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(54) **GRAIN-ORIENTED ELECTRICAL STEEL SHEET AND METHOD OF MANUFACTURING SAME**

(57) A grain-oriented electrical steel sheet according to an embodiment of the present invention comprises, in wt%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, with the balance being Fe and in-

evitable impurities, wherein a fraction of textures in which an angle between the <110> direction and the Normal Direction (ND) is 5° or less is 60 area% or more.

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Description**[Technical Field]**

5 **[0001]** An embodiment of the present invention relates to a grain-oriented electrical steel sheet and a manufacturing method thereof. Specifically, an embodiment of the present invention relates to a manufacturing method of grain-oriented electrical steel sheet having excellent magnetic properties, comprising appropriately controlling conditions during hot rolling to stably form secondary recrystallization into the Goss $\{110\}<001>$ orientation.

10 **[Background Art]**

[0002] A grain-oriented electrical steel sheet is a soft magnetic material that is used as a core for electromagnetic devices requiring excellent unidirectional magnetic properties, such as transformers, and it exhibits excellent magnetic properties in a rolling direction by forming a Goss texture ($\{110\}<001>$ texture) throughout a steel sheet using an abnormal grain growth phenomenon called secondary recrystallization. In general, magnetic properties may be expressed by magnetic flux density and iron loss, and high magnetic flux density may be obtained by accurately aligning the crystal grains in the $\{110\}<001>$ orientation. An electrical steel sheet having high magnetic flux density may not only reduce the size of the core material of an electromagnetic device but also lower the hysteresis loss, thereby achieving miniaturization and high efficiency of the electromagnetic device simultaneously. Iron loss is a power loss consumed as thermal energy when an arbitrary alternating magnetic field is applied to a steel sheet, and it varies greatly depending on the magnetic flux density, the sheet thickness, the amount of impurities in the steel sheet, the electrical resistivity, and the secondary recrystallized grain size of the steel sheet. The higher the magnetic flux density and electrical resistivity, and the lower the sheet thickness and the amount of impurities in the steel sheet, the lower the iron loss, which increases the efficiency of the electromagnetic device.

25 **[0003]** Secondary recrystallization of grain-oriented electrical steel sheet, unlike typical crystal grain growth, occurs when the movement of a normally growing grain boundary is suppressed by precipitates, inclusions, or elements that are dissolved or segregated at the grain boundaries. In addition, in order to grow crystal grains having a high degree of texture with respect to the Goss orientation, complex processes such as composition control in steelmaking, slab reheating in hot rolling and control of hot rolling process factors, hot-rolled sheet annealing heat treatment, primary recrystallization annealing, and secondary recrystallization annealing are required, and these processes must also be managed very precisely and strictly. Such precipitates or inclusions that suppress crystal grain growth are specifically called a grain growth inhibitor, and research on the manufacturing technology of a grain-oriented electrical steel sheet by secondary recrystallization of the Goss orientation has focused on securing excellent magnetic properties by forming secondary recrystallization having a high degree of texture with respect to the Goss orientation using a strong grain growth inhibitor.

35 **[0004]** In the grain-oriented electrical steel sheet developed in the early stages, MnS was used as a grain growth inhibitor, and it was manufactured by a two-stage cold rolling method. As a result, secondary recrystallization was stably formed, but the magnetic flux density was not very high and the iron loss was also relatively high. Later, a method of manufacturing a grain-oriented electrical steel sheet by using AlN and MnS precipitates in combination and performing single heavy cold rolling at a cold rolling reduction of 80% or more was proposed. Recently, a method of manufacturing a grain-oriented electrical steel sheet has been proposed, in which secondary recrystallization is caused by Al-based nitrides that exhibit a strong crystal grain growth inhibition effect by supplying nitrogen into the interior of the steel sheet through a separate nitriding process using ammonia gas after decarburization and subsequent to single heavy cold rolling without using MnS.

45 **[0005]** Until now, almost all steel sheet companies manufacturing grain-oriented electrical steel sheet have mainly used a manufacturing method that causes secondary recrystallization by using precipitates such as AlN or MnS[Se] as grain growth inhibitors. This manufacturing method has the advantage of being able to stably cause secondary recrystallization; however, in order to exhibit a strong crystal grain growth inhibition effect, the precipitates must be distributed very finely and uniformly in the steel sheet. In order to uniformly distribute such fine precipitates, the slab must be heated to a high temperature for a long time before hot rolling to dissolve coarse precipitates present in the steel sheet, and then hot rolling must be performed within a very short time to finish the hot rolling in a state where precipitation has not occurred. For this purpose, large-scale slab heating facilities are required, and there are constraints such that the hot rolling and coiling processes must be managed very strictly to suppress precipitation as much as possible, and the dissolved precipitates must be managed to be finely precipitated in the hot-rolled sheet annealing process after hot rolling. In addition, when the slab is heated to a high temperature, a slab washing phenomenon occurs as Fe_2SiO_4 having a low melting point is formed, which reduces the yield.

55 **[0006]** A recently developed grain-oriented electrical steel sheet manufacturing technology utilizing a low-temperature slab heating method forms secondary recrystallization via Al-based nitrides, achieved through nitriding treatment

following decarburization annealing and cold rolling. This method has improved many issues, such as difficulties in operating slab heating facilities and a decrease in yield at the hot rolling stage, by relatively lowering the slab heating temperature. However, to utilize this method, an additional process for forming a nitride-based inhibitor during the annealing process after slab heating is required. To this end, nitriding treatment is performed using ammonia gas during the primary recrystallization annealing process. Ammonia gas possesses the property of decomposing into hydrogen and nitrogen at temperatures of about 500°C or higher; this property is utilized to perform nitridation, whereby the permeated nitrogen reacts with nitride-forming elements in the steel sheet to form nitrides, such as AlN and (Al,Si)N, which serve as inhibitors.

