7	0.7	57	0.02	0.02	0.001	0.9	0.01	0.07
19	3.1	1	1.3	67	0.04	0.04	0.02	-1	0.02	0.02
20	3.1	1	1.3	67	0.04	0.04	0.02	-1	-	0.005
21	3.1	1	1.3	67	0.04	0.04	0.02	-1	0.08	0.01
22	3.1	1	1.3	67	0.04	0.04	0.02	-1	0.05	0.06
23	3.1	1	1.3	67	0.04	0.04	0.02	-1	0.003	0.001

[Table 4]

Steel grade	Sn+Sb	Heating rate ($^{\circ}\text{C}/\text{sec}$)	Dew point ($^{\circ}\text{C}$)	Thickness of inner oxide layer (μm)	Insulation resistance (Ωcm^2)	W10/400 (W/kg)	B50 (T)	Note
14	0.02	15	-5	1.5	7.8	14.8	1.67	Example
15	0.14	15	-5	0.05	2.8	14.8	1.62	Comparative Example
16	0.01	15	-5	2.5	8.9	14.8	1.64	Example
17	0.07	15	-5	1.8	8.2	14.2	1.68	Example
18	0.08	15	-5	0.15	3.1	14.8	1.63	Comparative Example
19	0.04	18	35	1.7	8.5	13.5	1.64	Example
20	0.005	18	35	2.3	10.3	14.8	1.64	Example
21	0.09	18	35	2.2	9.5	13.1	1.66	Example
22	0.11	18	35	0.03	2.7	15.5	1.61	Comparative Example
23	0.004	18	35	2.5	9.5	14.8	1.62	Comparative Example

[0096] As shown in Tables 3 and 4, it can be seen that in steel grades of Examples and Examples satisfying heating rate and dew point conditions at the time of rapid heating, an appropriate inner oxide layer is formed therein, and both insulation resistance properties and magnetic properties are excellent.

[0097] It can be seen that steel grades 15, 18, and 22 containing an excessive amount of one kind of Sn and Sb have poor insulation resistance properties because the inner oxide layer is not properly formed. In addition, the magnetic properties were poor, but it is analyzed that fine inclusions are formed by the excessive addition of Sn and Sb, thereby deteriorating the magnetic properties.

[0098] It can be seen that a steel grade 23 containing traces of both Sn and Sb has poor magnetic properties.

[0099] The present invention is not limited to the exemplary embodiments, but may be manufactured in various different forms, and those of ordinary skill in the art to which the present invention pertains will appreciate that the present invention may be implemented in other specific forms without changing the technical spirit or essential features of the present invention. Therefore, it should be understood that the exemplary embodiments described above are illustrative and not limited in all respects.

<Description of symbols>

100: Non-oriented electrical steel sheet	10: Base steel sheet
11: Inner oxide layer	12: Surface oxide layer
20: Insulating layer	

Claims

1. A non-oriented electrical steel sheet comprising, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, and the balance of Fe and inevitable impurities, satisfying the following Equation 1, having an inner oxide layer formed inside a base steel sheet and having a thickness of 0.2 to 5 μm , and further comprising at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb.

[Equation 1]

$$-2.5 \leq [P] / [Cr] - [Mg] \times 100 \leq 6.5$$

(In Equation 1, [P], [Cr] and [Mg] represent contents (wt%) of P, Cr and Mg, respectively.)

2. The non-oriented electrical steel sheet of claim 1, wherein: the total content of Sn and Sb is 0.005 to 0.1 wt%.
3. The non-oriented electrical steel sheet of claim 1, wherein: 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb are included.
4. The non-oriented electrical steel sheet of claim 1, wherein: the inner oxide layer is formed in a range of 5 μm or less from the surface of the base steel sheet to an inner direction of the base steel sheet.
5. The non-oriented electrical steel sheet of claim 1, wherein: the inner oxide layer includes at least one kind of oxide of Cr_2O_3 or MgO .
6. The non-oriented electrical steel sheet of claim 1, wherein: the average roughness of an interface between the inner oxide layer and the base steel sheet is 1 to 5 μm .
7. The non-oriented electrical steel sheet of claim 1, further comprising: a surface oxide layer formed in the inner direction of the base steel sheet by coming into contact with the surface of the base steel sheet.
8. The non-oriented electrical steel sheet of claim 7, wherein: the inner oxide layer and the surface oxide layer include 0.05 wt% or more of oxygen.
9. The non-oriented electrical steel sheet of claim 7, wherein: the thickness of the inner oxide layer is greater than the thickness of the surface oxide layer.
10. The non-oriented electrical steel sheet of claim 1, wherein: the specific resistance of the non-oriented electrical steel sheet is 45 $\mu\Omega\cdot\text{cm}$ or higher.
11. The non-oriented electrical steel sheet of claim 1, wherein:

the non-oriented electrical steel sheet further includes at least one kind of C, S, N, Ti, Nb and V in an amount of 0.004 wt% or less, respectively.

