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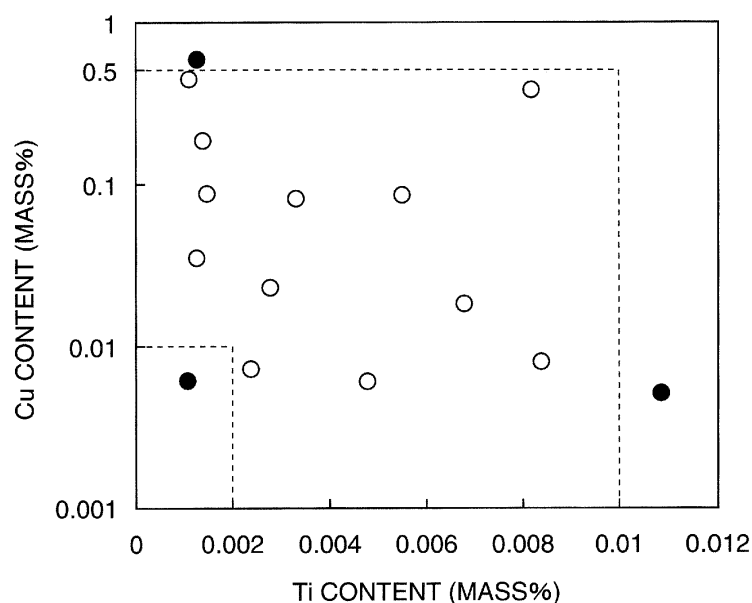
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(54) **MANUFACTURING METHOD FOR GRAIN-ORIENTED ELECTROMAGNETIC STEEL SHEET**

(57) Hot rolling is performed on a steel with a predetermined composition containing Ti: 0.0020 mass% to 0.010 mass% and/or Cu: 0.010 mass% to 0.50 mass% to obtain a hot-rolled steel sheet. Annealing is performed on the hot-rolled steel sheet to obtain an annealed steel sheet. Cold rolling is performed on the annealed steel

sheet to obtain a cold-rolled steel sheet. Decarburization annealing is performed on the cold-rolled steel sheet at a temperature of 800°C to 950°C to obtain a decarburization annealed steel sheet. Then, nitridation treatment is performed on the decarburization annealed steel sheet at 700°C to 850°C to obtain a nitrided steel sheet. Finish annealing is performed on the nitrided steel sheet.

FIG. 1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method of manufacturing a grain-oriented electrical steel sheet in which the variation in magnetic property is suppressed.

BACKGROUND ART

10 **[0002]** A grain-oriented electrical steel sheet is a steel sheet which contains Si and in which crystal grains are highly integrated in a {110}<001> orientation, and is used as a material of a wound core of a stationary induction apparatus such as a transformer. The control of the orientation of the crystal grains is conducted with catastrophic grain growth phenomenon called secondary recrystallization.

15 **[0003]** As a method of controlling the secondary recrystallization, the following two methods can be cited. In one method, heating is performed on a slab at a temperature of 1280°C or higher to almost completely solid-solve fine precipitates called inhibitors, and thereafter hot rolling, cold rolling, annealing and so on are performed to cause the fine precipitates to precipitate during the hot rolling and the annealing. In the other method, heating is performed on a slab at a temperature of lower than 1280°C, and thereafter hot rolling, cold rolling, decarburization annealing, nitridation, finish annealing and so on are performed to cause AlN (Al, Si)N and the like to precipitate as inhibitors during the nitridation.

20 **[0004]** In recent years, it has been requested to reduce a time taken for a decarburization annealing in a manufacturing process of a grain-oriented electrical steel sheet from a point of view of reduction in CO₂ emissions. Accordingly, it has been studied to use a slab whose C content is low.

25 **[0005]** However, lowering the C content of the slab causes a remarkable variation in magnetic property (magnetic property deviation) depending on site, after the finish annealing performed with the steel being coiled.

CITATION LIST

PATENT LITERATURE

30 **[0006]**

Patent Literature 1: Japanese Laid-open Patent Publication No. 03-122227

Patent Literature 2: Japanese Laid-open Patent Publication No. 11-323437

Patent Literature 3: Japanese Laid-open Patent Publication No. 06-256847

35 Patent Literature 4: Japanese National Publication of International Patent Application No. 2001-515540

Patent Literature 5: Japanese Laid-open Patent Publication No. 2000-199015

Patent Literature 6: Japanese Laid-open Patent Publication No. 2007-254829

SUMMARY OF INVENTION

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TECHNICAL PROBLEM

[0007] An object of the present invention is to provide a method of manufacturing a grain-oriented electrical steel sheet, capable of suppressing the variation in magnetic property.

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SOLUTION TO PROBLEM

[0008] It turned out that the above-described variation in magnetic properties after the finish annealing is remarkable when the C content is 0.06 mass% or less, and further, it is particularly noticeable when the C content is 0.048 mass% or less. Although the cause of the variation in magnetic property after the finish annealing is not exactly known, the variation is considered to occur because the crystal grains sometimes do not uniformly grow during the finish annealing even if the crystal grains seem to be uniform before the finish annealing. Further, it may be considered that the reason why the crystal grains do not uniformly grow is because, due to the low C content, a phase transformation during the hot rolling is not sufficiently performed, so that an amount of austenite transformation is small, resulting in that a hot-rolled texture becomes unstable. Specifically, it may be considered that a sufficient secondary recrystallization does not occur in a portion in which the hot-rolled texture becomes nonuniform, resulting in that sufficient magnetic properties are not obtained.

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[0009] The present inventors thought, based on such knowledge, that it is possible to sufficiently cause the secondary

recrystallization through forming an effective precipitate in order to make the crystal grain growth uniform during the finish annealing. Then, the present inventors repeatedly carried out an experiment of measuring the magnetic properties of the grain-oriented electrical steel sheets obtained through adding various kinds of elements to slabs. As a result, the present inventors found that addition of Ti and Cu was effective to make the secondary recrystallization uniform.

[0010] The present invention has been made based on the above-described knowledge, and a summary thereof is as follows.

[0011] (1) A method of manufacturing a grain-oriented electrical steel sheet, comprising:

performing hot rolling of a steel containing Si: 2.5 mass% to 4.0 mass%, C: 0.01 mass% to 0.060 mass%, Mn: 0.05 mass% to 0.20 mass%, acid-soluble Al: 0.020 mass% to 0.040 mass%, N: 0.002 mass% to 0.012 mass%, S: 0.001 mass% to 0.010 mass%, and P: 0.01 mass% to 0.08 mass%, further containing at least one kind selected from a group consisting of Ti: 0.0020 mass% to 0.010 mass% and Cu: 0.010 mass% to 0.50 mass%, and a balance composed of Fe and inevitable impurities, to obtain a hot-rolled steel sheet;

performing annealing on the hot-rolled steel sheet to obtain an annealed steel sheet;

performing cold rolling on the annealed steel sheet to obtain a cold-rolled steel sheet;

performing decarburization annealing on the cold-rolled steel sheet at a temperature of 800°C to 950°C to obtain a decarburization annealed steel sheet;

then, performing nitridation treatment on the decarburization annealed steel sheet at 700°C to 850°C to obtain a nitrided steel sheet; and

performing finish annealing on the nitrided steel sheet.

