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(71) Applicant: **JFE Steel Corporation**
**Tokyo, 100-0011 (JP)**

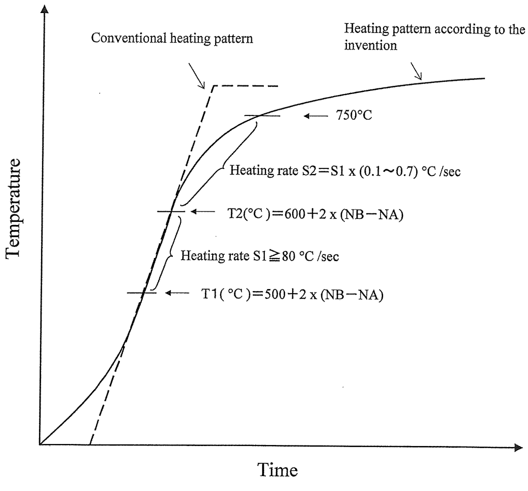
(72) Inventors:
- **SHINGAKI, Yukihiro**
  **Tokyo 100-0011 (JP)**
- **WATANABE, Makoto**
  **Tokyo 100-0011 (JP)**
- **SENDA, Kunihiro**
  **Tokyo 100-0011 (JP)**

(74) Representative: **HOFFMANN EITLE**
**Patent- und Rechtsanwälte**
**Arabellastrasse 4**
**81925 München (DE)**

## (54) PROCESS FOR PRODUCING GRAIN-ORIENTED ELECTROMAGNETIC STEEL SHEET WITH EXCELLENT CORE LOSS CHARACTERISTICS

(57) In the production of a grain-oriented electrical steel sheet by hot rolling a steel slab comprising C: 0.001~0.10 mass%, Si:1.0~5.0 mass%, Mn:0.01~0.5 mass%, sol. Al: 0.003~0.050 mass%, N: 0.0010~0.020 mass%, one or two selected from S and Se: 0.005~0.040 mass% in total, cold rolling, primary recrystallization annealing, and final annealing, a heating rate S1 between a temperature T1 (°C): 500+2 x (NB - NA) and a temperature T2 (°C): 600 +2 x (NB - NA) in a heating process of the primary recrystallization annealing is set to not less than 80°C/sec, and an average heating rate S2 from the temperature T2 to 750°C is set to 0.1~0.7 times of S1, whereby a grain-oriented electrical steel sheet having a low iron loss over a full length of a product coil is obtained. In the equations, NA represents N amount (massppm) precipitated after the final cold rolling and NB represents N amount (massppm) precipitated after the primary recrystallization annealing.

[Fig.1]



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## Description

### TECHNICAL FIELD

**[0001]** This invention relates to a method of producing a grain-oriented electrical steel sheet, and more particularly to a method of producing a grain-oriented electrical steel sheet being excellent in the iron loss properties throughout the whole length of a product coil.

### BACKGROUND ART

**[0002]** The grain-oriented electrical steel sheet is a soft magnetic material where its crystal orientation is highly oriented in the Goss orientation ({110} <001>) and is mainly used as cores for transformers or the like. The grain-oriented electrical steel sheet used in the transformer is required to have low iron loss $W_{17/50}$ (W/kg) representing magnetic loss when being magnetized to 1.7 T at a frequency of 50 Hz in order to reduce no-load loss (energy loss).

**[0003]** The iron loss of the electrical steel sheet is represented as the sum of hysteresis loss depending on crystal orientation, purity and the like and eddy-current loss depending on specific resistance, sheet thickness, magnetic domain size and the like. Therefore, as a method for reducing the iron loss are known a method of enhancing an accumulation degree of crystal orientation to improve a magnetic flux density, a method of increasing Si content for enhancing an electric resistance, a method of reducing a thickness of a steel sheet, a method of refining secondary recrystallized grains, a method of refining magnetic domain and so on.

**[0004]** Among them, as a technique for refining the secondary recrystallized grains is known a method of rapidly heating during the decarburization annealing or a method of conducting a rapidly heating treatment just before the decarburization annealing to improve primary recrystallized texture. For example, Patent Document 1 discloses that the grain-oriented electrical steel sheet having extremely low iron loss can be obtained by heating the steel sheet rolled to a final thickness to a temperature of not lower than 700°C at a heating rate of not less than 100°C/sec in a non-oxidizing atmosphere having $PH_2O/PH_2$ of not more than 0.2 just before decarburization annealing, and also Patent Document 2 discloses that the grain-oriented electrical steel sheet having extremely low iron loss can be obtained by rapidly heating the steel sheet rolled to a final thickness to 800~950°C at a heating rate of not less than 100°C/sec in an atmosphere having an oxygen concentration of not more than 500 ppm before the decarburization annealing, and conducting decarburization annealing wherein a temperature of a preceding zone at the decarburization annealing step is 775~840°C lower than a temperature achieved by the rapid-heating and a temperature of subsequent latter zone is 815~875 °C higher than the temperature of the preceding zone. Further, Patent Documents 3 and 4 disclose that grain-oriented electrical steel sheets being excellent in the film properties and magnetic properties can be obtained by heating a temperature zone of at least not less than 600°C at a heating stage of decarburization annealing step to not lower than 800°C at a heating rate of not less than 95°C/s or not less than 100°C/s and properly controlling an atmosphere of this temperature zone.

### PRIOR ART DOCUMENTS

### PATENT DOCUMENTS

**[0005]**

Patent Document 1: JP-A-H07-062436
Patent Document 2: JP-A-H10-298653
Patent Document 3: JP-A-2003-027194
Patent Document 4: JP-A-2000-204450

### SUMMARY OF THE INVENTION

### PROBLEMS TO BE SOLVED BY THE INVENTION

**[0006]** Most of the conventional techniques are intended to improve the primary recrystallization texture and refine secondary recrystallized grains by unambiguously determining the starting temperature of the rapid-heating and defining the achieving temperature of the rapid-heating as not lower than 700°C. According to the inventors' studies, it becomes clear that the secondary recrystallized grains can be surely refined to improve the iron loss by applying the above conventional techniques in most cases, but there is a case that secondary recrystallization behavior is not stabilized and the above improvement effect cannot be obtained over a full length of a coil depending on the precipitation states before the rapid-heating.

**[0007]** The invention is made in view of the above problems inherent to the conventional techniques and is to propose a method of producing a grain-oriented electrical steel sheet which is capable of stabilizing secondary recrystallization behavior to refine secondary recrystallized grains over a full length of a product coil to thereby make the iron loss of the full length of the product coil lower.