12. A method for manufacturing a non-oriented electrical steel sheet comprising the steps of:

preparing a slab including, by wt%, 2.5 to 6.0% of Si, 0.2 to 3.5% of Al, 0.2 to 4.5% of Mn, 0.01 to 0.2% of Cr, 0.005 to 0.08% of P, 0.0005 to 0.05% of Mg, and the balance of Fe and inevitable impurities, satisfying the following Equation 1, and further including at least one kind of 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb; heating the slab; preparing a hot-rolled sheet by hot-rolling the slab; preparing a cold-rolled sheet by cold-rolling the hot-rolled sheet; and finally annealing the cold-rolled sheet, wherein the final annealing step includes a rapid heating step of heating at a heating rate of 15°C/sec or more, a general heating step, and a cracking step, and the rapid heating step is performed at a dew point temperature of -10 to 60°C.

[Equation 1]

$$-2.5 \leq [P] / [Cr] - [Mg] \times 100 \leq 6.5$$

(In Equation 1, [P], [Cr] and [Mg] represent contents (wt%) of P, Cr and Mg, respectively.)

13. The method for manufacturing the non oriented electrical steel sheet of claim 12, wherein: the slab includes the total content of Sn and Sb of 0.005 to 0.1 wt%.

14. The method for manufacturing the non oriented electrical steel sheet of claim 12, wherein: the slab includes 0.01 to 0.08 wt% of Sn and 0.005 to 0.05 wt% of Sb.

15. The method for manufacturing the non-oriented electrical steel sheet of claim 12, wherein: the rapid heating step is performed by heating the cold-rolled sheet to 450 to 600°C.

16. The method for manufacturing the non-oriented electrical steel sheet of claim 12, wherein: the general heating step is performed at a heating rate of 1 to 15°C/sec and a dew point temperature of -50 to -20°C.

17. The method for manufacturing the non-oriented electrical steel sheet of claim 12, wherein: the cracking temperature of the cracking step is 850 to 1050°C.

FIG. 1

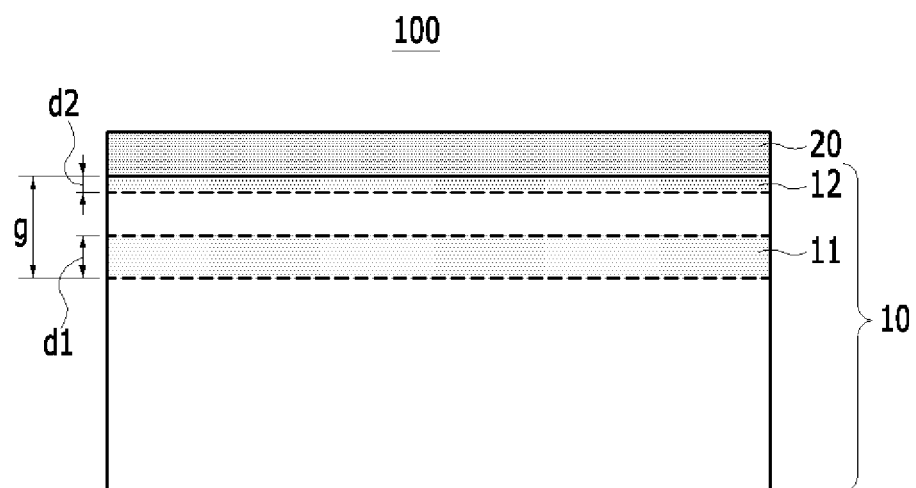
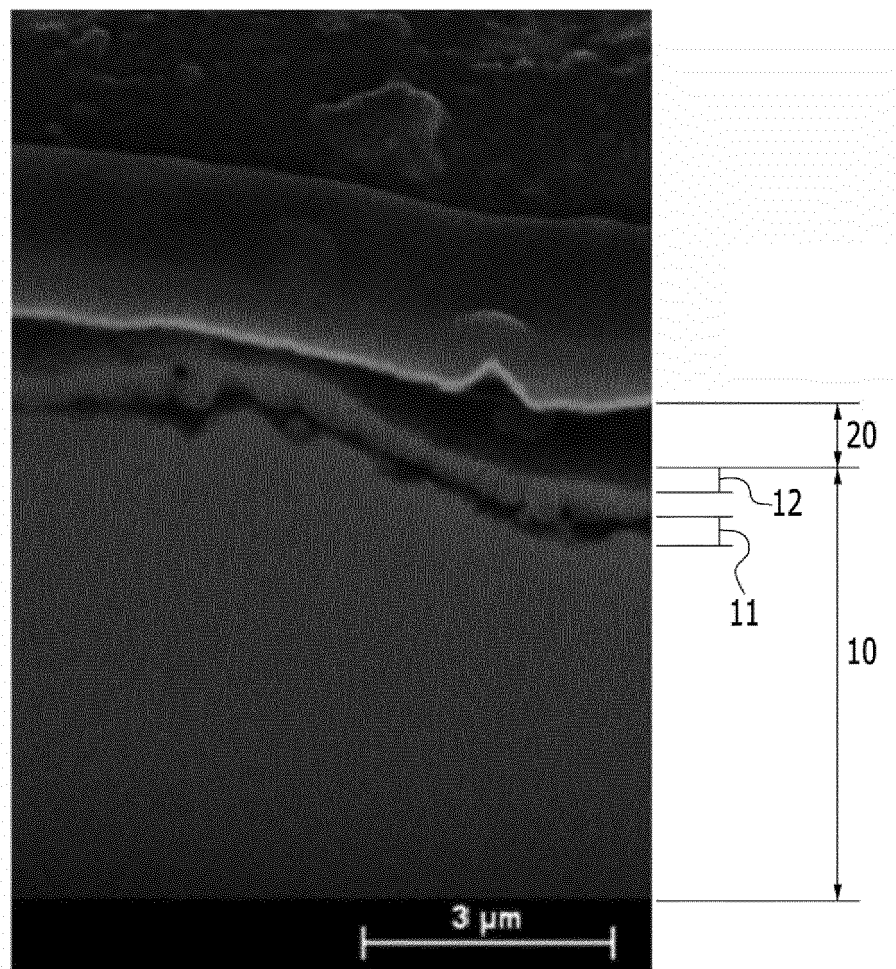