[0012] (2) The method of manufacturing a grain-oriented electrical steel sheet according to (1), wherein the hot rolling on the steel is performed after heating the steel to a temperature of 1250°C or lower.

[0013] (3) The method of manufacturing a grain-oriented electrical steel sheet according to (1) or (2), wherein the steel further contains at least one kind selected from a group consisting of Cr: 0.010 mass% to 0.20 mass%, Sn: 0.010 mass% to 0.20 mass%, Sb: 0.010 mass% to 0.20 mass%, Ni: 0.010 mass% to 0.20 mass%, Se: 0.005 mass% to 0.02 mass%, Bi: 0.005 mass% to 0.02 mass%, Pb: 0.005 mass% to 0.02 mass%, B: 0.005 mass% to 0.02 mass%, V: 0.005 mass% to 0.02 mass%, Mo: 0.005 mass% to 0.02 mass%, and As: 0.005 mass% to 0.02 mass%.

[0014] (4) The method of manufacturing a grain-oriented electrical steel sheet according to any one of (1) to (3), wherein a Ti content in the steel is 0.0020 mass% to 0.0080 mass%, a Cu content in the steel is 0.01 mass% to 0.10 mass%, and a relation of $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ is established where the Ti content (mass%) in the steel is expressed as [Ti] and the Cu content (mass%) is expressed as [Cu].

[0015] (5) The method of manufacturing a grain-oriented electrical steel sheet according to (4), wherein a relation of $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ is established.

ADVANTAGEOUS EFFECTS OF INVENTION

[0016] According to the present invention, appropriate amounts of Ti and/or Cu are contained in the steel, and decarburization annealing and nitridation treatment are performed at appropriate temperatures, thereby making it possible to suppress the variation in magnetic property.

BRIEF DESCRIPTION OF DRAWINGS

[0017]

[Fig. 1] Fig. 1 is a chart representing the relation between a Ti content and a Cu content and the magnetic flux density and the evaluation of its variation.

[Fig. 2] Fig. 2 is a flowchart illustrating a method of manufacturing a grain-oriented electrical steel sheet according to an embodiment of the present invention.

DESCRIPTION OF EMBODIMENTS

[0018] As described above, the present inventors repeatedly conducted the experiments of measuring the magnetic properties of the grain-oriented electrical steel sheets obtained through adding various kinds of elements to slabs and found out that addition of Ti and Cu is effective to make the secondary recrystallization uniform.

[0019] In the experiment, silicon steel with a composition used for manufacturing a grain-oriented electrical steel sheet based on a low-temperature slab heating method in which a C content was 0.06 mass% or less was used, for example.

Further, Ti and Cu were contained at various ratios into the carbon steel to produce steel ingots with various compositions. Further, the steel ingots were heated at a temperature of 1250°C or lower and subjected to hot rolling, and then subjected to cold rolling. Further, decarburization annealing was performed after the cold rolling, and thereafter, nitridation treatment and finish annealing were performed. Then, the magnetic flux densities B₈ of the obtained grain-oriented electrical steel sheets were measured and the variations in the magnetic flux densities B₈ in coils after the finish annealing were checked. The magnetic flux density B₈ is the magnetic flux density occurring in the grain-oriented electrical steel sheet when a magnetic field of 800 A/m at 50 Hz is applied thereto.

[0020] As a result of the experiment, it was found out that the variation in the magnetic flux density B₈ in the coil after the finish annealing is remarkably reduced when the steel ingot contains 0.0020 mass% to 0.010 mass% of Ti and/or 0.010 mass% to 0.50 mass% of Cu.

[0021] An example of the results obtained through the above-described experiments is illustrated in Fig. 1. Though details of the experiments will be described later, an open circle mark in Fig. 1 indicates that the average value of the magnetic flux densities B₈ of five single-plate samples was 1.90 T or more and the difference between the maximum value and the minimum value of the magnetic flux density B₈ was 0.030 T or less. Further, a filled circle mark in Fig. 1 indicates that at least the average value of the magnetic flux densities B₈ of the five single-plate samples was less than 1.90 T or the difference between the maximum value and the minimum value of the magnetic flux densities B₈ was more than 0.030 T. It is apparent from Fig. 1 that when the steel ingot contains 0.0020 mass% to 0.010 mass% of Ti and/or 0.010 mass% to 0.50 mass% of Cu, the average value of the magnetic flux densities B₈ is high and the variation in the magnetic flux densities B₈ is small.

[0022] Next, a method of manufacturing a grain-oriented electrical steel sheet according to an embodiment of the present invention will be described. Fig. 2 is a flowchart illustrating the method of manufacturing a grain-oriented electrical steel sheet according to the embodiment of the present invention.

[0023] In the present embodiment, first, a slab is produced through casting of molten steel for a grain-oriented electrical steel sheet with a predetermined composition (Step 1). The casting method therefor is not particularly limited. The molten steel contains, for example, Si: 2.5 mass% to 4.0 mass%, C: 0.01 mass% to 0.060 mass%, Mn: 0.05 mass% to 0.20 mass%, acid-soluble Al: 0.020 mass% to 0.040 mass%, N: 0.002 mass% to 0.012 mass%, S: 0.001 mass% to 0.010 mass%, and P: 0.01 mass% to 0.08 mass%. The molten steel further contains at least one kind selected from a group consisting of Ti: 0.0020 mass% to 0.010 mass% and Cu: 0.010 mass% to 0.50 mass%. In short, the molten steel contains one or both of Ti and Cu in ranges of Ti: 0.010 mass% or less and Cu: 0.50 mass% or less to satisfy at least one of Ti: 0.0020 mass% or more or Cu: 0.010 mass% or more. The balance of the molten steel may be composed of Fe and inevitable impurities. Note that the inevitable impurities may include an element(s) forming an inhibitor in the manufacturing process of the grain-oriented electrical steel sheet and remaining in the grain-oriented electrical steel sheet after purification is performed through a high-temperature annealing.

[0024] Here, reasons for numerical limitations of the composition of the above-described molten steel will be described.

[0025] Si is an element that is extremely effective to enhance the electrical resistance of the grain-oriented electrical steel sheet to reduce the eddy current loss constituting a part of the core loss. When the Si content is less than 2.5 mass%, the eddy current loss cannot be sufficiently suppressed. On the other hand, when the Si content is more than 4.0 mass%, the processability is lowered. Accordingly, the Si content is set to 2.5 mass% to 4.0 mass%.

[0026] C is an element that is effective to control the structure (primary recrystallization structure) obtained through primary recrystallization. When the C content is less than 0.01 mass%, the effect cannot be sufficiently obtained. On the other hand, when the C content is more than 0.06 mass%, the time required for decarburization annealing increases, resulting in a larger exhaust amount of CO₂. Note that when the decarburization annealing is insufficient, the grain-oriented electrical steel sheet with excellent magnetic properties is less likely to be obtained. Accordingly, the C content is set to 0.01 mass% to 0.06 mass%. Further, since the variation in magnetic property after finish annealing is particularly prominent when the C content is 0.048 mass% or less in the conventional technique as described above, the embodiment is particularly effective in the case where the C content is 0.048 mass% or less.