## MEANS FOR SOLVING PROBLEMS

**[0008]** In order to solve the above problems, the inventors have made various studies from various viewpoints over an influence of precipitation state of nitrogen (N) in steel sheet in the raid-heating temperature zone, fixed in the conventional techniques, on primary recrystallization behavior. As a result, it has been found that a preferable rapid-heating temperature zone may vary depending on the precipitation state (precipitation amount) of N in the steel sheet. In general, solute nitrogen in the steel sheet is unevenly distributed on a crystal grain boundary or a dislocation, while solute nitrogen retained in the steel sheet after the cold rolling precipitates in the heating process of subsequent heat treatment, but most of them precipitate on the dislocation to inhibit polygonization of the dislocation, which has effects of delaying recovery of microstructure and start of recrystallization. Such effects are considered to vary depending on the precipitation state.

**[0009]** Now, the inventors have made further studies in consideration that the refining of secondary recrystallized grains can be stably attained by accurately understanding and controlling a relation between recovery temperature zone or recrystallization temperature zone and heating rate. Consequently, it has been found out that the refining of secondary recrystallized grains can be stably attained by setting an optimum heating rate with respect to each of the recovery temperature zone and the recrystallization temperature zone, i.e., as shown in FIG. 1, by setting a high heating rate with respect to a relatively low temperature zone mainly enhancing only the recovery (hereinafter referred to as "low temperature zone") and setting a heating rate lower than that of the above low temperature zone with respect to a relatively high temperature zone enhancing both of the recovery and the recrystallization (hereinafter referred to as "high temperature zone") and as a result, the invention has been accomplished.

**[0010]** That is, the invention is a method of producing a grain-oriented electrical steel sheet which comprises a series of steps of hot rolling a steel slab having a chemical composition of C: 0.001~0.10 mass%, Si:1.0~5.0 mass%, Man:0.01~0.5 mass%, sol. Al: 0.003~0.050 mass%, N: 0.0010~0.020 mass%, one or two selected from S and Se: 0.005~0.040 mass% in total, and the remainder being Fe and inevitable impurities, subjecting the resulting sheet to a hot band annealing if necessary, conducting a single cold rolling or two or more cold rollings with an intermediate annealing therebetween to form a cold rolled sheet having a final thickness, conducting a primary recrystallization annealing, applying an annealing separator and conducting a final annealing, characterized in that in a heating process of the primary recrystallization annealing, a heating rate S 1 from a temperature T1 to a temperature T2, which are determined by the following equations (1) and (2):

$$\mathrm{T1}\ (^\circ\mathrm{C}):\ 500+2 \times (\mathrm{NB} - \mathrm{NA}) \quad \cdot\cdot\cdot\ (1);$$

$$\mathrm{T2}\ (^\circ\mathrm{C}):\ 600 + 2 \times (\mathrm{NB} - \mathrm{NA}) \quad \cdot\cdot\cdot\ (2)$$

is set to not less than 80°C/sec, and an average heating rate S2 from the temperature T2 to 750°C is set to 0.1~0.7 times of S1, wherein NA represents N amount (massppm) precipitated after the final cold rolling and NB represents N amount (massppm) precipitated after the primary recrystallization annealing in the equations (1) and (2).

**[0011]** The method of producing a grain-oriented electrical steel sheet according to the invention is characterized in that a total N content in the steel slab NB'(massppm) is used instead of the N amount precipitated after the primary recrystallization annealing NB (massppm).

**[0012]** Also, the method of producing a grain-oriented electrical steel sheet according to the invention is characterized in that the steel slab contains one or more selected from Cu: 0.01~0.2 mass%, Ni: 0.01~0.5 mass%, Cr: 0.01~0.5 mass%, Mo: 0.01~0.5 mass%, Sb: 0.01~0.1 mass%, Sn: 0.01~0.5 mass%, Bi: 0.001~0.1 mass%, P: 0.001~0.05 mass%, Ti: 0.005~0.02 mass% and Nb: 0.0005~0.100 mass% in addition to the above chemical composition.

## EFFECT OF THE INVENTION

**[0013]** According to the invention, the secondary recrystallized grains can be stably refined over the full length of the product coil, so that it is possible to produce a grain-oriented electrical steel sheet having low iron loss in a high yield.

## BRIEF DESCRIPTION OF THE DRAWING

**[0014]** FIG. 1 is a view illustrating a comparison between heating pattern of the invention and heating pattern of the conventional technique in primary recrystallization annealing.

## EMBODIMENTS FOR CARRYING OUT THE INVENTION

**[0015]** First, there will be explained the basic technical concept of the invention that the refining of the secondary recrystallized grains can be stably attained by setting a high heating rate with respect to a relatively low temperature zone mainly enhancing only the recovery (low temperature zone) and setting a heating rate lower than that of the low temperature zone with respect to a relatively high temperature zone enhancing both of the recovery and the recrystallization (high temperature zone).

**[0016]** It is necessary to control primary recrystallization texture in order to improve secondary recrystallization behavior. In particular, in order to refine the secondary recrystallized grains, the number of nuclei of Goss orientation ({110}<041>) is important. Also, in order to stably induce the secondary recrystallization and to prevent secondary recrystallized grains from coarsening, the amount of {111} primary recrystallization texture encroached by the Goss orientation is greatly concerned.

**[0017]** First, the reason why the heating rate in the low temperature zone mainly enhancing only the recovery is increased will be explained below.

**[0018]** It is known that a nucleus of the Goss orientation ({110}<001>) is located in a deformation band formed in {111} fiber structure easily storing strain energy of rolling structure. The deformation band is a region particularly storing strain energy in the {111} fiber structure.

**[0019]** When the heating rate of the low temperature zone in the primary recrystallization annealing is low, a deformation band having extremely high strain energy is preferentially recovered to release the strain energy, so that the recrystallization of the Goss orientation nucleus is hardly caused. While when the heating rate of the low temperature zone is high, the deformation band can be kept at a state of the high strain energy to a high temperature, so that the recrystallization of the Goss orientation nucleus can be preferentially caused.

**[0020]** Next, the reason why the heating rate in the high temperature zone subsequent to the above low temperature zone is made lower than that of the low temperature zone and the heating rate is limited to a specific range will be explained below.

**[0021]** In general, when the amount of {111} primary recrystallization texture easily encroached by the Goss orientation ({110} <001>) is too large, the growth of the secondary recrystallized grains (Goss orientation grains) is promoted, so that there is a fear that even if there are many nuclei of the Goss orientation, one crystal grain is coarsened before the growth of these nuclei. On the other hand, when the amount of the {111} primary recrystallization texture is too small, the growth of the secondary recrystallized grains is difficult and the failure of secondary recrystallization is caused. Therefore, it is necessary to control the {111} primary recrystallization texture to a proper amount.

