

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
23 July 2009 (23.07.2009)

PCT

(10) International Publication Number
WO 2009/091127 A2

(51) International Patent Classification:

C21D 8/12 (2006.01) **B21B 3/00** (2006.01)
C22C 38/00 (2006.01)

10-2008-0119207

27 November 2008 (27.11.2008) KR

10-2008-0119201

27 November 2008 (27.11.2008) KR

(21) International Application Number:

PCT/KR2008/007727

10-2008-0119202

27 November 2008 (27.11.2008) KR

(22) International Filing Date:

27 December 2008 (27.12.2008)

(71) Applicant (for all designated States except US): **POSCO**
[KR/KR]; 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do 790-300 (KR).

(25) Filing Language:

Korean

(72) Inventors; and

(26) Publication Language:

English

(75) Inventors/Applicants (for US only): **JOO, Hyung-Don**

(30) Priority Data:

10-2007-0140116	28 December 2007 (28.12.2007)	KR
10-2008-0119208	27 November 2008 (27.11.2008)	KR
10-2008-0119209	27 November 2008 (27.11.2008)	KR
10-2008-0119200	27 November 2008 (27.11.2008)	KR
10-2008-0119204	27 November 2008 (27.11.2008)	KR
10-2008-0119203	27 November 2008 (27.11.2008)	KR

PARK, Jong-Tae [KR/KR]; c/o POSCO, 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do 790-300 (KR). **KIM, Chang-Soo** [KR/KR]; c/o POSCO, 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do 790-300 (KR). **HAN, Kyu-Seok** [KR/KR]; c/o POSCO, 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do 790-300 (KR). **KIM, Jae-Kwan** [KR/KR]; c/o POSCO, 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do 790-300 (KR). **SEO, Jin-Wook** [KR/KR]; c/o POSCO, 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do 790-300 (KR). **LIM, Jae-Soo** [KR/KR]; c/o POSCO, 1 Koedong-dong, Nam-gu, Pohang, Kyung-sang-book-do

[Continued on next page]

(54) Title: GRAIN ORIENTED ELECTRICAL STEEL HAVING EXCELLENT MAGNETIC PROPERTIES AND MANUFACTURING METHOD FOR THE SAME

[Fig. 4]

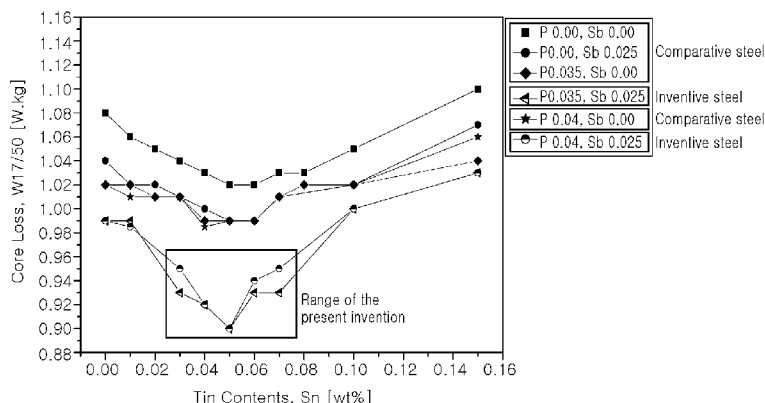


FIG. 4

(57) Abstract: There are provided a grain-oriented electrical steel sheet having excellent magnetic properties and a method for manufacturing the same. More particularly, there are provided a grain-oriented electrical steel sheet whose magnetic properties are remarkably improved to the extent that is unexpected in similar component systems in the prior art by adjusting contents of the components and improving the manufacturing method and, a method for manufacturing the same. The grain-oriented electrical steel sheet essentially comprises 0.03 to 0.07% by weight of Sn, 0.01 to 0.5% by weight of Sb, and 0.01 to 0.05% by weight of P.

WO 2009/091127 A2



790-300 (KR). **KIM, Byeong-Goo** [KR/KR]; c/o POSCO,
1 Koedong-dong, Nam-gu, Pohang, Kyungsangbook-do
790-300 (KR). **KWON, Min-Serk** [KR/KR]; c/o POSCO,
1 Koedong-dong, Nam-gu, Pohang, Kyungsangbook-do
790-300 (KR). **CHOI, Heon-Jo** [KR/KR]; c/o POSCO,
1 Koedong-dong, Nam-gu, Pohang, Kyungsangbook-do
790-300 (KR). **PARK, Soon-Bok** [KR/KR]; c/o POSCO,
1 Koedong-dong, Nam-gu, Pohang, Kyungsangbook-do
790-300 (KR).