[0027] Mn increases the specific resistance of the grain-oriented electrical steel sheet to reduce the core loss. Mn also functions to prevent occurrence of cracks in the hot rolling. When the Mn content is less than 0.05 mass%, the effects cannot be sufficiently obtained. On the other hand, when the Mn content is more than 0.20 mass%, the magnetic flux density of the grain-oriented electrical steel sheet is lowered. Accordingly, the Mn content is set to 0.05 mass% to 0.20 mass%.

[0028] Acid-soluble Al is an important element forming AlN serving as an inhibitor. When the acid-soluble Al content is less than 0.020 mass%, a sufficient amount of AlN cannot be formed, resulting in insufficient inhibitor strength. On the other hand, when the acid-soluble Al content is more than 0.040 mass%, AlN becomes coarse, resulting in a decrease in inhibitor strength. Accordingly, the acid-soluble Al content is set to 0.020 mass% to 0.040 mass%.

[0029] N is an important element forming AlN through reacting with the acid-soluble Al. Though a large amount of N does not need to be contained in the grain-oriented electrical steel sheet because nitridation treatment is performed after the cold rolling as will be described later, a great load may be required in steelmaking in order to make the N content

less than 0.002 mass%. On the other hand, when the N content is more than 0.012 mass%, a hole called blister is generated in the steel sheet in the cold rolling. Accordingly, the N content is set to 0.002 mass% to 0.012 mass%. The N content is preferably 0.010 mass% or less in order to further reduce the blister.

[0030] S is an important element forming a MnS precipitate through reacting with Mn. The MnS precipitate mainly affects the primary recrystallization and functions to suppress the variation depending on site in grain growth in the primary recrystallization due to the hot rolling. When the Mn content is less than 0.001 mass%, the effect cannot be sufficiently obtained. On the other hand, when the Mn content is more than 0.010 mass%, the magnetic property is likely to decrease. Accordingly, the Mn content is set to 0.001 mass% to 0.010 mass%. The Mn content is preferably 0.009 mass% or less in order to further improve the magnetic property.

[0031] P increases the specific resistance of the grain-oriented electrical steel sheet to reduce the core loss. When the P content is less than 0.01 mass%, the effect cannot be sufficiently obtained. On the other hand, when the P content is more than 0.08 mass%, the cold rolling may become difficult to perform. Accordingly, the P content is set to 0.01 mass% to 0.08 mass%.

[0032] Ti forms a TiN precipitate through reacting with N. Further, Cu forms a CuS precipitate through reacting with S. These precipitates function to make the growth of the crystal grains in the finish annealing uniform irrespective of the site of the coil and suppress the variation in magnetic property of the grain-oriented electrical steel sheet. In particular, the TiN precipitate is considered to suppress the variation in grain growth in a high temperature region in the finish annealing to decrease the deviation of the magnetic property of the grain-oriented electrical steel sheet. Further, the CuS precipitate is considered to suppress the variation in grain growth in a low temperature region in the decarburization annealing and the finish annealing to decrease the deviation of the magnetic property of the grain-oriented electrical steel sheet. When the Ti content is less than 0.0020 mass% and the Cu content is less than 0.010 mass%, the effects cannot be sufficiently obtained. On the other hand, when the Ti content is more than 0.010 mass%, the TiN precipitate is excessively formed and remains even after the finish annealing. Similarly, when the Cu content is more than 0.50 mass%, the CuS precipitate is excessively formed and remains even after the finish annealing. If these precipitates remain in the grain-oriented electrical steel sheet, it is difficult to obtain a high magnetic property. Accordingly, the molten steel contains one or both of Ti and Cu in ranges of Ti: 0.010 mass% or less and Cu: 0.50 mass% or less to satisfy at least one of Ti: 0.0020 mass% or more or Cu: 0.010 mass% or more. In short, the molten steel contains at least one kind selected from a group consisting of Ti: 0.0020 mass% to 0.010 mass% and Cu: 0.010 mass% to 0.50 mass%.

[0033] Note that the lower limit of the Ti content is preferably 0.0020 mass%, and the upper limit of the Ti content is preferably 0.0080 mass%. Further, the lower limit of the Cu content is preferably 0.01 mass%, and the upper limit of the Cu content is preferably 0.10 mass%. Further, where the Ti content (mass%) is expressed as [Ti] and the Cu content (mass%) is expressed as [Cu], it is more preferable that the relation of " $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ " is established and, preferably, the relation of " $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ " is established.

[0034] Note that at least one kind of the following various kinds of elements may be contained in the molten steel.

[0035] Cr and Sn improve the quality of an oxide layer to be formed in the decarburization annealing and improve the quality of a glass film to be formed of the oxide layer in the finish annealing. In other words, Cr and Sn improve the magnetic property through stabilization of the formation of the oxide layer and the glass film to suppress the variation in the magnetic property. However, when the Cr content is more than 0.20 mass%, the formation of the glass film may be unstable. Further, when the Sn content is more than 0.20 mass%, the surface of the steel sheet may be less likely to be oxidized to result in insufficient formation of the glass film. Accordingly, each of the Cr content and the Sn content is preferably 0.20 mass% or less. Further, in order to sufficiently obtain the above effects, each of the Cr content and the Sn content is preferably 0.01 mass% or more. Note that Sn is a grain boundary segregation element and thus also has an effect to stabilize secondary recrystallization.

[0036] Further, the molten steel may contain Sb: 0.010 mass% to 0.20 mass%, Ni: 0.010 mass% to 0.20 mass%, Se: 0.005 mass% to 0.02 mass%, Bi: 0.005 mass% to 0.02 mass%, Pb: 0.005 mass% to 0.02 mass%, B: 0.005 mass% to 0.02 mass%, V: 0.005 mass% to 0.02 mass%, Mo: 0.005 mass% to 0.02 mass%, and/or As: 0.005 mass% to 0.02 mass%. These elements may be inhibitor strengthening elements.

[0037] In the embodiment, after the slab is produced from the molten steel with the composition, the slab is heated (Step S2). The temperature of the heating is preferably set to 1250°C or lower from the viewpoint of energy saving.

[0038] Next, hot rolling is performed on the slab to obtain a hot-rolled steel sheet (Step S3). The thickness of the hot-rolled steel sheet is not particularly limited, and may be set to 1.8 mm to 3.5 mm.

[0039] Thereafter, annealing is performed on the hot-rolled steel sheet to obtain an annealed steel sheet (Step S4). The condition of the annealing is not particularly limited, and the annealing may be performed, for example, at a temperature of 750°C to 1200°C for 30 seconds to 10 minutes. The annealing improves the magnetic property.

[0040] Subsequently, cold rolling is performed on the annealed steel sheet to obtain a cold-rolled steel sheet (Step S5). The cold rolling may be performed only once or a plurality of times while an intermediate annealing is performed therebetween. The intermediate annealing is preferably performed at a temperature of 750°C to 1200°C for 30 seconds to 10 minutes.

[0041] Note that if the cold rolling is performed without performing the above-described intermediate annealing, it may be difficult to obtain uniform properties. On the other hand, if the cold rolling is performed a plurality of times while the intermediate annealing is performed therebetween, the uniform properties are easily obtained but the magnetic flux density may decrease. Accordingly, it is preferable to determine the number of times of the cold rolling and the presence or absence of the intermediate annealing according to the property required for and the cost of the finally obtained grain-oriented electrical steel sheet.