**[0022]** Here, the {111} primary recrystallization texture is produced by the recrystallization of the {111} fiber structure in the rolling texture. Also, since the rolling texture is oriented in the {111} fiber structure, the main orientation of the primary recrystallization texture is the {111} primary recrystallization texture unless any special heat treatment is conducted. Also, the {111} fiber structure is high in the strain energy as compared to other surrounding textures though the energy is not so much as that of the deformation band generating nuclei of the Goss orientation. Therefore, it is said to be a crystal orientation easy to be recrystallized next to the Goss orientation under a heat treatment condition that the rapid-heating is conducted in the low temperature zone mainly enhancing only the recovery.

**[0023]** It is possible to promote the recrystallization from the deformation band keeping the strain energy or the {111} fiber structure by making slow the heating rate in the high temperature zone after the rapid-heating in the low temperature zone. However, when the heating rate is made too slow, the number of the nuclei of the Goss orientation is somewhat increased, while the {111} primary recrystallization structure originally being a main orientation of the structure is further increased in excess. As a result, the {111} primary recrystallization structure becomes too much and the Goss orientation grains are coarsened in the secondary recrystallization annealing.

**[0024]** However, when the heating in the relatively high temperature zone simultaneously enhancing the recovery and the recrystallization is conducted at the same heating rate as in the low temperature zone, crystals in all orientations start the primary recrystallization before the recrystallization in the Goss orientation or the {111} primary recrystallization structure and hence the texture is randomized. As a result, the {111} primary recrystallization structure becomes decreased and the secondary recrystallization itself may not be generated.

**[0025]** Here, the ranges of the low temperature zone and the high temperature zone have a close relation to the recovery temperature and recrystallization temperature of the material, so that they vary depending on the precipitation state of solute nitrogen having an effect of inhibiting polygonization of dislocation in the primary recrystallization annealing to delay the recovery of the structure and the start of the recrystallization, concretely by N amount precipitated in the primary recrystallization annealing. Therefore, it is necessary to change the heating rate depending on the above precipitated N amount.

**[0026]** The invention is based on the technical idea described above.

**[0027]** Next, the chemical composition of the steel slab used as a raw material for the grain-oriented electrical steel sheet of the invention will be explained below.

C: 0.001~0.10 mass%

**[0028]** C is an element useful for generating the Goss orientation grains and is necessary to be included in an amount of not less than 0.001 mass% in order to develop such an effect. On the other hand, when the C amount exceeds 0.10 mass%, there is a risk of deteriorating the magnetic properties due to an insufficient decarburization in the decarburization annealing. Therefore, the C amount is in the range of 0.001 to 0.10 mass%. Preferably, it is in the range of 0.005 to 0.08 mass%.

Si: 1.0~5.0 mass%

**[0029]** Si has an effect of increasing an electrical resistance of steel to reduce iron loss and is necessary to be added in an amount of at least 1.0 mass% in the invention. On the other hand, when it is added in an amount exceeding 5.0 mass%, it is difficult to conduct the cold rolling. Therefore, the Si amount is in the range of 1.0 to 5.0 mass%. Preferably, it is in the range of 2.0 to 4.5 mass%.

Mn: 0.01 - 0.5 mass%

**[0030]** Mn not only effectively contributes to the improvement of the hot brittleness of steel, but also forms precipitates of MnS, MnSe or the like to develop a function as an inhibitor when S and Se are included. When the Mn content is less than 0.01 mass%, the above effect is not sufficient, while when the addition amount exceeds 0.5 mass%, the slab heating temperature required for dissolving the precipitates such as MnS, MnSe or the like becomes extremely high, which is not preferable. Therefore, the Mn content is in the range of 0.01 to 0.5 mass%. Preferably, it is in the range of 0.01 to 0.3 mass%.

sol. Al: 0.003 - 0.050 mass%

**[0031]** Al is a useful element forming AlN in steel and precipitating as a second dispersion phase to act as an inhibitor. However, when the content as sol. Al is less than 0.003 mass%, the sufficient precipitation amount cannot be ensured and the above effect is not obtained. While when it exceeds 0.050 mass% as sol. Al, the slab heating temperature necessary for solid solution of AlN becomes extremely high and also AlN is coarsened by the heat treatments after the hot rolling to lose the function as an inhibitor. Therefore, Al content is in the range of 0.003 to 0.050 mass% as sol. Al. Preferably, it is in the range of 0.005 to 0.040 mass%.

N: 0.0010~0.020 mass%

**[0032]** N is an element required for forming AlN as an inhibitor like Al. However, when the addition amount is less than 0.0010 mass%, the precipitation of AlN is insufficient, while when it exceeds 0.020 mass%, blistering or the like is caused in heating the slab. Therefore, N content is in the range of 0.0010 to 0.020 mass%. Preferably, it is in the range of 0.0030 to 0.015 mass%.

S and Se: 0.005 - 0.040 mass% in total

**[0033]** S and Se are useful elements which are precipitated as a second dispersion phase in steel by bonding to Mn or Cu to form MnS, MnSe, $Cu_{2-x}S$ or $Cu_{2-x}Se$ to thereby act as an inhibitor. When the addition amount of S and Se in total is less than 0.005 mass%, the above addition effect is not obtained sufficiently, while when it exceeds 0.040 mass%, not only solving S and Se to steel is insufficient in the heating of the slab, but also surface defects are caused in a product. Therefore, the addition amount of S and Se is in the range of 0.005 to 0.040 mass% without regard for the single addition and the composite addition. Preferably, it is in the range of 0.005 to 0.0030 mass%.

**[0034]** In addition to the above chemical composition, the grain-oriented electrical steel sheet of the invention may contain at least one selected from Cu: 0.01~0.2 mass%, Ni: 0.01~0.5 mass%, Cr: 0.01~0.5 mass%, Mo: 0.01~0.5 mass%, Sb: 0.01~0.1 mass%, Sn: 0.01~0.5 mass%, Bi: 0.001~0.1 mass%, P: 0.001~0.05 mass%, Ti: 0.005~0.02 mass% and Nb: 0.0005~0.0100 mass%.

**[0035]** Cu, Ni, Cr, Mo, Sb, Sn, Bi, P, Ti and Nb are elements easily segregating into crystal grain boundary or surface or elements forming carbonitride and have a subsidiary action as an inhibitor. Therefore, the addition of these elements can further improve the magnetic properties. However, when the addition amount is less than the above lower limit, the effect of suppressing the coarsening of the primary recrystallized grains is not obtained sufficiently at a higher temperature zone of the secondary recrystallization process, while when it exceeds the above upper limit, there is a risk of causing poor secondary recrystallization or poor appearance of the coating. Therefore, if such elements are added, it is preferable to be added in the aforementioned range.