[0007] As regulations on transformer efficiency are tightened worldwide, the demand for thin grain-oriented electrical steel sheet is increasing. In general, as the thickness decreases, the precipitates lose their grain growth inhibition force relatively quickly during secondary recrystallization annealing, rendering the secondary recrystallization behavior unstable. As a result, the degree of texture for the Goss orientation is inferior, and the hysteresis loss increases, which offsets the eddy current loss improvement effect resulting from the reduced thickness. To address this, technologies for strengthening the grain growth inhibition force by using precipitates other than Al-based nitrides have been developed, but there remains a problem in that purification annealing may not be performed perfectly.

[Disclosure]

[Technical Problem]

[0008] An embodiment of the present invention provides a method of manufacturing a grain-oriented electrical steel sheet. Specifically, an embodiment of the present invention provides a method of manufacturing a grain-oriented electrical steel sheet having excellent magnetic properties by appropriately controlling conditions during hot rolling to stably form secondary recrystallization into the Goss {110}<001> orientation.

[Technical Solution]

[0009] A grain-oriented electrical steel sheet according to an embodiment of the present invention comprises, in wt%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, with the balance being Fe and inevitable impurities, wherein a fraction of textures in which an angle between the <110> direction and the Normal Direction (ND) is 5° or less is 60 area% or more.

[0010] The grain-oriented electrical steel sheet according to an embodiment of the present invention, a fraction of textures in which an angle between the <001> direction and ND is 5° or less is 70 area% or more.

[0011] The grain-oriented electrical steel sheet according to an embodiment of the present invention may further include at least one of C: 0.005 wt% or less, N: 0.01 wt% or less, and S: 0.01 wt% or less.

[0012] The grain-oriented electrical steel sheet according to an embodiment of the present invention may further include at least one of P: 0.0005 to 0.045 wt%, Sn: 0.03 to 0.08 wt%, and Cr: 0.01 to 0.20 wt%.

[0013] A manufacturing method of grain-oriented electrical steel sheet according to an embodiment of the present invention comprises: a step of manufacturing a hot-rolled sheet by hot rolling a slab comprising, in wt%, C: 0.03 to 0.07%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, with a balance of Fe and inevitable impurities; a step of manufacturing a preliminary rolled sheet by preliminary rolling the hot-rolled sheet; a hot-rolled sheet annealing step of annealing the preliminary rolled sheet; a step of manufacturing a cold-rolled sheet by cold rolling the annealed preliminary rolled sheet; a step of primary recrystallization annealing the cold-rolled sheet; and a step of secondary recrystallization annealing the primary recrystallization annealed steel sheet.

[0014] The step of manufacturing a hot-rolled sheet comprises a step of manufacturing a bar by rough rolling a slab and a step of finish rolling the bar to manufacture a hot-rolled sheet, wherein in the step of manufacturing the bar, an average A value calculated by the following Equation 1 is 1.35 to 1.65.

$$A = 2 \times (\text{work roll diameter} \times (\text{thickness before rolling} - \text{thickness after rolling}))^{0.5} / (\text{thickness before rolling} + \text{thickness after rolling}) \quad \text{[Equation 1]}$$

(In Equation 1, the units of the work roll diameter, thickness before rolling, and thickness after rolling are all mm.)

[0015] The slab may further comprise at least one of N: 0.01 wt% or less and S: 0.01 wt% or less.

[0016] The slab may further comprise at least one of P: 0.0005 to 0.045 wt%, Sn: 0.03 to 0.08 wt%, and Cr: 0.01 to 0.20 wt%.

[0017] In the step of manufacturing the bar, the total passes may be 3 to 8 times.

[0018] In the step of manufacturing a preliminary rolled sheet, the reduction ratio may be 20 to 50%.

[0019] After the hot-rolled sheet annealing step, in the ODF analysis of the steel sheet, the intensity of orientation at

$\phi_1=90^\circ$, $\Phi=65^\circ$, and $\phi_2=45^\circ$ may be 2.0 or more.

[Advantageous Effects]

[0020] A grain-oriented electrical steel sheet and a manufacturing method thereof according to an embodiment of the present invention exhibit excellent magnetic properties by stably growing crystal grains having a very high degree of texture in the Goss orientation.

[Mode for Invention]

[0021] 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 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.

[0022] The terminology used herein is for the purpose of referring to specific embodiments only and is not intended to be limiting of the present invention. As used herein, the singular forms include the plural forms as well unless the phrases clearly indicate the opposite. The meaning of "comprising" as 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.

[0023] When a part is referred to as being "on" or "over" another part, it may be directly on or over the other part, or another part may be interposed therebetween. In contrast, when a part is referred to as being "directly on" another part, no other part is interposed therebetween.

[0024] Unless otherwise defined, all terms, including technical and scientific terms, used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Terms defined in a commonly used dictionary shall be interpreted as having a meaning consistent with their meaning in the context of the related technical literature and the present disclosure, and shall not be interpreted in an ideal or overly formal sense unless explicitly defined herein.

[0025] In addition, unless otherwise specifically mentioned, % means wt%, and 1 ppm is 0.0001 wt%.

[0026] In an embodiment of the present invention, the term 'further including an additional element' means including the additional element by replacing the balance iron (Fe) by an amount equal to the additional amount of the additional element.

[0027] Hereinafter, embodiments of the present invention will be described in detail so that a person of ordinary skill in the art to which the present invention belongs may easily implement the same. However, the present invention may be implemented in various different forms and is not limited to the embodiments described herein.

[0028] A grain-oriented electrical steel sheet according to an embodiment of the present invention comprises, in wt%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, and balance Fe and inevitable impurities, wherein a fraction of textures where the <110> direction makes an angle of 5° or less with the Normal Direction (ND) is 60 area% or more.

[0029] The reasons for limiting the alloying elements of the steel sheet will be described below.