[0042] Further, in any case, it is preferable to set the rolling reduction at the final cold rolling to 80% to 95%.

[0043] The decarburization annealing is performed on the cold-rolled steel sheet in a wet atmosphere containing hydrogen and nitrogen at 800°C to 950°C after the cold rolling to obtain a decarburization annealed steel sheet (step S6). The decarburization annealing removes carbon in the steel sheet and causes primary recrystallization. When the temperature of the decarburization annealing is lower than 800°C, the crystal grain obtained through the primary recrystallization (primary recrystallization grain) is small so that the subsequent secondary recrystallization does not sufficiently appear. On the other hand, when the temperature of the decarburization annealing is higher than 950°C, the primary recrystallization grain is large so that the subsequent secondary recrystallization does not sufficiently appear.

[0044] Next, nitridation treatment is performed on the decarburization annealed steel sheet in an atmosphere containing hydrogen, nitrogen and a gas having a nitriding capability such as ammonia at 700°C to 850°C to obtain a nitrided steel sheet (step S7). The nitridation treatment increases the nitrogen content in the steel sheet. When the temperature of the nitridation treatment is lower than 700°C or high than 850°C, nitrogen is difficult to be diffused to the inner part of the steel sheet so that the subsequent secondary recrystallization does not sufficiently appear.

[0045] After that, an annealing separating agent containing MgO as a main component is applied, in a water slurry, to the surface of the nitrided steel sheet, and the nitrided steel sheet is coiled. Then, batch-type finish annealing is performed on the coiled nitrided steel sheet to obtain a coiled finish-annealed steel sheet (Step S8). The finish annealing causes secondary recrystallization.

[0046] Thereafter, the coiled finish-annealed steel sheet is uncoiled, and the annealing separating agent is removed. Subsequently, a coating solution containing aluminum phosphate and colloidal silica as main components is applied to the surface of the finish-annealed steel sheet, and baking is performed thereon to form an insulating film (step S9).

[0047] In the above manner, the grain-oriented electrical steel sheet can be manufactured.

[0048] Note that the steel being an object for the hot rolling is not limited to the slab obtained through casting of the molten steel, but a so-called thin slab may be used. Further, when using the thin slab, it is not always necessary to perform the slab heating at 1250°C or lower.

EXAMPLE

[0049] Next, experiments conducted by the present inventors will be described. Conditions and so on in these experiments are examples employed to verify practicality and effects of the present invention, and the present invention is not limited to these examples.

(First Experiment)

[0050] First, 15 kinds of steel ingots each containing Si: 3.2 mass%, C: 0.055 mass%, Mn: 0.10 mass%, acid-soluble Al: 0.028 mass%, N: 0.003 mass%, S: 0.0060 mass%, and P: 0.030 mass%, further containing Ti and Cu in amounts listed in Table 1, and the balance composed of Fe and inevitable impurities were produced using a vacuum melting furnace. Then, annealing was performed on the steel ingots at 1150°C for one hour, and then hot rolling was performed thereon to obtain hot-rolled steel sheets with a thickness of 2.3 mm.

[0051] Subsequently, annealing was performed on the hot-rolled steel sheets at 1100°C for 120 seconds to obtain annealed steel sheets. Next, acid pickling was performed on the annealed steel sheets, and then cold rolling was performed on the annealed steel sheets to obtain cold-rolled steel sheets with a thickness of 0.23 mm. Subsequently, decarburization annealing was performed on the cold-rolled steel sheets in an atmosphere containing water vapor, hydrogen, and nitrogen at 860°C for 100 seconds to obtain decarburization annealed steel sheets. Next, nitridation treatment was performed on the decarburization annealed steel sheets in an atmosphere containing hydrogen, nitrogen, and ammonia at 770°C for 20 seconds to obtain nitrided steel sheets.

[0052] Thereafter, an annealing separating agent containing MgO as a main component was applied, in a water slurry, to the surfaces of the decarburized nitrided steel sheets. Then, finish annealing was performed on them at 1200°C for 20 hours to obtain finish-annealed steel sheets. Subsequently, the finish-annealed steel sheets were washed with water, and then cutout into a single-plate magnetic measurement size with a width of 60 mm and a length of 300 mm. Subsequently, a coating solution containing aluminum phosphate and colloidal silica as main components was applied to the surfaces of the finish-annealed steel sheets, and baking was performed thereon to form an insulating film. In this manner, samples of the grain-oriented electrical steel sheets were obtained.

[0053] Then, the magnetic flux density B8 of each of the grain-oriented electrical steel sheets was measured. The magnetic flux density B8 is the magnetic flux density occurring in the grain-oriented electrical steel sheet when a magnetic field of 800 A/m at 50 Hz is applied thereto as described above. Note that the magnetic flux densities B8 of five single-plate samples for measurement were measured for each of the samples. Then, for each sample, the average value "average B8," the maximum value "B8max," and the minimum value "B8min" were obtained. The difference " $\Delta B8$ " between the maximum value "B8max" and the minimum value "B8min" was also obtained. The difference " $\Delta B8$ " is an index indicating the fluctuation range of the magnetic property. These results are listed in Table 1 together with the Ti contents and the Cu contents. Further, the evaluation results based on the average value "average B8" and the difference " $\Delta B8$ " are indicated in Fig. 1. As described above, an open circle mark in Fig. 1 indicates that the average value "average B8" was 1.90 T or more and the difference " $\Delta B8$ " was 0.030 T or less. Further, a filled circle mark in Fig. 1 indicates that the average value "average B8" was less than 1.90 T or the difference " $\Delta B8$ " was more than 0.030 T.

[0054] [Table 1]

TABLE 1

SAMPLE No	Ti CONTENT (MASS%)	Cu CONTENT (MASS%)	20× [Ti]+[Cu]	10×[Ti]+[Cu]	AVERAGEB8(T)	B8max (T)	B8min (T)	ΔB8 (T)	NOTE
1	0.0011	0.006	0.028	0.017	1914	1931	1890	0.041	COMPARATIVE EXAMPLE
2	0.0024	0.007	0.055	0.031	1913	1923	1902	0.021	EMBODIMENT
3	0.0048	0.006	0.102	0.054	1911	1919	1897	0.022	EMBODIMENT
4	0.0084	0.008	0.176	0.092	1902	1915	1889	0.026	EMBODIMENT
5	0.0109	0.005	0.223	0.114	1877	1887	1866	0.021	COMPARATIVE EXAMPLE
6	0.0013	0.033	0.059	0.046	1914	1924	1901	0.023	EMBODIMENT
7	0.0015	0.083	0.133	0.098	1913	1922	1895	0.027	EMBODIMENT
8	0.0014	0.182	0.210	0.196	1911	1919	1894	0.025	EMBODIMENT
9	0.0011	0.430	0.452	0.441	1901	1908	1884	0.024	EMBODIMENT
10	0.0013	0.576	0.602	0.589	1876	1884	1861	0.023	COMPARATIVE EXAMPLE
11	0.0033	0.079	0.145	0.112	1911	1921	1901	0.020	EMBODIMENT
12	0.0055	0.084	0.194	0.139	1903	1910	1891	0.019	EMBODIMENT
13	0.0068	0.018	0.154	0.086	1912	1921	1899	0.022	EMBODIMENT
14	0.0082	0.380	0.544	0.462	1902	1908	1893	0.015	EMBODIMENT
15	0.0028	0.022	0.078	0.050	1914	1927	1907	0.020	EMBODIMENT

[0055] As presented in Table 1 and Fig. 1, in the samples No. 2 to No. 4, No. 6 to No. 9, and No. 11 to No. 15, in each of which the Ti content and the Cu content were within the range of the present invention, the average value "average B8" was large to be 1.90 T or more, and the difference " $\Delta B8$ " was small to be 0.030 T or less. In short, high magnetic property was obtained and the variation in magnetic property was small.