**[0036]** As described above, the steel slab used as a raw material of the grain-oriented electrical steel sheet according to the invention is necessary to contain N in an amount of not less than 0.0010 mass% and a nitride-forming element such as Al or the like precipitating by forming nitride.

**[0037]** Moreover, the remainder other than the aforementioned components is Fe and inevitable impurities. However, other components may be contained within the scope not damaging the effect of the invention.

**[0038]** The method of producing the grain-oriented electrical steel sheet according to the invention will be explained below.

**[0039]** The method of producing the grain-oriented electrical steel sheet according to the invention comprises a series of steps of hot-rolling a steel slab having the above chemical composition suitable for the invention, subjecting the hot rolled sheet to a hot band annealing if necessary, subjecting the sheet to a single cold rolling or two or more cold rollings with an intermediate annealing therebetween to obtain a cold rolled sheet having a final thickness, subjecting the cold rolled sheet to primary recrystallization annealing, applying an annealing separator composed mainly of MgO, $Al_2O_3$ or the like, and subjecting the sheet to a final annealing.

**[0040]** The method of producing the steel slab is not particularly limited except that it is necessary to adjust the chemical composition so as to conform with the invention, and well-known production methods can be used. Also, the reheating temperature of the steel slab prior to the hot rolling is preferable to be not lower than 1300°C because it is necessary to solve the inhibitor-forming elements completely.

**[0041]** Further, the conditions of the hot rolling, the conditions of the hot band annealing conducted if necessary, and the conditions of the single cold rolling or two or more cold rollings with an intermediate annealing therebetween for the formation of a cold rolled sheet having a final thickness are not particularly limited as long as they are conducted according to the usual manner. Moreover, aging between rolling passes or warm rolling may be properly adopted in the cold rolling. The production conditions after the cold rolling will be explained below.

**[0042]** In the primary recrystallization annealing after the cold rolling, it is necessary to properly control the heating rates in the low temperature zone mainly enhancing only the recovery and the high temperature zone enhancing primary recrystallization in addition to the recovery during the heating process in order to stably refine the secondary recrystallized grains and enhance a ratio of low iron loss zone in the coil. Concretely, the effect of stably reducing the iron loss can be obtained by setting the heating rate in the low temperature zone to not less than 80°C/sec which is higher than of the usual primary recrystallization annealing and setting the heating rate in the high temperature zone to the range of 0.1 to 0.7 times of the heating rate of the low temperature zone.

**[0043]** Here, the temperature ranges of the low temperature zone and high temperature zone during the heating process are determined based on the precipitation state of N in the steel sheet. The solute nitrogen existing after the cold rolling is unevenly distributed on the crystal grain boundary or dislocation and forms nitrides to be finely precipitated on the dislocation during the heating process of the primary recrystallization annealing so that it has an effect of limiting the movement of the dislocation to inhibit the polygonization, or an effect of recovering the rolled structure or delaying the recrystallization. Therefore, it is considered that the amount of N precipitated in the primary recrystallization annealing largely affects the recovery or the recrystallization.

**[0044]** Under such an idea, the inventors have measured N amount NA (massppm) precipitated in the steel sheet after the final cold rolling and N amount NB (massppm) precipitated in the steel sheet after the primary recrystallization annealing and presumed the difference (NB-NA) (massppm) to be N amount newly precipitated by the primary recrystallization annealing and made many experiments for studying a relation between the difference (NB-NA) and heating conditions for obtaining good magnetic properties (heating rate, temperature range). As a result, we have found that proper heating conditions exist depending on (NB-NA) as mentioned later.

**[0045]** Firstly, it has been found that a heating rate S1 between a temperature T1 determined from the following equation (1) and a temperature T2 determined from the following equation (2) is necessary to be not less than 80°C/sec.

$$T1(°C): 500 + 2 \times (NB\text{-}NA) \quad \cdots (1)$$

$$T2(°C): 600 + 2 \times (NB\text{-}NA) \quad \cdots (2)$$

**[0046]** The above equations (1) and (2) show that as the N amount precipitated in the primary recrystallization annealing is increased, the recovery and recrystallization are delayed and the temperature range in the low temperature zone is made higher.

**[0047]** Also, when the heating rate S 1 in this temperature range is slower than 80°C/sec, the recovery is caused in the deformation band producing the nucleus of the Goss orientation {110} <001>, and preferential recrystallization in the nucleus of the Goss orientation is not caused and the number of the nuclei of the Goss orientation cannot be increased, so that secondary recrystallized grains cannot be refined.

**[0048]** In the invention, the heating rate in the low temperature zone is sufficient to be not less than 80°C/sec, so that an average heating rate from a temperature lower than T1 may be not less than 80°C/sec.

**[0049]** It is preferable that the high temperature zone enhancing both the recovery and recrystallization is within a temperature range of the above T2 (=600 + 2(NB-NA)) to 750°C and the heating rate S2 thereof is in the range of 0.1 to 0.7 times of the heating rate S 1 in the low temperature zone.

**[0050]** Here, the lowest temperature of the temperature range in the high temperature zone is the highest temperature T2 in the low temperature zone and corresponds to the temperature starting recrystallization of only a specific crystal orientation (Goss orientation) when heated at the heating rate S1. On the other hand, the highest temperature is a temperature of 750°C recrystallizing almost all crystals.

**[0051]** Further, the reason why the heating rate S2 is related to S1 is considered due to the fact that as the heating rate in the low temperature zone becomes higher, the recovery of the Goss orientation being preferentially recrystallized can be at an inhibited state, and even if a retention time in the high temperature zone is made short, the recrystallization of the Goss orientation can be promoted and an optimum heating rate in the high temperature zone becomes high in accordance with the heating rate S 1 in the low temperature zone.

**[0052]** However, when the heating rate S2 in the high temperature zone is too high, the recrystallization of texture intended to preferentially recrystallize is also at an inhibited state, and all of orientations is recrystallized to randomize recrystallization texture to thereby cause poor secondary recrystallization. Therefore, it is preferable to limit the heating rate S2 to not more than 0.7 times of S1. Inversely, when the heating rate S2 is too slow, {111} primary recrystallized texture is increased and the effect of refining secondary grains is not obtained, so that it is preferable to be not less than 0.1 times of S1. The preferable S2 is in the range of 0.2 to 0.6 times of S1.

**[0053]** In the invention, it is assumed that N unevenly distributed on the dislocation introduced by the cold rolling is precipitated by forming nitrides on the dislocation in the primary recrystallization annealing. Therefore, the invention cannot be applied when nitriding for increasing N amount in steel is carried out in the primary recrystallization annealing.