Si: 2.0 to 5.0 wt%

[0030] Silicon (Si) is a base component of an electrical steel sheet and serves to lower core loss, i.e., iron loss, by increasing the electrical resistivity of the material. If the Si content is too low, the electrical resistivity decreases and the iron loss characteristics may deteriorate. In addition, during decarburization annealing, phase transformation between ferrite and austenite becomes active, and the primary recrystallization texture may be severely damaged. Also, during secondary recrystallization annealing, phase transformation between ferrite and austenite occurs, so that secondary recrystallization becomes unstable and the Goss texture may be severely damaged. If Si is excessively added to the slab, SiO_2 and Fe_2SiO_4 oxide layers are excessively and densely formed during decarburization annealing, which may delay the decarburization behavior. Furthermore, the brittleness, which is a mechanical property of the electrical steel sheet, increases and the toughness decreases, such that the rate of sheet breakage during the rolling process may increase. Accordingly, the weldability between sheets may be inferior, making it difficult to ensure efficient workability. Therefore, in an embodiment of the present invention, Si may be included in an amount of 2.0 to 5.0 wt%. More specifically, it may be included in an amount of 2.5 to 4.5 wt%. More specifically, it may be included in an amount of 3.0 to 3.5 wt%.

Al: 0.005 to 0.040 wt%

[0031] Aluminum (Al) serves as a strong grain growth inhibitor by forming nitrides in the form of (Al, Si, Mn)N, (Al, Si)N, and AlN, as nitrogen ions introduced by ammonia gas during the annealing process after cold rolling combine with Al, Si, and Mn present in a solid solution state in the steel, in addition to the AlN finely precipitated during hot rolling and hot-rolled sheet annealing. If Al is included in an excessively small amount, it is difficult to expect a sufficient effect as an inhibitor because the number and volume of the nitrides formed are at a considerably low level. If Al is included in an excessively large amount, the grain growth inhibition force may decrease due to the formation of coarse nitrides. More specifically, Al may be included in an amount of 0.010 to 0.030 wt%.

Mn: 0.01 to 0.20 wt%

[0032] Manganese (Mn), like Si, has an effect of reducing iron loss by increasing electrical resistivity. It is an important element in causing secondary recrystallization by suppressing the growth of primary recrystallized grains through the formation of (Al, Si, Mn)N precipitates, which result from a reaction with nitrogen introduced by nitriding treatment in the presence of Si. If the Mn content is too low, it is difficult to expect a sufficient effect as an inhibitor because the number and volume of the precipitates formed are at a low level. If the content is too high, a large amount of (Fe, Mn) and Mn oxides are formed in addition to Fe_2SiO_4 on the surface of the steel sheet; this interferes with the formation of the base coating during secondary recrystallization annealing, thereby deteriorating the surface quality. Furthermore, it causes nonuniformity of phase transformation between ferrite and austenite in the primary recrystallization annealing process, resulting in non-uniform size of the primary recrystallized grains, and as a result, secondary recrystallization becomes unstable. Therefore, the content of Mn may be 0.01 to 0.20 wt%. Preferably, the content may be 0.05 to 0.15 wt%.

[0033] The grain-oriented electrical steel sheet according to an embodiment of the present invention may further include at least one of C: 0.005 wt% or less, N: 0.01 wt% or less, and S: 0.01 wt% or less.

C: 0.005 wt% or less

[0034] Carbon (C) is an element that contributes to refining crystal grains and improving elongation by inducing a phase transformation between ferrite and austenite. C is an essential element for improving the rollability of an electrical steel sheet, which otherwise exhibits poor rollability due to high brittleness. However, if C remains in the final product, it is an element that deteriorates magnetic properties by causing carbides, which are formed due to a magnetic aging effect, to precipitate in the product sheet; therefore, the content of C must be controlled to an appropriate level.

[0035] If the content of C in the slab is too low within the above-described Si content range, the inter-austenite phase transformation does not sufficiently occur, causing nonuniformity in the microstructures of the slab and the hot-rolled material. This also deteriorates cold rolling properties.

[0036] If the C content is too high within the above-described Si content range, sufficient decarburization may not be obtained in the decarburization annealing process. Due to the phase transformation phenomenon caused thereby, the secondary recrystallization texture may be severely damaged. Furthermore, when the final product is applied to power equipment, it may cause deterioration of magnetic properties due to magnetic aging.

[0037] Therefore, the content of C in the slab may be 0.03 to 0.07 wt%. More specifically, it may be 0.050 to 0.065 wt%.

[0038] In an embodiment of the present invention, a decarburization annealing is performed during the manufacturing process, and a C content in the final grain-oriented electrical steel sheet manufactured after the decarburization annealing may be 0.005 wt% or less. More specifically, the C content may be 0.003 wt% or less. Even more specifically, the C content may be 0.0001 to 0.0030 wt%.

N: 0.0100 wt% or less

[0039] Nitrogen (N) is an important element that reacts with Al to form an AlN precipitate. If an excessive amount of N is added, it causes a surface defect called 'blister' due to nitrogen diffusion in processes after hot rolling; furthermore, since an excessive amount of nitrides is formed in the slab state, rolling becomes difficult, which complicates subsequent processes and may cause manufacturing costs to rise. Meanwhile, additional N required to form nitrides, such as those selected from the group consisting of (Al, Si, Mn)N, (Al, Si)N, AlN, (B, Si, Mn)N, (Al, B)N, and BN, may be supplemented by performing a nitriding treatment on the steel using ammonia gas in an annealing process after cold rolling. Thereafter, a portion of the N is removed in a secondary recrystallization annealing process, and the N may be included in the finally manufactured grain-oriented electrical steel sheet in an amount of 0.0100 wt% or less. More

specifically, the N may be included in an amount of 0.0001 to 0.0070 wt%. Even more specifically, the N may be included in an amount of 0.001 to 0.005 wt%.

S: 0.010 wt% or less

[0040] Sulfur (S) is an element that has a high solid solution temperature and exhibits severe segregation during hot rolling; therefore, it is preferable to minimize its content. Sulfur is a type of inevitable impurity present during steelmaking. In addition, since S forms MnS, which affects the primary grain size, the content of S may be limited to 0.01 wt% or less. More specifically, S may be included in an amount of 0.0001 to 0.0070 wt%. Still more specifically, it may be included in an amount of 0.001 to 0.005 wt%.