[0056] In particular, the balance between the average value "average B8" and the difference " $\Delta B8$ " was excellent in the samples No. 11, No. 13, and No. 15, in which the relation of " $20 \times [Ti] + [Cu] \leq 0.18$ " was established where the Ti content (mass%) was expressed as [Ti] and the Cu content (mass%) was expressed as [Cu]. Among them, the balance between the average value "average B8" and the difference " $\Delta B8$ " was extremely excellent in the sample No. 15, in which the relation of " $10 \times [Ti] + [Cu] \leq 0.07$ " was established.

[0057] On the other hand, in the sample No. 1, in which the Ti content was less than 0.0020 mass% and the Cu content was less than 0.010 mass%, the difference " $\Delta B8$ " was large to be more than 0.030 T. In short, the variation in magnetic property was large. Further, in the sample No. 5, in which the Ti content was more than 0.010 mass% and the sample No. 10, in which the Cu content was more than 0.50 mass%, a large amount of precipitate was contained to affect the finish annealing, with the result that the average value "average B8" was small to be less than 1.90 T. In short, a sufficiently high magnetic property could not be obtained.

(Second Experiment)

[0058] First, a steel ingot containing Si: 3.2 mass%, C: 0.051 mass%, Mn: 0.09 mass%, acid-soluble ΔI : 0.026 mass%, N: 0.004 mass%, S: 0.0053 mass%, P: 0.027 mass%, Ti: 0.0024 mass%, Cu: 0.029 mass%, and the balance composed of Fe and inevitable impurities was produced using a vacuum melting furnace. Then, annealing was performed on the steel ingot at 1150°C for one hour, and then hot rolling was performed thereon to obtain a hot-rolled steel sheet with a thickness of 2.4 mm.

[0059] Subsequently, annealing was performed on the hot-rolled steel sheet at 1090°C for 120 seconds to obtain an annealed steel sheet. Then, acid pickling was performed on the annealed steel sheet, and then cold rolling was performed on the annealed steel sheet to obtain a cold-rolled steel sheet with a thickness of 0.23 mm. Subsequently, eight pieces of steel sheets for annealing were cutout from the cold-rolled steel sheet, and decarburization annealing was performed on each of the steel sheets in an atmosphere containing water vapor, hydrogen, and nitrogen at a temperature T1 ranging from 790°C to 960°C listed in Table 2 for 80 seconds to obtain decarburization annealed steel sheets. Next, nitridation treatment was performed on each of the decarburization annealed steel sheets in an atmosphere containing water vapor, hydrogen, nitrogen, and ammonia at a temperature T2 ranging from 680°C to 880°C listed in Table 2 for 20 seconds to obtain nitrided steel sheets.

[0060] Thereafter, an annealing separating agent containing MgO as a main component was applied, in a water slurry, to the surfaces of the nitrided steel sheets. Then, finish annealing was performed on them at 1200°C for 20 hours to obtain finish annealed steel sheets. Subsequently, treatments from the water washing to the formation of the insulating film were performed similarly to the first experiment to obtain samples of the grain-oriented electrical steel sheets.

[0061] Then, for each of the samples, the average value "average B8," the maximum value "B8max," the minimum value "B8min," and the difference " $\Delta B8$ " were obtained similarly to the first experiment. These results are listed in Table 2 together with the temperatures T1 and the temperatures T2.

[0062] [Table 2]

TABLE 2

SAMPLE No	T1 (°C)	T2 (°C)	AVERAGE B8 (T)	B8 max (T)	B8minn (T)	$\Delta B8$ (T)	NOTE
21	790	780	1.840	1 859	1832	0.027	COMPARATIVE EXAMPLE
22	820	780	1.911	1.918	1 895	0023	EMBODIMENT
23	870	780	1.924	1 931	1 908	0.023	EMBODIMENT
24	930	780	1.925	1 937	1 908	0.029	EMBODIMENT
25	960	780	1.824	1.872	1 770	0102	COMPARATIVE EXAMPLE
26	860	670	1.896	1 907	1 880	0027	COMPARATIVE EXAMPLE
27	860	750	1.922	1 930	1.906	0024	EMBODIMENT

(continued)

SAMPLE No	T1 (°C)	T2 (°C)	AVERAGE B8 (T)	B8 max (T)	B8minn (T)	ΔB8 (T)	NOTE
28	860	860	1.823	1 872	1 777	0.095	COMPARATIVE EXAMPLE

[0063] As presented in Table 2, in the samples No. 22 to No. 24, and No. 27, in which the temperature T1 of the decarburization annealing and the temperature T2 of the nitridation treatment were within the range of the present invention, the average value "average B8" was large to be 1.90 T or more, and the difference "ΔB8" was small to be 0.030 T or less. In short, a high magnetic property was obtained and the variation in the magnetic property was small.

[0064] On the other hand, in the sample No. 21, in which the temperature T1 of the decarburization annealing was less than 800°C, the average value "average B8" was small to be less than 1.90 T. In the sample No. 25, in which the temperature T1 of the decarburization annealing was higher than 950°C, the difference "ΔB8" was large to be over 0.030 T, and the average value "average B8" was small to be less than 1.90 T. Further, in the sample No. 26, in which the temperature T2 of the nitridation treatment was less than 700°C, the average value "average B8" was small to be less than 1.90 T. In the sample No. 28, in which the temperature T2 of the nitridation treatment is higher than 850°C, the difference "ΔB8" was large to be high than 0.030 T, and the average value "average B8" was small to be less than 1.90 T.

(Third Experiment)

[0065] First, 20 kinds of steel ingots each containing Si: 3.2 mass%, Mn: 0.09 mass%, acid-soluble Al: 0.026 mass%, N: 0.004 mass%, S: 0.0053 mass%, and P: 0.027 mass%, further containing C, Ti and Cu in amounts listed in Table 3, and the balance composed of Fe and inevitable impurities were produced using a vacuum melting furnace. Then, annealing was performed on the steel ingots at 1150°C for one hour, and then hot rolling was performed to obtain hot-rolled steel sheets with a thickness of 2.4 mm.

[0066] Subsequently, annealing was performed on the hot-rolled steel sheets at 1090°C for 120 seconds to obtain annealed steel sheets. Then, acid pickling was performed on the annealed steel sheets, and then, cold rolling was performed on the annealed steel sheets to obtain cold-rolled steel sheets with a thickness of 0.23 mm. Subsequently, steel sheets for annealing were cutout from the cold-rolled steel sheets, and decarburization annealing was performed on the steel sheets in an atmosphere containing water vapor, hydrogen, and nitrogen at 860°C for 80 seconds to obtain decarburization annealed steel sheets. Next, nitridation treatment was performed on the decarburization annealed steel sheets in an atmosphere containing water vapor, hydrogen, nitrogen, and ammonia at 760°C for 20 seconds to obtain nitrided steel sheets.