**[0054]** In general, the primary recrystallization annealing is ordinarily conducted in combination with decarburization annealing. Even in the invention, the primary recrystallization annealing combined with decarburization annealing may be conducted. In this case, it is preferable that the decarburization annealing is conducted by heating at a heating rate suitable for the invention under such a wet hydrogen atmosphere that an oxidation potential $PH_2O/PH_2$ of the atmosphere is not less than 0.1. Furthermore, when there is restriction on the annealing facility, the decarburization annealing may be performed after the heating treatment at the temperature range and heating rate suitable for the invention is conducted in a non-oxidizing atmosphere.

**[0055]** The steel sheet subjected to the primary recrystallization annealing as described above is subsequently coated on the steel sheet surface with an annealing separator and then subjected to a final annealing of generating secondary recrystallization. As the annealing separator can be used, for example, ones composed mainly of MgO and added with $TiO_2$ if necessary, in case of forming forsterite coating or ones composed mainly of $SiO_2$ or $Al_2O_3$ in case of forming no forsterite coating.

**[0056]** After the unreacted annealing separator is removed from the surface of the finish annealed steel sheet, a product sheet is obtained by applying and baking an insulation coating on the surface of the steel sheet or subjecting to flattening annealing for correcting the shape if necessary. Moreover, the kind of the insulation coating is not particularly limited, but it is preferable to use a tension coating for providing tensile force to the surface of the steel sheet in order to further reduce the iron loss. For example, there can be preferably used an insulation coating formed by baking a coating liquid containing phosphate, chromic acid and colloidal silica as described in JP-A-S50-79442, JP-A-S48-39338 or the like. Further, when the annealing separator forming no forsterite coating is used, the insulation coating may be formed by again applying an aqueous slurry composed mainly of MgO onto the surface of the steel sheet after the final annealing and subjecting to an annealing for forming a forsterite coating. Furthermore, in order to further reduce the iron loss, the steel sheet after the final annealing may be subjected to a well-known magnetic domain subdividing treatment by lineally conducting plasma jet or laser irradiation or electron beam irradiation or by providing linear strain with a protruded roll.

**[0057]** According to the production method of the invention, the secondary recrystallization texture can be stably refined over the full length of the product coil, so that grain-oriented electrical steel sheets having low iron loss can be produced in a high yield.

EXAMPLE 1

**[0058]** A steel slab containing C: 0.06 mass%, Si: 3.3 mass%, Mn: 0.08 mass%, S: 0.023 mass%, sol. Al: 0.03 mass%, N: 0.008 mass%, Cu: 0.2 mass% and Sb: 0.02 mass% is heated to 1430 °C and soaked for 30 minutes and hot rolled to obtain a hot rolled sheet having a sheet thickness of 2.2 mm, which is subjected to a hot band annealing at 1000°C for 1 minute, cold rolled to obtain an intermediate cold rolled sheet having a sheet thickness of 1.5 mm and subjected to an intermediate annealing. The intermediate annealing is conducted under two conditions that the sheet is heated to 1100°C and cooled at a rate of 30°C/sec to promote the precipitation of N and that the sheet is heated to 1150°C and cooled at a rate of 100°C/sec to keep N at a solid solution state. Thereafter, the sheet is further cold rolled to obtain a cold rolled sheet having a final thickness of 0.23 mm.

**[0059]** A test specimen of 100mm x 300mm is taken out from a central portion in longitudinal and widthwise directions of each of the cold rolled sheet coils thus obtained and subjected to a primary recrystallization annealing combined with a primary recrystallization and decarburization in a laboratory. Moreover, the primary recrystallization annealing is conducted with an electrical heating furnace by heating while varying heating rates from 300°C and 800°C as shown in Table 1 and then promoting decarburization while keeping at 840°C for 2 minutes. In this case, $PH_2O/PH_2$ of the atmosphere is controlled to 0.3.

**[0060]** Also, the test specimen taken out from the cold rolled sheet is electrolyzed, filtered and extracted with an AA-based electrolytic solution (acetylacetone) of 10 mass%, and then N amount precipitated in the cold rolled sheet is quantified from the remaining residue to determine N amount precipitated in the cold rolled sheet NA. Also, N amount precipitated in the steel sheet after the primary recrystallization annealing is measured in the same way to determine N amount precipitated after the primary recrystallization annealing NB. The difference between NA and NB (NB-NA) is determined as N amount newly precipitated by the primary recrystallization annealing.

**[0061]** Next, 50 test specimens subjected to the primary recrystallization annealing (decarburization annealing) are prepared with respect to each of the respective heating conditions. After an annealing separator composed mainly of MgO and added with 10 mass% of $TiO_2$ is applied onto each surface of these test specimens in form of an aqueous slurry and dried, the test specimen is subjected to a final annealing to conduct secondary recrystallization and then coated and baked with a phosphate-based insulation tension coating.

**[0062]** With respect to all of the 50 test specimens thus obtained for each heating condition, iron loss $W_{17/50}$ is measured with a single sheet tester to determine an average value and a standard deviation. After the measurement of the iron loss, the coating is removed from the test specimen by pickling, and then a secondary recrystallized grain size in a length range of 300 mm is measured by a linear analysis to determine an average value on the 50 test specimens. The results are also shown in Table.1. As seen from these results, the steel sheets subjected to the heating in the primary recrystallization annealing under conditions according to the invention are small in the secondary recrystallized grain size and good in the iron loss properties and show reduced dispersion.