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2018/016039

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/34(2006.01)i, C22C 38/04(2006.01)i, C22C 38/06(2006.01)i, C22C 38/00(2006.01)i, C22C 38/60(2006.01)i, C21D 8/12(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 38/34; C21D 8/12; C21D 9/46; C22C 38/00; C22C 38/02; C22C 38/60; C22C 38/04; C22C 38/06

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: non-oriented, electrical steel sheet, P, Cr, Mg, Sn, Sb, Si, Al, Mn, oxidized layer, temperature rising, crack, annealing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2018-0011809 A (JFE STEEL CORPORATION) 02 February 2018 See paragraphs [0065]-[0066], [0071], [0074] and claims 1, 3-5.	1-17
A	JP 2016-156044 A (NIPPON STEEL & SUMITOMO METAL) 01 September 2016 See paragraph [0017] and claims 1, 3.	1-17
A	JP 2006-213975 A (NIPPON STEEL CORP.) 17 August 2006 See paragraph [0014] and claims 1, 2, 4.	1-17
A	KR 10-2018-0070951 A (POSCO) 27 June 2018 See paragraphs [0105]-[0110] and claims 1, 6, 7, 9, 12.	1-17
A	KR 10-2018-0078306 A (JFE STEEL CORPORATION) 09 July 2018 See paragraphs [0064]-[0071] and claims 1-3.	1-17

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

* Special categories of cited documents:

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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

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"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

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Date of the actual completion of the international search

18 APRIL 2019 (18.04.2019)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2018/016039

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-2018-0011809 A	02/02/2018	CN 107849632 A EP 3333271 A1 EP 3333271 A4 JP 6390876 B2 JP WO2017-022360 A1 TW 201710524 A TW 1641704 B US 2018-230564 A1 WO 2017-022360 A1	27/03/2018 13/06/2018 04/07/2018 19/09/2018 10/08/2017 16/03/2017 21/11/2018 16/08/2018 09/02/2017
JP 2016-156044 A	01/09/2016	None	
JP 2006-213975 A	17/08/2006	JP 4589747 B2	01/12/2010
KR 10-2018-0070951 A	27/06/2018	KR 10-1918720 B1 WO 2018-117602 A1	14/11/2018 28/06/2018
KR 10-2018-0078306 A	09/07/2018	BR 112018010370 A2 CA 3006620 A1 CN 108368561 A EP 3388537 A1 JP 2017-106073 A JP 6406522 B2 MX 2018006883 A TW 201720935 A TW 1605128 B US 2018-355454 A1 WO 2017-098800 A1	04/12/2018 15/06/2017 03/08/2018 17/10/2018 15/06/2017 17/10/2018 06/09/2018 16/06/2017 11/11/2017 13/12/2018 15/06/2017