[0067] Thereafter, an annealing separating agent containing MgO as a main component was applied, in a water slurry, to the surfaces of the nitrided steel sheets. Then, finish annealing was performed on them at 1200°C for 20 hours to obtain finish annealed steel sheets. Subsequently, treatments from the water washing to the formation of insulating film were performed similarly to the first experiment to obtain samples of the grain-oriented electrical steel sheets.

[0068] Then, for each of the samples, the average value "average B8," the maximum value "B8max," the minimum value "B8min," and the difference "ΔB8" were obtained similarly to the first experiment. These results are listed in Table 3 together with the C contents, the Ti contents and the Cu contents.

[0069] [Table 3]

TABLE 3

SAMPLE No	C CONTENT (MASS%)	Ti CONTENT (MASS%)	Cu CONTENT (MASS%)	20 × [Ti]+ [Cu]	10 × [T i]+ [Cu]	AVERAGE B8 (T)	Δ B8 (T)	NOTE
31	0028	00014	0006	0034	0020	1 868	0051	COMPARATIVE EXAMPLE
32	0028	00024	0024	0.072	0.048	1.911	0024	EMBODIMENT
33	0028	00042	0051	0135	0.093	1906	0021	EMBODIMENT
34	0028	0.0070	0390	0530	0460	1 901	0018	EMBODIMENT
35	0028	00105	0560	0770	0.665	1 822	0016	COMPARATIVE EXAMPLE

(continued)

SAMPLE No	C CONTENT (MASS%)	Ti CONTENT (MASS%)	Cu CONTENT (MASS%)	20 × [Ti]+ [Cu]	10 × [T i]+ [Cu]	AVERAGE B8 (T)	Δ B8 (T)	NOTE
36	0039	00015	0005	0035	0.020	1 892	0.046	COMPARATIVE EXAMPLE
37	0039	00023	0022	0068	0.045	1 913	0022	EMBODIMENT
38	0039	00044	0053	0141	0097	1 907	0.019	EMBODIMENT
39	0039	00075	0350	0500	0425	1 902	0017	EMBODIMENT
40	0039	0.0110	0590	0810	0700	1 843	0.015	COMPARATIVE EXAMPLE
41	0.048	00018	0007	0.043	0025	1 904	0042	COMPARATIVE EXAMPLE
42	0.048	0.0026	0025	0.077	0051	1 914	0021	EMBODIMENT
43	0.048	00043	0052	0138	0095	1 908	0019	EMBODIMENT
44	0048	00072	0370	0514	0442	1 903	0.017	EMBODIMENT
45	0048	00122	0550	0794	0672	1.852	0.014	COMPARATIVE EXAMPLE
46	0057	00017	0008	0042	0025	1.912	0037	COMPARATIVE EXAMPLE
47	0057	00024	0026	0074	0.050	1 915	0.020	EMBODIMENT
48	0057	00046	0054	0146	0100	1 908	0017	EMBODIMENT
49	0057	00074	0380	0528	0454	1.907	0015	EMBODIMENT
50	0057	00109	0540	0758	0649	1 871	0013	COMPARATIVE EXAMPLE

[0070] As presented in Table 3, in the samples No. 32 to No. 34, No. 37 to No. 39, No. 42 to No. 44, and No. 47 to No. 49, in each of which the C content, the Ti content and the Cu content were within the range of the present invention, the average value "average B8" was large to be 1.90 T or more, and the difference "ΔB8" was small to be 0.025 T or less. In short, a high magnetic property was obtained and the variation in magnetic property was small. Particularly, when the C content was small, a good result was obtained.

[0071] Further, the balance between the average value "average B8" and the difference "ΔB8" was excellent in the samples No. 32, No. 33, No. 37, No. 38, No. 42, No. 43, No. 47, and No. 48, in each of which the Ti content was 0.0020 mass to 0.080 mass%, the Cu content was 0.010 mass to 0.10 mass%, and the relation of " $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ " was established. Among them, the balance between the average value "average B8" and the difference "ΔB8" was extremely excellent in the samples No. 32, No. 37, No. 42, and No. 47, in each of which the relation of " $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ " was established.

[0072] On the other hand, in the samples No. 31, No. 36, No. 41, and No. 46, in each of which the Ti content was less than 0.010 mass%, and the Cu content was less than 0.50 mass%, the difference "ΔB8" was large to be higher than 0.030 T. Among them, in the samples No. 31 and No. 36, in each of which the C content was low, the average value "average B8" was further small to be less than 1.90 T. Further, in the samples No. 35, No. 40, No. 45, and No. 50, in each of which the Ti content was higher than 0.010 mass%, and the Cu content was higher than 0.50 mass%, the average value "average B8" was small to be less than 1.90 T.

(Fourth Experiment)

[0073] First, 10 kinds of steel ingots each containing Si: 3.2 mass%, C: 0.048 mass%, Mn: 0.08 mass%, acid-soluble Al: 0.028 mass%, N: 0.004 mass%, S: 0.0061 mass%, P: 0.033 mass%, Ti: 0.0024 mass%, and Cu: 0.029 mass%, further containing Cr and Sn in amounts listed in Table 4, and the balance composed of Fe and inevitable impurities were produced using a vacuum melting furnace. Then, annealing was performed on the steel ingots at 1100°C for one

hour, and then hot rolling was performed thereon to obtain hot-rolled steel sheets with a thickness of 2.3 mm.

[0074] Subsequently, annealing was performed on the hot-rolled steel sheets at 1080°C for 120 seconds to obtain annealed steel sheets. Then, acid pickling was performed on the annealed steel sheets, and then cold rolling was performed on the annealed steel sheets to obtain cold-rolled steel sheets with a thickness of 0.23 mm. Subsequently, decarburization annealing was performed on the cold-rolled steel sheets in an atmosphere containing water vapor, hydrogen, and nitrogen at 870°C for 90 seconds to obtain decarburization annealed steel sheets. Next, nitridation treatment was performed on the decarburization annealed steel sheets in an atmosphere containing hydrogen, nitrogen, and ammonia at 760°C for 20 seconds to obtain nitrided steel sheets.

[0075] Thereafter, an annealing separating agent containing MgO as a main component was applied, in a water slurry, to the surfaces of the nitrided steel sheets. Then, finish annealing was performed on them at 1200°C for 20 hours to obtain finish annealed steel sheets. Subsequently, treatments from the water washing to the formation of the insulating film were performed similarly to the first experiment to obtain samples of the grain-oriented electrical steel sheets.

[0076] Then, for each of the samples, the average value "average B8," the maximum value "B8max," the minimum value "B8min," and the difference "ΔB8" were obtained similarly to the first experiment. These results are listed in Table 4 together with the Cr contents and the Sn contents.