Table 1

| No | N amount precipitated (massppm) | | Heating rate and temperature range of controlling heating rate | | | | | Average heating rate (°C / s) | | | | Iron loss $W_{17/50}$ (W/kg) | | Secondary grain size (mm) | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NA | NB | Starting temperature (°C) | Heating rate 1 (°C/s) | Switching temperature (°C) | Heating rate 2 (°C/s) | End temperature (°C) | S1 | S2 | S1×0.1 | S1×0.7 | Average value | Standard deviation | | |
| 1 | 53 | 74 | 300 | 80 | 520 | 50 | 800 | 50 | 50 | 5 | 35 | 0.851 | 0.025 | 16.8 | Comparative Example |
| 2 | 54 | 73 | 300 | 80 | 550 | 50 | 800 | 50 | 50 | 5 | 35 | 0.853 | 0.022 | 17.5 | Comparative Example |
| 3 | 52 | 71 | 300 | 80 | 600 | 50 | 800 | 69 | 50 | 7 | 48 | 0.832 | 0.018 | 16.1 | Comparative Example |
| 4 | 53 | 75 | 300 | 80 | 650 | 50 | 800 | 80 | 51 | 8 | 56 | 0.802 | 0.019 | 11.2 | Invention Example |
| 5 | 50 | 73 | 300 | 80 | 700 | 50 | 800 | 80 | 62 | 8 | 56 | 0.820 | 0.028 | 10.0 | Comparative Example |
| 6 | 55 | 72 | 300 | 80 | 800 | - | 800 | 80 | 80 | 8 | 56 | 0.825 | 0.042 | 9.7 | Comparative Example |
| 7 | 54 | 75 | 300 | 100 | 600 | 50 | 800 | 70 | 50 | 7 | 49 | 0.844 | 0.023 | 18.5 | Comparative Example |
| 8 | 52 | 74 | 300 | 100 | 650 | 50 | 800 | 100 | 51 | 10 | 70 | 0.805 | 0.015 | 10.3 | Invention Example |
| 9 | 51 | 72 | 300 | 100 | 700 | 50 | 800 | 100 | 68 | 10 | 70 | 0.811 | 0.018 | 8.4 | Invention Example |
| 10 | 51 | 73 | 300 | 200 | 700 | 50 | 800 | 200 | 83 | 20 | 140 | 0.814 | 0.020 | 9.4 | Invention Example |
| 11 | 32 | 75 | 300 | 80 | 550 | 50 | 800 | 50 | 50 | 5 | 35 | 0.881 | 0.027 | 15.3 | Comparative Example |
| 12 | 30 | 74 | 300 | 80 | 600 | 50 | 800 | 52 | 50 | 5 | 36 | 0.877 | 0.026 | 15.6 | Comparative Example |

(continued)

| No | N amount precipitated (massppm) | | Heating rate and temperature range of controlling heating rate | | | | | Average heating rate (°C / s) | | | | Iron loss $W_{17/50}$ (W/kg) | | Secondary grain size (mm) | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NA | NB | Starting temperature (°C) | Heating rate 1 (°C/s) | Switching temperature (°C) | Heating rate 2 (°C/s) | End temperature (°C) | S1 | S2 | S1×0.1 | S1×0.7 | Average value | Standard deviation | | |
| 13 | 29 | 72 | 300 | 80 | 650 | 50 | 800 | 65 | 50 | 7 | 46 | 0.883 | 0.020 | 15.9 | Comparative Example |
| 14 | 31 | 73 | 300 | 80 | 700 | 50 | 800 | 80 | 55 | 8 | 56 | 0.840 | 0.022 | 10.8 | Invention Example |
| 15 | 32 | 72 | 300 | 80 | 800 | - | 800 | 80 | 80 | 8 | 56 | 0.888 | 0.102 | 7.5 | Comparative Example |
| 16 | 33 | 75 | 300 | 100 | 600 | 20 | 800 | 23 | 20 | 2 | 16 | 0.872 | 0.030 | 14.9 | Comparative Example |
| 17 | 28 | 73 | 300 | 100 | 650 | 20 | 800 | 38 | 20 | 4 | 27 | 0.870 | 0.023 | 14.5 | Comparative Example |
| 18 | 25 | 73 | 300 | 100 | 700 | 20 | 800 | 100 | 21 | 10 | 70 | 0.847 | 0.019 | 11.0 | Invention Example |
| 19 | 25 | 71 | 300 | 300 | 650 | 20 | 800 | 43 | 20 | 4 | 30 | 0.865 | 0.022 | 14.1 | Comparative Example |
| 20 | 32 | 74 | 300 | 300 | 700 | 20 | 800 | 300 | 23 | 30 | 210 | 0.863 | 0.021 | 14.7 | Comparative Example |

Note) NA : Nitrogen amount precipitated after final cold rolling (massppm)
NB : Nitrogen amount precipitated after primary recrystallization annealing (massppm)
S1=Heating rate (°C/sec) from 500+2(NB-NA) to 600+2(NB-NA))
S2=Heating rate (°C/sec) from 600+2(NB-NA) to 750°C

EXAMPLE 2

**[0063]** A steel slab having a chemical composition shown in Table 2 and Table 3 is heated at 1400°C for 20 minutes, hot rolled to obtain a hot rolled sheet of 2.0 mm in thickness, subjected to a hot band annealing at 1000°C for 1 minute, cold rolled to obtain an intermediate cold rolled sheet of 1.5 mm in thickness, subjected to an intermediate annealing at 1100°C for 2 minutes, cold rolled to obtain a final cold rolled sheet having a thickness of 0.23 mm, and then subjected to a magnetic domain subdividing treatment by forming linear grooves through electrolytic etching.

**[0064]** Next, the cold rolled sheet is heated to 750°C at a heating rate shown in Table 2 and Table 3 in a non-oxidizing atmosphere, and heated from 750°C to 840°C at an average heating rate of 10°C/sec, and then subjected to a primary recrystallization annealing combined with decarburization by keeping the sheet in an atmosphere of $PH_2O/PH_2 = 0.3$ for 2 minutes. Thereafter, an aqueous slurry of an annealing separator composed mainly of MgO and added with 10 mass% of $TiO_2$ is applied and dried on the surface of the steel sheet after the primary recrystallization, and the sheet is wound in a coil, subjected to a final annealing, and subjected to a flattening annealing for the purpose of applying and baking a phosphate-based insulation tension coating and flattening the steel sheet to thereby produce a product sheet.

**[0065]** In the production process, N amount precipitated in the steel sheet after the cold rolling NA and N amount precipitated in the steel sheet after the primary recrystallization NB are determined by analyzing the test specimens cut out from longitudinal end portions and widthwise central portion of the coil.

**[0066]** 30 Epstein test pieces each having mass of not less than 500 g are taken out from each of the thus obtained product coils at a constant interval in the longitudinal direction thereof and iron loss $W_{17/50}$ is measured over a full length of the coil to determine a worst value of iron loss in the full length of the coil and a ratio of a portion having iron loss $W_{17/50}$ of not more than 0.8 W/kg to the full length of the coil (achievement ratio: %). The results are also shown in Table 2.

**[0067]** As seen from Table 2, the sheets of Invention Examples heated under the conditions according to the invention are good in the worst value of iron loss $W_{17/50}$ and high in the ratio of the portion having iron loss $W_{17/50}$ of not more than 0.80 w/kg (achievement ratio).