[0041] The grain-oriented electrical steel sheet according to an embodiment of the present invention may further include at least one of P: 0.0005 to 0.045 wt%, Sn: 0.03 to 0.08 wt%, and Cr: 0.01 to 0.20 wt%.

P: 0.0005 to 0.0450 wt%

[0042] Phosphorus (P) segregates at the grain boundary to hinder the movement of the grain boundary and at the same time may serve an auxiliary role in suppressing grain growth, and has the effect of improving the {110}<001> texture in terms of microstructure. If the P content is too low, the addition effect may not be sufficient. If too much P is included, brittleness increases and rollability may deteriorate significantly. Therefore, when P is further included, it may be included in an amount of 0.0005 to 0.0450 wt%. More specifically, it may be included in an amount of 0.0010 to 0.0400 wt%. Even more specifically, it may be included in an amount of 0.0100 to 0.0300 wt%.

Sn: 0.03 to 0.08 wt%

[0043] Tin (Sn), like P, is a grain boundary segregation element and is known as a grain growth inhibitor because it is an element that hinders the movement of the grain boundary. In the Si content range proposed in an embodiment of the present invention, since the grain growth inhibition force for smooth secondary recrystallization behavior during secondary recrystallization annealing is insufficient, it may be supplemented by further adding Sn, which hinders the movement of the grain boundary by segregating at the grain boundary. When Sn is further added, if too little Sn is added, the effect may not be sufficient. If too much Sn is added, it may become difficult to obtain stable secondary recrystallization because the growth inhibition force is too strong. Therefore, when Sn is further added, the content of Sn may be 0.03 to 0.08 wt%. More specifically, Sn may be included in an amount of 0.05 to 0.07 wt%.

Cr: 0.01 to 0.20 wt%

[0044] Chromium (Cr) promotes the formation of a hard phase in the hot-rolled annealed sheet to promote the formation of the Goss texture during cold rolling, and promotes decarburization of C during the decarburization annealing process, thereby exhibiting the effect of reducing the austenite phase transformation maintenance time to prevent the phenomenon in which the texture is damaged due to the long austenite phase transformation maintenance time, which is a disadvantage when the C content is high. In addition, Cr may be additionally added as it may solve the disadvantage that the formation of the oxide layer is inhibited by Sn among alloying elements used as auxiliary grain growth inhibitors by promoting the formation of the oxide layer on the surface formed during the decarburization annealing process. If Cr is added in too small an amount, its addition effect may not be sufficient. If too much Cr is included, it promotes the formation of a denser oxide layer when forming the oxide layer during the decarburization process of primary recrystallization annealing, so that the oxide layer formation is rather inferior and may even interfere with decarburization and nitridation. Therefore, when Cr is further included, the content of Cr may be 0.01 to 0.20 wt%. More specifically, Cr may be further included in an amount of 0.05 to 0.15 wt%.

[0045] In addition to the above-described components, alloying elements advantageous for the formation of the Goss texture may be added as needed. For example, it may further include at least one of Cu: 0.001 to 0.050 wt%, Se: 0.001 to 0.050 wt%, Sb: 0.01 to 0.08 wt%, and Ni: 0.02 to 0.5 wt%.

[0046] The balance consists of Fe and inevitable impurities. The inevitable impurities are impurities incorporated during the steelmaking stage and the manufacturing process of the grain-oriented electrical steel sheet, and since this is widely known in the art, a specific description thereof will be omitted. Specifically, components such as Ti, Mg, and Ca react with oxygen in the steel to form oxides, so it is necessary to suppress them strongly; accordingly, each component may be managed at 0.005 wt% or less. In an embodiment of the present invention, the addition of elements other than the aforementioned alloying elements is not excluded, and such elements may be included in various ways within a range that does not depart from the technical spirit of the present invention. When additional elements are further included, they are included in place of the balance Fe.

[0047] In the grain-oriented electrical steel sheet according to an embodiment of the present invention, a fraction of textures where the <110> direction makes an angle of 5.000° or less with the Normal Direction (ND) is 60 area% or more. In an embodiment of the present invention, a large number of crystal grains more accurately aligned such that the <110> direction makes an angle of 5.000° or less with the Normal Direction (ND) may be generated, through which magnetic properties may be improved. More specifically, the fraction of textures where the <110> direction makes an angle of 5.000° or less with the Normal Direction (ND) may be 75 to 90 area %.

[0048] In the grain-oriented electrical steel sheet according to an embodiment of the present invention, a fraction of textures where the <001> direction makes an angle of 5° or less with the Normal Direction (ND) may be 70 area% or more. In an embodiment of the present invention, a large number of crystal grains more accurately aligned such that the <001> direction makes an angle of 5° or less with the Normal Direction (ND) may be generated, through which magnetic properties may be improved. If the fraction of the crystal grains is small, it is difficult to obtain sufficient improvement in magnetic properties. More specifically, the fraction of textures where the <001> direction makes an angle of 5° or less with the Normal Direction (ND) may be 72 to 90 area %. The fraction of textures where the <001> direction makes an angle of 5° or less with the Normal Direction (ND) may be measured using an X-ray Laue method.

[0049] The grain-oriented electrical steel sheet according to an embodiment of the present invention simultaneously exhibits excellent magnetic flux density and iron loss characteristics. The grain-oriented electrical steel sheet according to an embodiment of the present invention may have a magnetic flux density (B_8) of 1.91 T or more. Here, the magnetic flux density B_8 is the magnitude (Tesla) of the magnetic flux density induced under a magnetic field of 800 A/m. More specifically, the grain-oriented electrical steel sheet according to an embodiment of the present invention may have a magnetic flux density (B_{10}) of 1.91 to 2.00 T. In addition, the grain-oriented electrical steel sheet according to an embodiment of the present invention may have an iron loss ($W_{17/50}$) of 0.67 W/kg or less. The iron loss $W_{17/50}$ is the iron loss measured at 1.7 Tesla and 50 Hz. More specifically, the iron loss ($W_{17/50}$) may be 0.50 to 0.65 W/kg. In this case, the thickness of the steel sheet may be 0.20 mm.