[0077] [Table 4]

TABLE 4

SAMPLE No.	Cr CONTENT (MASS%)	Sn CONTENT (wt%)	AVERAGE B8 (T)	B8 max (T)	B8min (T)	ΔB8 (T)	NOTE
51	0007	0.008	1.904	1 918	1.890	0.028	EMBODIMENT
52	0068	0.003	1.915	1 927	1.903	0024	EMBODIMENT
53	0141	0.008	1 915	1 928	1.904	0024	EMBODIMENT
54	0214	0.006	1 903	1 917	1.888	0029	EMBODIMENT
55	0003	0.042	1 917	1 928	1.906	0.022	EMBODIMENT
56	0006	0087	1 918	1 928	1 907	0021	EMBODIMENT
57	0005	0.264	1 902	1 915	1.888	0.027	EMBODIMENT
58	0070	0124	1 913	1 922	1.898	0.024	EMBODIMENT
59	0150	0035	1 914	1 924	1 901	0023	EMBODIMENT
60	0170	0.154	1 912	1 922	1897	0.025	EMBODIMENT

[0078] As presented in Table 4, in any of the samples Nos. 51 to 60, the average value *average B8* was large to be 1.90 T or more and the difference "ΔB8" was small to be 0.030 T or less. In short, a high magnetic property was obtained and the variation in the magnetic property was small. Among them, in the samples No. 52, No. 53, No. 55, No. 56, and No. 58 to No. 60, each of which contains 0.010 mass% to 0.20 mass% of Cr and/or 0.010 mass% to 0.20 mass% of Sn, the average value "average B8" was particularly large to be 1.91 T or more, and the difference "ΔB8" was particularly small to be 0.025 T or less.

INDUSTRIAL APPLICABILITY

[0079] The present invention is applicable, for example, in electrical steel sheet manufacturing industries and electrical steel sheet using industries.

Claims

1. A method of manufacturing a grain-oriented electrical steel sheet, comprising:

performing hot rolling of a steel containing Si: 2.5 mass% to 4.0 mass%, C: 0.01 mass% to 0.060 mass%, Mn: 0.05 mass% to 0.20 mass%, acid-soluble Al: 0.020 mass% to 0.040 mass%, N: 0.002 mass% to 0.012 mass%, S: 0.001 mass% to 0.010 mass%, and P: 0.01 mass% to 0.08 mass%, further containing at least one kind

selected from a group consisting of Ti: 0.0020 mass% to 0.010 mass% and Cu: 0.010 mass% to 0.50 mass%,
 and a balance composed of Fe and inevitable impurities, to obtain a hot-rolled steel sheet;
 performing annealing on the hot-rolled steel sheet to obtain an annealed steel sheet;
 performing cold rolling on the annealed steel sheet to obtain a cold-rolled steel sheet;
 performing decarburization annealing on the cold-rolled steel sheet at a temperature of 800°C to 950°C to obtain
 a decarburization annealed steel sheet;
 then, performing nitridation treatment on the decarburization annealed steel sheet at 700°C to 850°C to obtain
 a nitrided steel sheet; and
 performing finish annealing on the nitrided steel sheet.

2. The method of manufacturing a grain-oriented electrical steel sheet according to claim 1, wherein the hot rolling on the steel is performed after heating the steel to a temperature of 1250°C or lower.
3. The method of manufacturing a grain-oriented electrical steel sheet according to claim 1, wherein the steel further contains at least one kind selected from a group consisting of Cr: 0.010 mass% to 0.20 mass%, Sn: 0.010 mass% to 0.20 mass%, Sb: 0.010 mass% to 0.20 mass%, Ni: 0.010 mass% to 0.20 mass%, Se: 0.005 mass% to 0.02 mass%, Bi: 0.005 mass% to 0.02 mass%, Pb: 0.005 mass% to 0.02 mass%, B: 0.005 mass% to 0.02 mass%, V: 0.005 mass% to 0.02 mass%, Mo: 0.005 mass% to 0.02 mass%, and As: 0.005 mass% to 0.02 mass%.
4. The method of manufacturing a grain-oriented electrical steel sheet according to claim 2, wherein the steel further contains at least one kind selected from a group consisting of Cr: 0.010 mass% to 0.20 mass%, Sn: 0.010 mass% to 0.20 mass%, Sb: 0.010 mass% to 0.20 mass%, Ni: 0.010 mass% to 0.20 mass%, Se: 0.005 mass% to 0.02 mass%, Bi: 0.005 mass% to 0.02 mass%, Pb: 0.005 mass% to 0.02 mass%, B: 0.005 mass% to 0.02 mass%, V: 0.005 mass% to 0.02 mass%, Mo: 0.005 mass% to 0.02 mass%, and As: 0.005 mass% to 0.02 mass%.
5. The method of manufacturing a grain-oriented electrical steel sheet according to claim 1, wherein
 a Ti content in the steel is 0.0020 mass% to 0.0080 mass%,
 a Cu content in the steel is 0.01 mass% to 0.10 mass%, and
 a relation of $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ is established where the Ti content (mass%) in the steel is expressed as [Ti] and the Cu content (mass%) is expressed as [Cu].
6. The method of manufacturing a grain-oriented electrical steel sheet according to claim 2, wherein
 a Ti content in the steel is 0.0020 mass% to 0.0080 mass%,
 a Cu content in the steel is 0.01 mass% to 0.10 mass%, and
 a relation of $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ is established where the Ti content (mass%) in the steel is expressed as [Ti] and the Cu content (mass%) is expressed as [Cu].
7. The method of manufacturing a grain-oriented electrical steel sheet according to claim 3, wherein
 a Ti content in the steel is 0.0020 mass% to 0.0080 mass%,
 a Cu content in the steel is 0.01 mass% to 0.10 mass%, and
 a relation of $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ is established where the Ti content (mass%) in the steel is expressed as [Ti] and the Cu content (mass%) is expressed as [Cu].
8. The method of manufacturing a grain-oriented electrical steel sheet according to claim 4, wherein
 a Ti content in the steel is 0.0020 mass% to 0.0080 mass%,
 a Cu content in the steel is 0.01 mass% to 0.10 mass%, and
 a relation of $20 \times [\text{Ti}] + [\text{Cu}] \leq 0.18$ is established where the Ti content (mass%) in the steel is expressed as [Ti] and the Cu content (mass%) is expressed as [Cu].
9. The method of manufacturing a grain-oriented electrical steel sheet according wherein a relation of $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ is established to claim 5,
10. The method of manufacturing a grain-oriented electrical steel sheet according to claim 6, wherein a relation of $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ is established.
11. The method of manufacturing a grain-oriented electrical steel sheet according to claim 7, wherein a relation of $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ is established.

12. The method of manufacturing a grain-oriented electrical steel sheet according to claim 8, wherein a relation of " $10 \times [\text{Ti}] + [\text{Cu}] \leq 0.07$ " is established.