(74) **Agent: C & S LOGOS PATENT AND LAW OFFICE;**
13th Floor, Seocho-Pyunghwa Building, 1451-34 Seocho-
dong, Seocho-gu, Seoul 137-070 (KR).

(81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE,
EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID,

IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR,
LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX,
MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO,
RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished
upon receipt of that report*

Description

GRAIN ORIENTED ELECTRICAL STEEL HAVING EXCELLENT MAGNETIC PROPERTIES AND MANU- FACTURING METHOD FOR THE SAME

Technical Field

- [1] The present invention relates to a grain-oriented electrical steel sheet having excellent magnetic properties and a method for manufacturing the same, and more particularly, to a grain-oriented electrical steel sheet whose magnetic properties is remarkably improved to the extent that is unexpected in similar component systems in the prior art by adjusting contents of the components and improving the manufacturing method and, a method for manufacturing the same.

[2]

Background Art

- [3] An electrical steel sheet is referred to as a silicon steel sheet used to manufacture electrical machines or devices. The electrical steel sheet may be broadly divided into a grain-oriented electrical steel sheet and a non-oriented electrical steel sheet. In particular, the grain-oriented electrical steel sheets is composed of crystal grains having a so-called Goss texture in which the orientation of the crystal plane of the grain is a {110} plane and the crystal orientation of the grain in the rolling direction is parallel to a <001> axis, as discovered and suggested by Goss. Thus, these steel sheets have excellent magnetic properties in the rolling direction.
- [4] The effect of the crystal orientation of a grain-oriented electrical steel sheet on magnetic properties thereof is briefly described with reference to FIG. 1 (cited literature: Arai ken et. al, Recent Development of Electrical Steel Sheets, the Iron & Steel Institute of Japan, pp 15, 1995). FIG. 1 is a graph illustrating the results of experiments conducted on single crystals to identify the relationship between iron loss and a deviation of the actual crystal orientation of a steel sheet from the Goss orientation. As seen from the graph of FIG. 1, a deviation of approximately 2° (i.e., so-called an absolute value of an angle β , which will be described later) from the Goss orientation indicates the lowest iron loss. Therefore, grain-oriented electrical steel sheets are generally manufactured such that their crystal orientations deviate from the Goss orientation by angles as close to 2 as possible. The orientation of an electrical steel sheet, which is polycrystalline material, may be obtained by calculating an area-

weight average of the absolute values of the angle β among the angles by which the orientation of each grain deviates from the Goss orientation in consideration of the grain area. For simplicity, the phrase 'an area-weight average of absolute values of the angle β among angles by which the orientation of each of grain deviates from the Goss orientation will be shortened to 'a deviation from the Goss orientation'.

- [5] Referring to FIG. 2, the deviation from the Goss orientation is represented by angles α , β and γ . It is generally known that controlling the angle β is the most effective way to control magnetic properties of an electrical steel sheet. Therefore, a deviation of the angle β from the Goss orientation will be simplified into 'a deviation from the Goss orientation' throughout the specification of the present invention.
- [6] In order to manufacture a steel sheet having an orientation close to the Goss orientation, it is necessary for the orientations of all crystals to match the Goss orientation. However, since electrical steel sheets are manufactured by rolling slabs, they should inevitably have a polycrystalline structure. Accordingly, each crystal has a different orientation, and special operations are required to make the orientation of each crystal close to the Goss orientation.
- [7] That is, while a rolled steel sheet having the polycrystalline structure includes crystals having orientations close to the Goss orientation, it mostly includes crystals having orientations largely different from the Goss orientation. Therefore, when the crystals whose orientations are different from the Goss orientation are used as they are, it is difficult to produce an electrical steel sheet having excellent magnetic properties. For this reason, the steel sheet having the polycrystalline structure must be re-crystallized so that only the crystals whose orientations are close to the Goss orientation can remain in the steel sheet. The orientations of crystals that grow preferentially during the recrystallization are determined by the recrystallization temperature. Thus, when the recrystallization temperature is controlled properly, crystals having orientations close to the Goss orientation can grow preferentially. Consequently, the steel sheet has a low fraction of crystals having orientations close to the Goss orientation before the recrystallization process, but has a high fraction of crystals having orientations close to the Goss orientation after the recrystallization process. This recrystallization process is referred to as secondary recrystallization, so that it can be distinguished from preceding primary recrystallization (which will be described later).
- [8] Before the secondary recrystallization, primary recrystallization is performed to distribute crystals uniformly. Generally, the primary recrystallization is performed im-