[0050] A manufacturing method of a grain-oriented electrical steel sheet according to an embodiment of the present invention comprises: a step of manufacturing a hot-rolled sheet by hot rolling a slab comprising, in wt%, C: 0.03 to 0.07%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, with the balance being Fe and inevitable impurities; a step of manufacturing a preliminary rolled sheet by preliminary rolling the hot-rolled sheet; a hot-rolled sheet annealing step of annealing the preliminary rolled sheet; a step of manufacturing a cold-rolled sheet by cold rolling the annealed preliminary rolled sheet; a step of primary recrystallization annealing the cold-rolled sheet; and a step of secondary recrystallization annealing the primary recrystallization annealed steel sheet.

[0051] First, a hot-rolled sheet is manufactured by hot rolling a slab. Since the steel composition of the slab has been described in the above-described grain-oriented electrical steel sheet, redundant description will be omitted. Components other than C may be substantially the same.

[0052] A step of heating the slab before hot rolling the slab may be further included.

[0053] Slab heating may be performed at a temperature range of 1000 to 1250°C, a range in which N and S undergo incomplete solutionization. When N and S undergo complete solutionization, a large amount of nitrides or sulfides are finely precipitated after hot-rolled sheet annealing, rendering the subsequent single heavy cold rolling impossible, and the primary grain size is formed to be excessively fine, such that appropriate secondary recrystallization may not be formed. More specifically, the slab heating temperature may be 1050 to 1200°C.

[0054] In an embodiment of the present invention, the step of manufacturing a hot-rolled sheet includes a step of manufacturing a bar by rough rolling a slab and a step of finish rolling the bar to manufacture the hot-rolled sheet. Rough rolling is a step of manufacturing a bar having a thickness of 40 mm to 70 mm by rolling the slab. If the rough rolling thickness is too high, the latent heat on the surface of the steel sheet is high, and the rolling speed decreases, thereby increasing the growth of scale during rolling, which is disadvantageous for descaling of a hot-rolled coil. On the other hand, if the rough rolling thickness is too thin, the cooling of the steel material becomes fast, such that rollability may be lowered. More specifically, the thickness may be 45 mm to 65 mm. Finish rolling is a step of manufacturing the hot-rolled steel sheet by rolling the bar. The method may further include a coiling step of coiling the steel sheet manufactured after finish rolling.

[0055] In an embodiment of the present invention, the step of manufacturing the bar is characterized in that the average A value, calculated by the following Equation 1, is 1.35 to 1.65.

$$A = 2 \times (\text{work roll diameter} \times (\text{thickness before rolling} - \text{thickness after rolling}))^{0.5} / (\text{thickness before rolling} + \text{thickness after rolling}) \quad [\text{Equation 1}]$$

(In Equation 1, the units of the work roll diameter, thickness before rolling, and thickness after rolling are all mm.)

[0056] The 'average A value' refers to the average obtained by dividing the total sum of the A values for each pass by the number of passes, when the step of manufacturing the bar comprises a plurality of passes. A 'pass' refers to the number of times the bar passes through a work roll.

[0057] If the average of A value is too small, it means that the number of passes is large, which leads to a small reduction ratio per pass, or that the reduction ratio per pass at the front end of rough rolling is low while the reduction ratio per pass at the rear end is high. In the former case, the reduction ratio per pass decreases, whereby the shear deformation applied to the steel sheet decreases, leading to a problem in which the Goss fraction in the hot-rolled sheet decreases. In the latter case, the rolling load at the rear end of rough rolling is excessively high, which leads to difficulties in production. If the average of A value is too large, it means that the number of passes is small, which leads to an excessively high reduction ratio per pass, or that the total reduction ratio of rough rolling is high. In both the former and latter cases, difficulties in production occur due to an excessively high rolling load, and in the latter case in particular, there is a problem in which the Goss fraction in the hot-rolled sheet decreases as the total reduction ratio of finish rolling decreases. More specifically, the average of A value may be 1.35 to 1.60.

[0058] The total reduction ratio of rough rolling may be 70% or more. The step of manufacturing the bar may involve a total number of passes of 3 to 8.

[0059] The hot-rolled sheet may be manufactured to a thickness of 1.5 to 5.0 mm so that pre-rolling and final cold rolling may be applied.

[0060] The hot rolling temperature or cooling temperature is not particularly limited, but as an example of excellent magnetic properties, the hot rolling finishing temperature may be 950°C or lower, and cooling may be performed by quenching with water to coil at 600°C or lower.

[0061] A preliminary rolled sheet is manufactured by preliminary rolling the hot-rolled sheet. Before manufacturing the preliminary rolled sheet, pickling may be performed as needed. By adding the step of manufacturing a preliminary rolled sheet, the thickness of the finally manufactured grain-oriented electrical steel sheet may be further reduced without adding to the load in cold rolling, which will be described later. The reduction ratio during preliminary rolling may be 20.0 to 50.0%. If the reduction ratio is too small, the effect of improving the texture by preliminary rolling is small, and if the reduction ratio is too large, the hot-rolled sheet thickness becomes excessively thick, and edge cracks or the like may occur. More specifically, the reduction ratio during preliminary rolling may be 20.0 to 45.0%. The reduction ratio may be calculated as (thickness before rolling - thickness after rolling) / (thickness before rolling) × 100.

[0062] Next, in the hot-rolled sheet annealing step, the hot-rolled sheet is annealed. The hot-rolled sheet annealing is performed to control microstructure and precipitates, and after heating to a temperature of 1,000 to 1,250°C, the annealing may be performed at a soaking temperature of 950°C or lower.