Table 2

| No. | Chemical Composition (mass%) | | | | | | | | N amount precipitated (massppm) | | Heating rate(°C/s) | | | | | | Iron loss $W_{17/50}$ | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | S | Se | sol. A1 | N | Others | NA | NB | ~ 700°C | 700~ 750°C | S1 | S2 | S1×0.1 | S1×0.7 | Best value (W/kg) | Achievement rate (%) | |
| 1 | 0.06 | 3.25 | 0.01 | 0.0013 | 0.0170 | 0.0150 | 0.0040 | - | 10 | 38 | 200 | 80 | 200 | 111 | 20 | 140 | 0.781 | 80 | Invention Example |
| 2 | 0.06 | 3.25 | 0.01 | 0.0013 | 0.0170 | 0.0150 | 0.0040 | - | 9 | 37 | 200 | 200 | 200 | 200 | 20 | 140 | 0.785 | 45 | Comparative Example |
| 3 | 0.06 | 3.25 | 0.01 | 0.0013 | 0.0170 | 0.0150 | 0.0040 | - | 11 | 36 | 50 | 30 | 50 | 38 | 5 | 35 | 0.811 | 0 | Comparative Example |
| 4 | 0.06 | 3.25 | 0.01 | 0.0013 | 0.0170 | 0.0150 | 0.0040 | Cu:0.02 | 13 | 38 | 200 | 80 | 200 | 114 | 20 | 140 | 0.770 | 90 | Invention Example |
| 5 | 0.06 | 3.25 | 0.01 | 0.0013 | 0.0170 | 0.0150 | 0.0040 | Ni:0.03 | 12 | 38 | 200 | 80 | 200 | 113 | 20 | 140 | 0.766 | 95 | Invention Example |
| 6 | 0.06 | 3.25 | 0.01 | 0.0013 | 0.0170 | 0.0150 | 0.0040 | Cr:0.04 | 9 | 35 | 200 | 80 | 200 | 113 | 20 | 140 | 0.764 | 90 | Invention Example |
| 7 | 0.04 | 3.33 | 0.03 | 0.0050 | 0.0050 | 0.0210 | 0.0100 | - | 74 | 92 | 300 | 80 | 300 | 136 | 30 | 210 | 0.775 | 90 | Invention Example |
| 8 | 0.04 | 3.33 | 0.03 | 0.0050 | 0.0050 | 0.0210 | 0.0100 | - | 72 | 93 | 300 | 10 | 300 | 21 | 30 | 210 | 0.798 | 5 | Comparative Example |
| 9 | 0.04 | 3.33 | 0.03 | 0.0050 | 0.0050 | 0.0210 | 0.0100 | Sb:0.02 | 78 | 95 | 300 | 80 | 300 | 137 | 30 | 210 | 0.770 | 100 | Invention Example |
| 10 | 0.04 | 3.33 | 0.03 | 0.0050 | 0.0050 | 0.0210 | 0.0100 | Sn:0.02 | 74 | 95 | 300 | 80 | 300 | 132 | 30 | 210 | 0.772 | 100 | Invention Example |
| 11 | 0.04 | 3.33 | 0.03 | 0.0050 | 0.0050 | 0.0210 | 0.0100 | Sb:0.02,<br>Sn:0.02 | 71 | 91 | 300 | 80 | 300 | 133 | 30 | 210 | 0.751 | 100 | Invention Example |

(continued)

| No. | Chemical Composition (mass%) | | | | | | | | N amount precipitated (massppm) | | Heating rate(°C/s) | | | | | | Iron loss $W_{17/50}$ | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | S | Se | sol. A1 | N | Others | NA | NB | ~ 700°C | 700~ 750°C | S1 | S2 | S1×0.1 | S1×0.7 | Best value (W/kg) | Achievement rate (%) | |
| 12 | 0.04 | 3.33 | 0.03 | 0.0050 | 0.0050 | 0.0210 | 0.0100 | Mo:0.01 | 75 | 94 | 300 | 80 | 300 | 134 | 30 | 210 | 0.769 | 100 | Invention Example |

Note) NA: Nitrogen amount precipitated after final cold rolling (massppm)
NB : Nitrogen amount precipitated after primary recrystallization annealing (massppm)
S1= Heating rate (°C/sec) from 500+2(NB-NA) to 600+2(NB-NA))
S2= Heating rate (°C/sec) from 600+2(NB-NA) to 750°C

Table 3

| No. | Chemical composition (mass%) | | | | | | | | N amount pre-cipitated (massppm) | | Heating rate(°C/s) | | | | | | Iron loss $W_{17/50}$ | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | S | Se | sol.Al | N | Others | NA | NB | ~ 600°C | 600~ 750°C | S1 | S2 | S1× 0.1 | S1× 0.7 | Best value (W/kg) | Achievement date (%) | |
| 13 | 0.03 | 3.05 | 0.05 | 0.0030 | 0.0160 | 0.0320 | 0.0150 | - | 122 | 138 | 120 | 70 | 105 | 70 | 11 | 74 | 0.783 | 75 | Invention Example |
| 14 | 0.03 | 3.05 | 0.05 | 0.0030 | 0.0160 | 0.0320 | 0.0150 | - | 125 | 136 | 100 | 70 | 91 | 70 | 9 | 64 | 0.790 | 30 | Comparative Example |
| 15 | 0.03 | 3.05 | 0.05 | 0.0030 | 0.0160 | 0.0320 | 0.0150 | Bi:0.001 | 120 | 140 | 120 | 70 | 102 | 70 | 10 | 71 | 0.780 | 80 | Invention Example |
| 16 | 0.03 | 3.05 | 0.05 | 0.0030 | 0.0160 | 0.0320 | 0.0150 | Ti:0.01 | 119 | 138 | 120 | 70 | 103 | 70 | 10 | 72 | 0.782 | 85 | Invention Example |
| 17 | 0.03 | 3.05 | 0.05 | 0.0030 | 0.0160 | 0.0320 | 0.0150 | P:0.008 | 126 | 139 | 120 | 70 | 108 | 70 | 11 | 76 | 0.783 | 85 | Invention Example |
| 18 | 0.03 | 3.05 | 0.05 | 0.0030 | 0.0160 | 0.0320 | 0.0150 | Nb:0.0010 | 124 | 137 | 120 | 70 | 108 | 70 | 11 | 76 | 0.778 | 80 | Invention Example |

Note) NA : Nitrogen amount precipitated after final cold rolling (massppm)
NB : Nitrogen amount precipitated after primary recrystallization annealing (massppm)
S1 = Heating rate (°C/sec) from 500+2(NB-NA) to 600+2(NB-NA))
S2=Heating rate (°C/sec) from 600+2(NB-NA) to 750°C

**[0068]** Moreover, when N in steel is not actively increased (not nitrided) in the primary recrystallization as in this example, it may be considered that all of the N amount in the steel slab is precipitated after the primary recrystallization annealing. In the actual operation, therefore, if the N amount precipitated after the cold rolling (before the primary recrystallization annealing) becomes clear, it is possible to set appropriate heating rate patterns. Also, if the production condition such as annealing pattern before the final cold rolling or the like is constant, it is possible to estimate N amount precipitated in the steel sheet after the cold rolling based on preliminary research.

## INDUSTRIAL APPLICABILITY

**[0069]** The technique of the invention is applicable to improve textures of non-oriented electrical steel sheets or to improve textures of thin steel sheets.