mediately after or at the same time as decarburization annealing which is performed after the cold rolling process. Grains having uniform and appropriate grain sizes are formed as a result of the primary recrystallization process. Of course, since the grains are oriented uniformly in various directions, the grains having the Goss orientation in the grain-oriented electrical steel sheet has a very low final fraction.

[9] As described above, the primarily recrystallized steel sheet may be manufactured into a steel sheet having the Goss orientation and excellent magnetic properties by secondarily recrystallizing the primarily recrystallized steel sheet at a suitable temperature to address the Goss orientation to the steel sheet. Meanwhile, when grains having different orientations in the primarily recrystallized steel sheet have different sizes, there is a higher probability that larger grains will outnumber smaller grains due to the so-called "size advantage" (i.e., the fact that larger grains are more stable than smaller grains), irrespective of their orientations, although the primarily recrystallized steel sheet is secondarily recrystallized at the suitable temperature to address the Goss orientation to the steel sheet. Consequently, the fraction of grains whose orientations deviate from the Goss orientation may be increased.

[10] Therefore, grains must be distributed with a uniform and appropriate size during the primary recrystallization. When grains are too fine, interfacial energy may be increased due to an increase of a crystal interfacial area, thereby making the grains unstable. In this case, secondary recrystallization occurs at an excessively low temperature, and thus grains whose orientations are out of the Goss orientation may be undesirably created in large numbers. The appropriate size of grains may be varied according to the kinds of elements (inhibitors) to be added, which will be described later.

[11] When the primarily recrystallized grains are recrystallized at an appropriate temperature, grains, which is suitable for a grain-oriented electrical steel sheet and has the Goss orientation, may be created in preferentially larger numbers. Therefore, it is necessary to heat the grains to the appropriate temperature. However, the grains are inevitably exposed to a low-temperature range before being heated to the appropriate temperature. When the grains are recrystallized in the low-temperature range, the grains having the Goss orientation cannot be obtained in preferentially larger numbers. For this reason, there is required a means for inhibiting the growth of crystal grains in order to prevent the recrystallization of the grains until the grains are heated to the appropriate temperature. A means that plays this role within the steel sheet may be obtained through segregation or precipitation of an element added to the steel sheet.

The element that plays this role is referred to as an inhibitor.

- [12] Before the grains are heated to the appropriate secondary recrystallization temperature, the inhibitor stays around grain boundaries in the form of precipitates or segregates to inhibit the further growth of the grains. Then, when the grains are heated to the appropriate (secondary recrystallization) temperature, the inhibitor is dissolved or decomposed, thereby facilitating the unrestricted growth of the grains.
- [13] Examples of the above-mentioned elements widely used as the inhibitor include MnS and MnSe.
- [14] For example, Japanese Patent Publication No. Sho 51-13469 discloses a method of manufacturing an electrical steel sheet. In this disclosure, a grain-oriented steel sheet is manufactured in a series of processes, including slab heating, hot rolling, annealing of hot rolled sheet, first cold rolling, intermediate annealing, second cold rolling, decarburization annealing and final annealing, and MnSe and Sb are used as inhibitors. In addition, Japanese Patent Publication No. Sho 30-3651 discloses a technology for manufacturing a grain-oriented electrical steel sheet. In this disclosure, the grain-oriented electrical steel sheet is manufacture through two cold rolling processes including intermediate annealing and MnS is used as an inhibitor. Another example of the method using MnS as an inhibitor is disclosed in Japanese Patent Publication No. Sho 40-15644. In this disclosure, MnS and AlN are used as inhibitors, and products having a high magnetic flux density are obtained at a high reduction rate of more than 80 % through the one-stage cold rolling process.
- [15] Meanwhile, the methods using MnS as an inhibitor have a drawback in that a slab must be reheated at a very high temperature to form MnS. That is, since MnS in a slab is present in the form of coarse precipitates, it may not act as an inhibitor that is used to manufacture a grain-oriented electrical steel sheet. Therefore, the MnS must be dissolved and then distributed uniformly. For this purpose, the slab must be heated to a temperature at which MnS may be dissolved. The temperature for dissolving MnS is very high, i.e., about 1300°C or more, even when thermodynamic equilibrium is taken into consideration. In reality, the slab must be reheated to a far higher temperature, e.g., approximately 1400°C, so as to dissolve MnS at a sufficiently high speed so that MnS can be used in the field of various industrial applications.
- [16] When the slab is heated to such a high temperature, however, a lot of energy may be consumed to heat the slab, and a surface of the slab may melt, which leads to the high cost of repairing a reheating furnace, and the reduced lifespan of the reheating furnace.
- [17] In this regard, there is a demand for an inhibitor that can lower the reheating