[0063] When hot rolling and pre-rolling are appropriately controlled, the ODF intensity of the orientation of $\phi_1=90^\circ$, $\Phi=65^\circ$, and $\phi_2=45^\circ$ in the hot-rolled sheet annealing develops to 2.0 or more. The orientation is formed by the rotation of Goss grains formed during hot rolling as they undergo pre-rolling, and they quickly rotate to $\{111\}<112>$ during cold rolling. In general cold rolling, since the friction between the surface portion in the thickness direction and the rolling roll is small, shear deformation barely occurs, unlike in hot rolling, and only plane deformation, in which the steel sheet thickness decreases and the length increases, is applied. As a result, Goss grains, which are a stable structure in shear deformation, rotate to $\{111\}<112>$ during cold rolling and disappear, while a small amount is formed by shear deformation of shear bands within the $\{111\}<112>$ deformed structure. When hot rolling and pre-rolling are appropriately controlled, not only does the fraction of the $\{111\}<112>$ deformed structure increase, but the amount of Goss grains formed in the shear bands also increases because they are formed quickly during cold rolling. More specifically, the ODF intensity of the orientation of $\phi_1=90^\circ$, $\Phi=65^\circ$, and $\phi_2=45^\circ$ may be 2.3 to 3.5. ODF analysis may be performed by EBSD such that the entire thickness is included in either a plane perpendicular to the TD (TD plane) or a plane perpendicular to the RD (RD plane). The scan size may be set to 'entire thickness' x '3 mm or more'.

[0064] Next, a cold-rolled sheet is manufactured by cold rolling the hot-rolled sheet.

[0065] Cold rolling is performed using a reverse rolling mill or a tandem rolling mill by a method of one-time cold rolling, or two or more cold rolling passes including an intermediate annealing, to manufacture a cold-rolled sheet having a final product thickness. Furthermore, performing warm rolling, in which the temperature of the steel sheet is maintained at 100°C or higher during the cold rolling, is advantageous for improving magnetic properties. Through the cold rolling, the cold-rolled sheet may be manufactured to have a final thickness of 0.10 to 0.50 mm, more specifically 0.15 to 0.35 mm.

[0066] Next, the cold-rolled sheet is subjected to primary recrystallization annealing. At this time, decarburization, nitridation, and primary recrystallization occur. The steel sheet may be heat-treated at an annealing temperature in a range of 800 to 950°C. If the annealing temperature of the steel sheet is low, it takes a long time for decarburization, and if the annealing temperature is too high, the crystal grains grow coarsely and the driving force for grain growth decreases, so that stable secondary recrystallization is not formed. And the annealing time does not matter much in exerting the effect of the present invention, but may be treated within 5 minutes.

[0067] Decarburization and nitridation may be performed by a nitriding treatment using ammonia gas after completing decarburization and recrystallization, or by a method of using ammonia gas concurrently so that decarburization and nitriding treatment may be performed simultaneously.

[0068] Next, the cold-rolled sheet that has been subjected to primary recrystallization annealing is subjected to secondary recrystallization annealing. The primary recrystallized steel sheet is subjected to secondary recrystallization annealing after applying an annealing separator so that a Goss $\{110\}<001>$ texture is formed, in which the $\{110\}$ plane is parallel to the rolling surface and the $<001>$ direction is parallel to the rolling direction. The annealing separator is not particularly limited, and an annealing separator containing MgO as a main component may be used. As annealing separators are widely known, a detailed description thereof will be omitted.

[0069] Secondary recrystallization high-temperature annealing may be performed by raising the temperature at an appropriate heating rate to induce secondary recrystallization of the $\{110\}<001>$ Goss orientation, followed by purification annealing as an impurity removal process and subsequent cooling. In this process, the annealing atmosphere gas used for heat treatment during the heating phase consists of a mixture of hydrogen and nitrogen as in a typical case, while during the purification annealing, the atmosphere is maintained with 100% hydrogen gas for a prolonged period to remove impurities.

[0070] Then, after removing unreacted MgO from the grain-oriented electrical steel sheet subjected to secondary recrystallization annealing, insulation coating and flattening annealing may be further performed. Flattening annealing is performed to remove residual stress generated during secondary recrystallization annealing and correct the shape, and may be performed at 800°C or higher.

[0071] The method may further include a step of irradiating a continuous wave mode CO₂ laser (TEM00) beam onto the surface of a grain-oriented electrical steel sheet subjected to flattening annealing and tension coating to improve iron loss through magnetic domain refinement. An optical system is configured such that the laser beam has an oval shape with a width of 0.05 to 0.20 mm and a length of 5 to 15 mm, and the laser is irradiated such that the longitudinal direction of the oval shape corresponds to the width direction of the steel sheet. The laser is irradiated at intervals of 3 to 7 mm in the longitudinal direction, and the laser may be irradiated at regular intervals throughout the steel sheet by controlling the rotation speed of a polygon mirror in conjunction with the speed of the steel sheet. The laser output intensity may be adjusted to an appropriate range where the iron loss improvement rate is favorable and the coating layer on the surface of the steel sheet is not excessively damaged.

[0072] Hereinafter, specific embodiments of the present invention will be described. However, the following embodiments are merely specific embodiments of the present invention, and the present invention is not limited to the following embodiments.