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FIG. 1

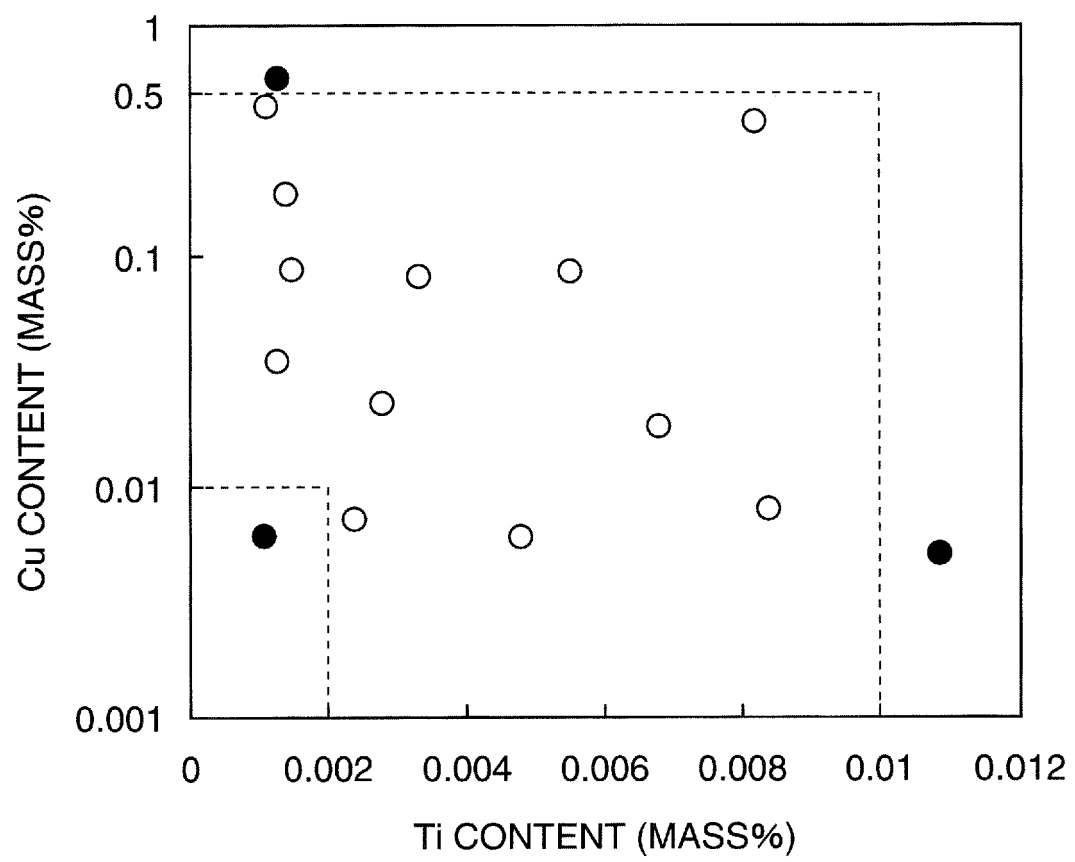
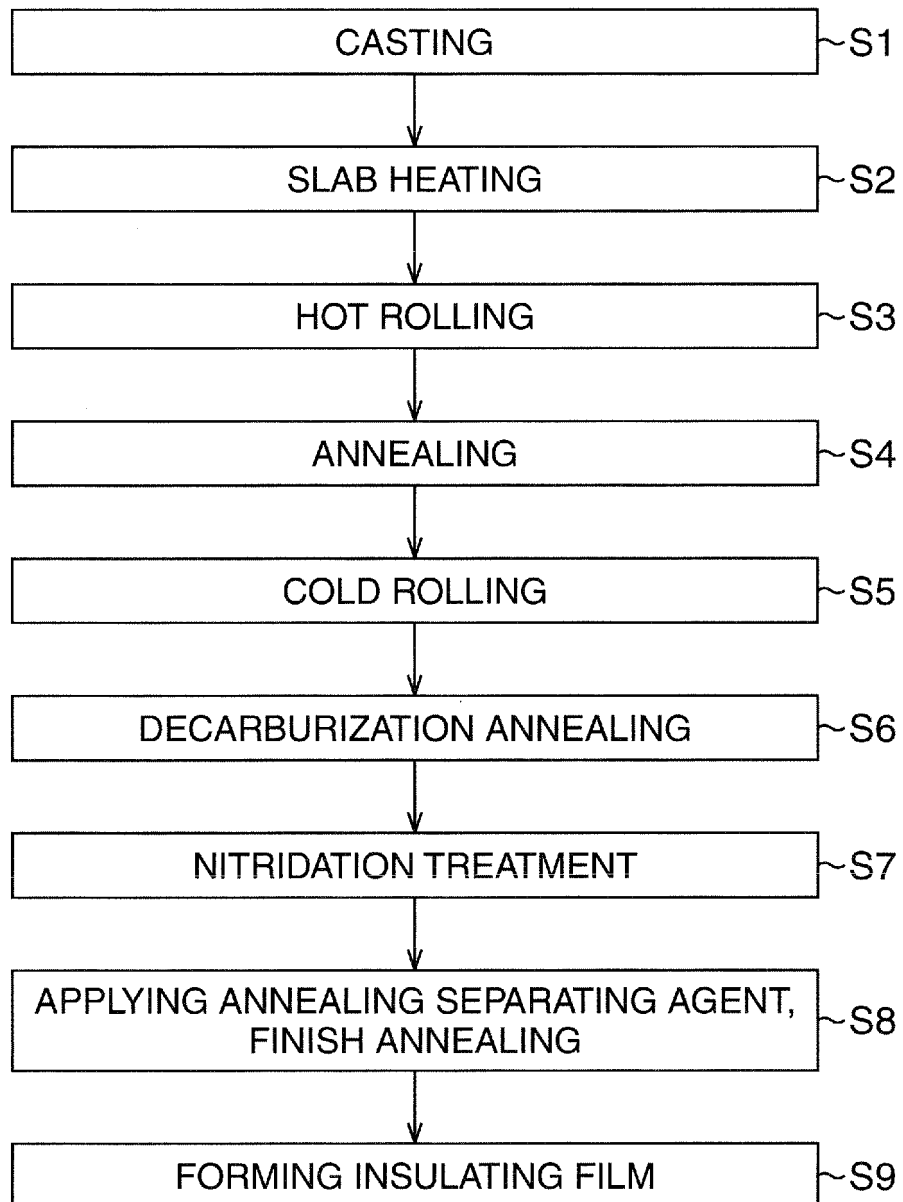


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/053491

A. CLASSIFICATION OF SUBJECT MATTER <i>C21D8/12</i> (2006.01) i, <i>C22C38/00</i> (2006.01) i, <i>C22C38/16</i> (2006.01) i, <i>C22C38/34</i> (2006.01) i, <i>H01F1/16</i> (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) <i>C21D8/12</i> , <i>C22C38/00-38/60</i> , <i>H01F1/16-1/18</i> Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2011 Kokai Jitsuyo Shinan Koho 1971-2011 Toroku Jitsuyo Shinan Koho 1994-2011 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 8-279408 A (Nippon Steel Corp.), 22 October 1996 (22.10.1996), claims 1 to 3; paragraphs [0013], [0026]; examples (Family: none)	1-12
X	JP 1-301820 A (Nippon Steel Corp.), 06 December 1989 (06.12.1989), claims 1, 2; page 5, upper left column, lines 3 to 7; examples & US 4938807 A1 & EP 326912 A2 & DE 68916980 C & KR 19930001331 B	1-12
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
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Date of the actual completion of the international search 07 April, 2011 (07.04.11)		Date of mailing of the international search report 19 April, 2011 (19.04.11)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/053491

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2009-256713 A (Nippon Steel Corp.), 05 November 2009 (05.11.2009), claims 1 to 3; paragraph [0031]; examples 7 to 9 (Family: none)	1-12
A	JP 6-228646 A (Nippon Steel Corp.), 16 August 1994 (16.08.1994), claims 1 to 5; paragraph [0026] (Family: none)	1-12

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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