## Claims

1. A method of producing a grain-oriented electrical steel sheet which comprises a series of steps of hot rolling a steel slab having a chemical composition of C: 0.001~0.10 mass%, Si:1.0~5.0 mass%, Mn:0.01~0.5 mass%, sol. Al: 0.003~0.050 mass%, N: 0.0010~0.020 mass%, one or two selected from S and Se: 0.005~0.040 mass% in total, and the remainder being Fe and inevitable impurities, subjecting the resulting sheet to a hot band annealing if necessary, conducting a single cold rolling or two or more cold rollings with an intermediate annealing therebetween to form a cold rolled sheet having a final thickness, conducting a primary recrystallization annealing, applying an annealing separator, and conducting a final annealing, **characterized in that** in a heating process of the primary recrystallization annealing, a heating rate S 1 from a temperature T1 to a temperature T2, which are determined by the following equations (1) and (2):

$$T1\ (°C): 500+2 \times (NB - NA) \quad \cdot\cdot\cdot (1);$$

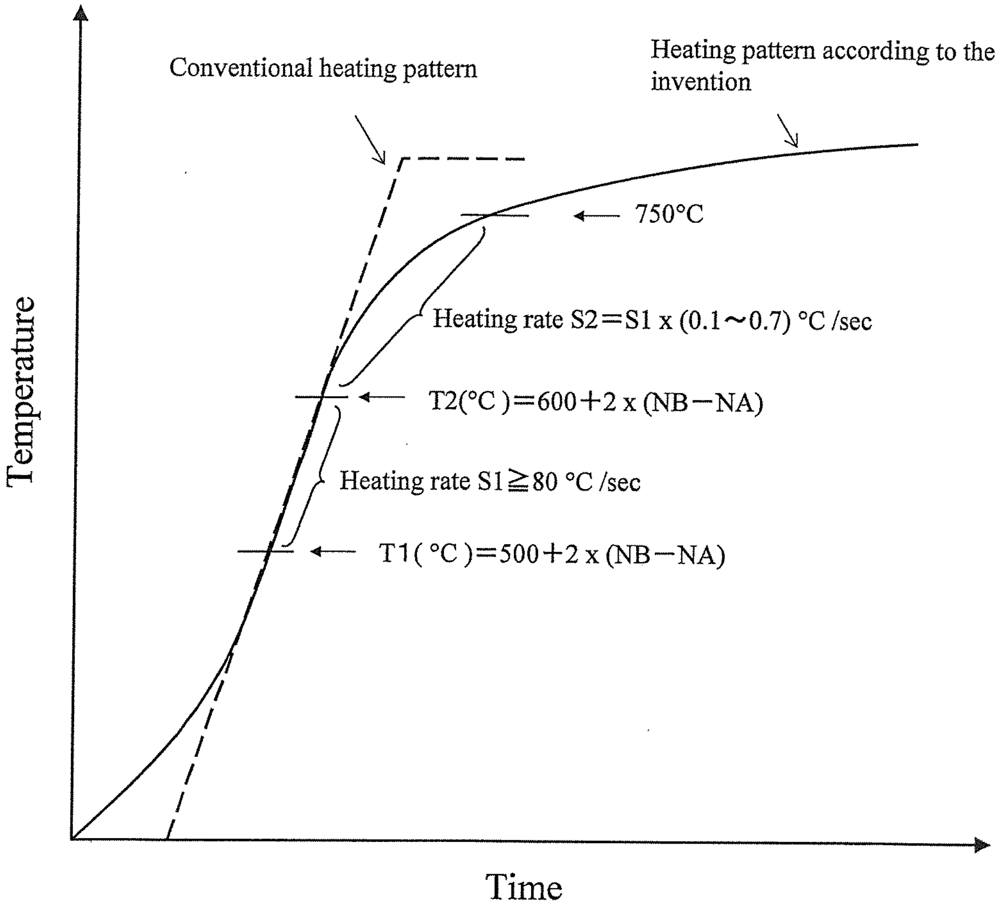
$$T2\ (°C): 600 +2 \times (NB - NA) \quad \cdot\cdot\cdot (2)$$

   is set to not less than 80°C/sec, and an average heating rate S2 from the temperature T2 to 750°C is set to 0.1~0.7 times of S1, wherein NA represents N amount (massppm) precipitated after the final cold rolling and NB represents N amount (massppm) precipitated after the primary recrystallization annealing in the equations (1) and (2).

2. The method of producing a grain-oriented electrical steel sheet according to claim 1, wherein a total N content in the steel slab NB'(massppm) is used instead of the N amount precipitated after the primary recrystallization annealing NB (massppm).

3. The method of producing a grain-oriented electrical steel sheet according to claim 1 or 2, wherein the steel slab contains one or more selected from Cu: 0.01~0.2 mass%, Ni: 0.01~0.5 mass%, Cr: 0.01~0.5 mass%, Mo: 0.01~0.5 mass%, Sb: 0.01~0.1 mass%, Sn: 0.01~0.5 mass%, Bi: 0.001~0.1 mass%, P: 0.001~0.05 mass%, Ti: 0.005~0.02 mass% and Nb: 0.0005~0.100 mass% in addition to the above chemical composition.

[ Fig.1]


Conventional heating pattern
Heating pattern according to the invention
750°C
Heating rate S2=S1 x (0.1~0.7) °C /sec
T2(°C )=600+2 x (NB−NA)
Heating rate S1≧80 °C /sec
T1( °C )=500+2 x (NB−NA)
Temperature
Time

| INTERNATIONAL SEARCH REPORT | International application No.<br>PCT/JP2012/073608 |
|---|---|

A. CLASSIFICATION OF SUBJECT MATTER

*C21D8/12*(2006.01)i, *C22C38/00*(2006.01)i, *C22C38/60*(2006.01)i, *H01F1/16*(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)

C21D8/12, C22C38/00, C22C38/60, H01F1/16

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 | 1996-2012 |
| Kokai Jitsuyo Shinan Koho | 1971-2012 | Toroku Jitsuyo Shinan Koho | 1994-2012 |

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | JP 2000-144249 A (Kawasaki Steel Corp.),<br>26 May 2000 (26.05.2000),<br>claims 1, 2; paragraph [0039]<br>(Family: none) | 1-3 |

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

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"&" document member of the same patent family

| | |
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| Date of the actual completion of the international search<br>04 December, 2012 (04.12.12) | Date of mailing of the international search report<br>11 December, 2012 (11.12.12) |
| Name and mailing address of the ISA/<br>Japanese Patent Office<br>Facsimile No. | Authorized officer<br>Telephone No. |

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

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2012/073608

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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