Example 1

[0073] A grain-oriented electrical steel comprising, in wt%, Si: 3.47%, Sol-Al: 0.029%, Mn: 0.097%, N: 0.005%, S: 0.005%, P: 0.028%, Sn: 0.063%, Cr: 0.11%, C: 0.063%, the balance being Fe and other inevitable impurities, was vacuum melted to form an ingot, which was subsequently heated to a temperature of 1150°C and hot rolled under the conditions shown in Table 1 below. Then, after pickling with a hydrochloric acid solution, pre-rolling was performed at the reduction ratio shown in Table 1 below. Next, the hot-rolled sheet was heated to a temperature of 1100°C, maintained at a soaking temperature of 900°C for 80 seconds, and quenched in water to perform hot-rolled sheet annealing. Subsequently, the hot-rolled annealed sheet was pickled and then cold rolled to the thickness shown in Table 1 below. The cold-rolled sheet was subjected to simultaneous decarburization and nitriding annealing in a humid mixed gas atmosphere of hydrogen, nitrogen, and ammonia at a temperature of 850°C for 180 seconds such that the nitrogen content was 200 ppm and the carbon content was 30 ppm. After applying MgO, as an annealing separator, to the steel sheet, final annealing was performed. The final annealing was carried out in a mixed gas atmosphere of 25 vol% nitrogen and 75 vol% hydrogen up to 1200°C, and after reaching 1200°C, the sheet was maintained in a 100% hydrogen gas atmosphere for 10 hours or more and then furnace-cooled. After the unreacted MgO was removed, an insulating coating composition containing phosphate and silica as main components was applied, followed by heat treatment to form an insulation film and subsequent flattening annealing. A continuous wave mode CO₂ laser (TEM00) beam was irradiated onto the surface of the grain-oriented electrical steel sheet, on which the insulation coating had been completed, for magnetic domain refinement. The laser beam was in an oval shape with a width and length of 0.1 mm and 10 mm, respectively, and was irradiated at intervals of 5.0 mm such that the longitudinal direction of the oval was the width direction of the steel sheet. The $<110>$ direction and $<001>$ direction of the crystal grains of the grain-oriented electrical steel sheet according to each condition, the angle with the Normal Direction (ND), and the magnetic properties are shown in Table 1.

[0074] The intensity of the orientation at ODF $\varphi_1=90^\circ$, $\Phi=65^\circ$, and $\varphi_2=45^\circ$ after hot-rolled sheet annealing was measured by EBSD on a plane perpendicular to the TD (TD plane) through the entire thickness $x \times 3$ mm.

[0075] The angles of the $<110>$ and $<001>$ directions of the crystal with respect to the Normal Direction (ND) were measured using the X-ray Laue method. The specimens for measuring magnetic properties were scanned at regular intervals, and the ratio of the number of points at which the angle of the $<110>$ and $<001>$ directions of the crystal with respect to the Normal Direction (ND) was 5° or less to the total number of points was calculated.

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[0076] Magnetic flux density and iron loss were measured using a single sheet measurement method, magnetic flux density B8 is the magnitude of magnetic flux density (Tesla) induced under a magnetic field of 800 A/m, and iron loss W17/50 is the loss (W/kg) when a magnetic flux density of 1.7 Tesla is induced at a frequency of 50 Hz.

[Table 1]

Steel No.	Number of rough rolling passes	Average A value	Pre-rolling reduction ratio (%)	ODF intensity of orientation at $\phi 1=90^\circ$, $\Phi=65^\circ$, and $\phi 2=45^\circ$ after hot-rolled sheet annealing	Cold-rolled sheet thickness (mm)
1	6	1.44	0.0	1.4	0.23
2	6	1.44	9.8	1.6	0.23
3	6	1.44	20.7	2.6	0.23
4	6	1.44	28.1	3.0	0.23
5	6	1.44	0.0	1.3	0.20
6	6	1.44	13.0	1.8	0.20
7	6	1.44	21.6	2.5	0.20
8	6	1.44	31.0	3.2	0.20
9	6	1.44	37.5	3.3	0.20
10	6	1.44	10.0	1.6	0.18
11	6	1.44	21.7	2.6	0.18
12	6	1.44	29.4	3.1	0.18
13	6	1.44	37.9	3.2	0.18
14	6	1.44	43.8	2.9	0.18
15	6	1.35	0.0	0.8	0.20
16	6	1.35	21.6	2.0	0.20
17	6	1.40	0.0	1.0	0.20
18	6	1.40	21.6	2.3	0.20
19	7	1.32	21.6	1.8	0.20
20	5	1.56	21.6	2.8	0.20

[Table 2]

Steel No.	Fraction where the <110> direction makes an angle of 5° or less with ND (area%)	Fraction where the <001> direction makes an angle of 5° or less with ND (area%)	Magnetic flux density (B8, Tesla)	Iron loss (W17/50, W/kg)	Classification
1	53	68	1.90	0.75	Comparative Example 1
2	56	69	1.90	0.75	Comparative Example 2
3	76	76	1.92	0.68	Inventive Example 1
4	84	82	1.93	0.66	Inventive Example 2
5	45	66	1.89	0.70	Comparative Example 3
6	58	69	1.90	0.69	Comparative Example 4
7	77	76	1.92	0.62	Inventive Example 3
8	87	82	1.93	0.60	Inventive Example 4
9	86	83	1.93	0.60	Inventive Example 5

(continued)

Steel No.	Fraction where the <110> direction makes an angle of 5° or less with ND (area%)	Fraction where the <001> direction makes an angle of 5° or less with ND (area%)	Magnetic flux density (B ₈ , Tesla)	Iron loss (W17/50, W/kg)	Classification
10	48	67	1.89	0.65	Comparative Example 5
11	76	78	1.92	0.58	Inventive Example 6
12	83	82	1.93	0.55	Inventive Example 7
13	84	81	1.93	0.56	Inventive Example 8
14	78	79	1.92	0.56	Inventive Example 9
15	32	62	1.88	0.73	Comparative Example 6
16	63	72	1.91	0.65	Inventive Example 10
17	45	65	1.89	0.71	Comparative Example 7
18	73	75	1.92	0.63	Inventive Example 11
19	55	68	1.90	0.69	Comparative Example 8
20	81	80	1.93	0.61	Inventive Example 12

[0077] As can be seen from Table 1 and Table 2, in the Inventive Examples in which process conditions were appropriately controlled, the texture may be appropriately formed, and it may be confirmed that magnetic flux density and iron loss are excellent simultaneously. On the other hand, in the Comparative Examples in which process conditions were not appropriately controlled, the texture may not be properly developed, and it may be confirmed that magnetic flux density and iron loss are inferior.

[0078] The present invention is not limited to the above-described embodiments and/or examples, but may be manufactured in various different forms, and a person of ordinary skill in the art to which the present invention belongs will understand that the present invention may be implemented in other specific forms without changing the technical spirit or essential features of the present invention. Therefore, the embodiments and/or examples described above should be understood as illustrative in all respects and not restrictive.

Claims

1. A grain-oriented electrical steel sheet comprising, in wt%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, the balance being Fe and inevitable impurities, wherein a fraction of textures in which an angle between <110> direction and Normal Direction is 5° or less is 60 area% or more.
2. The grain-oriented electrical steel sheet of Claim 1, wherein a fraction of textures in which an angle between <001> direction and Normal Direction is 5° or less is 70 area% or more.
3. The grain-oriented electrical steel sheet of Claim 1, further comprising at least one of C: 0.005 wt% or less, N: 0.01 wt% or less, and S: 0.01 wt% or less.
4. The grain-oriented electrical steel sheet of Claim 1, further comprising at least one of: P: 0.0005 to 0.045 wt%, Sn: 0.03 to 0.08 wt%, and Cr: 0.01 to 0.20 wt%.
5. A manufacturing method of grain-oriented electrical steel sheet comprising:
 - a step of manufacturing a hot-rolled sheet by hot rolling a slab comprising, in wt%, C: 0.03 to 0.07%, Si: 2.0 to 5.0%, Al: 0.005 to 0.04%, and Mn: 0.01 to 0.20%, with a balance of Fe and inevitable impurities;
 - a step of manufacturing a preliminary rolled sheet by preliminary rolling the hot-rolled sheet;

a hot-rolled sheet annealing step of annealing the preliminary rolled sheet;
a step of manufacturing a cold-rolled sheet by cold rolling the annealed preliminary rolled sheet;
a step of primary recrystallization annealing the cold-rolled sheet; and
a step of secondary recrystallization annealing the primary recrystallization annealed steel sheet;
wherein the step of manufacturing a hot-rolled sheet comprises a step of manufacturing a bar by rough rolling
a slab and a step of finish rolling the bar to manufacture a hot-rolled sheet,
wherein in the step of manufacturing the bar, an average A value calculated by the following Equation 1 is
1.35 to 1.65.

$$A = 2 \times (\text{work roll diameter} \times (\text{thickness before rolling} - \text{thickness after rolling}))^{0.5} / (\text{thickness before rolling} + \text{thickness after rolling}) \quad [\text{Equation 1}]$$

(In Equation 1, the units of the work roll diameter, thickness before rolling, and thickness after rolling are all mm.)

6. The manufacturing method of grain-oriented electrical steel sheet of Claim 5,
wherein the slab further comprises at least one of N: 0.01 wt% or less and S: 0.01 wt% or less.
7. The manufacturing method of grain-oriented electrical steel sheet of Claim 5,
wherein the slab further comprises at least one of P: 0.0005 to 0.045 wt%, Sn: 0.03 to 0.08 wt%, and Cr: 0.01 to 0.20 wt%.
8. The manufacturing method of grain-oriented electrical steel sheet of Claim 5,
wherein the step of manufacturing the bar comprises a total number of passes of 3 to 8.
9. The manufacturing method of grain-oriented electrical steel sheet of Claim 5,
wherein in the step of manufacturing a preliminary rolled sheet, the reduction ratio is 20 to 50%.
10. The manufacturing method of grain-oriented electrical steel sheet of Claim 1,
wherein, after the hot-rolled sheet annealing step, in the ODF analysis of the steel sheet, the intensity of orientation at $\phi 1=90^\circ$, $\Phi=65^\circ$, and $\phi 2=45^\circ$ is 2.0 or more.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2024/063279

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i; **C22C 38/04**(2006.01)i; **C22C 38/06**(2006.01)i; **C22C 38/00**(2006.01)i; **C22C 38/34**(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 38/02(2006.01); C21D 8/12(2006.01); C21D 9/46(2006.01); C22C 38/00(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: 방향성(orientation), 전기강판(electrical steel), 실리콘(silicon), 알루미늄(aluminum), 망간(manganese), 재결정 소둔(recrystallization annealing), 고스 집합조직(goss texture), 조압연(rough rolling)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-0347597 B1 (POSCO HOLDINGS INC. et al.) 23 November 2002 (2002-11-23) See paragraphs [0008]-[0009], [0013] and [0031] and claim 1.	1-10
Y	KR 10-2080166 B1 (POSCO) 21 February 2020 (2020-02-21) See paragraphs [0094]-[0098], [0112] and [0118], claim 4 and table 1.	1-10
A	KR 10-2020-0089321 A (JFE STEEL CORPORATION) 24 July 2020 (2020-07-24) See paragraphs [0103]-[0104].	1-10
A	JP 2015-098636 A (JFE STEEL CORP.) 28 May 2015 (2015-05-28) See paragraphs [0043]-[0045] and claim 1.	1-10
A	JP 2001-192785 A (KAWASAKI STEEL CORP.) 17 July 2001 (2001-07-17) See claims 1-4.	1-10

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

* Special categories of cited documents:

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

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“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
14 April 2025	14 April 2025
Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208	
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/IB2024/063279

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Patent document cited in search report				Publication date (day/month/year)		Patent family member(s)		Publication date (day/month/year)	
KR	10-0347597	B1		23 November 2002		KR	10-1997-0043184	A	26 July 1997
KR	10-2080166	B1		21 February 2020		KR	10-2019-0077890	A	04 July 2019
KR	10-2020-0089321	A		24 July 2020		CN	111417737	A	14 July 2020
						CN	111417737	B	02 November 2021
						EP	3733895	A1	04 November 2020
						EP	3733895	B1	30 March 2022
						JP	6601649	B1	06 November 2019
						KR	10-2437377	B1	26 August 2022
						RU	2744254	C1	04 March 2021
						US	11459633	B2	04 October 2022
						US	2020-0325555	A1	15 October 2020
						WO	2019-131853	A1	04 July 2019
JP	2015-098636	A		28 May 2015		JP	6079580	B2	15 February 2017
JP	2001-192785	A		17 July 2001		JP	4120121	B2	16 July 2008

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