temperature of slab. In response to this demand, a nitride-based inhibitor has been provided. The nitride-based inhibitor has advantages, as follows. Nitrogen can be introduced by the condition formed in the nitrogen atmosphere which enables nitrogen to be easily introduced into the steel sheet immediately after or at the same time as the decarburization annealing. Thus, the nitrogen introduced into the steel sheet reacts with a nitride-forming element in the steel sheet to form nitrides, which function as an inhibitor. Examples of the nitride include elements such as AlN, (Al,Si)N.

[18] Since the cold-rolled steel sheet may be nitrized at an appropriate temperature at the same time as or after the decarburization annealing thereof, the reheating temperature of the cold-rolled steel sheet may be close to a typical reheating temperature during the hot-rolling process. This reheating pattern is referred to as "low-temperature reheating" in the field of manufacturing a grain-oriented electrical steel sheet.

[19] Examples of the method of manufacturing a grain-oriented electrical steel sheet through the above-mentioned low-temperature reheating are disclosed in Japanese Patent Publication Nos. Hei 1-230721 and Hei 1-283324 and Korean Patent Laid-Open Publication Nos 97-48184 and 97-28305. In the above methods, an ammonia gas is used to create a nitrogen atmosphere. Generally, the ammonia gas tends to be decomposed into hydrogen and nitrogen at approximately 500°C or above. Thus, the characteristics of the ammonia gas may be used to supply nitrogen to a steel sheet.

[20] However, the low-temperature reheating process based on the above nitriding method also has a problem in that it is impossible to improve magnetic properties of a steel sheet only by the use of nitrogen.

[21] In order to further improve magnetic properties of a grain-oriented electrical steel sheet, a fraction of grains, which grow with Goss orientation during secondary recrystallization, may be increased by adding another element that can function as an inhibitor. Alternatively, a fraction of grains having the Goss orientation during secondary recrystallization may be increased by increasing a fraction of crystals having the Goss orientation during primary recrystallization. Furthermore, the size of primarily recrystallized grains may be uniformly distributed so as to prevent the grains, which have failed to have the Goss orientation, from growing larger during the secondary recrystallization due to their size advantage.

[22] The conventional proposed methods may be implemented by, for example, improving compositions of a steel sheet. That is, when elements such as Sn, Sb and P are added to an electrical steel sheet, the magnetic properties of the electrical steel sheet may be greatly improved for the following reasons.

- [23] That is, Sb and Sn function to increase a fraction of grains having a {110}<001> orientation in a primary recrystallization structure and allow sulfides to precipitate uniformly. In addition, when the content of the added Sb and Sn exceeds a pre-determined level, an oxidation reaction may be prevented during decarburization annealing. Thus, it is possible to raise the temperature for decarburization annealing which, in turn, makes it easier to form a first coating film on the grain-oriented electrical steel sheet. In addition, since the above-mentioned elements may prevent the growth of grains through the precipitation at grain boundaries, the particle size of secondarily recrystallized grains can be reduced. Here, the formation of the fine secondarily recrystallized grains leads to a magnetic-domain-minimizing effect.
- [24] It has been known that P functions to improve a texture during primary recrystallization. That is, P functions to increase a fraction of grains having the Goss orientation during primary recrystallization.
- [25] Japanese Patent Publication Nos. Hei 2-294428 and Hei 11-335794 and Nos. 2006-241503, 2007-254829, and 2007-051338 disclose that elements, such as Sn, Sb and P, are added to a grain-oriented electrical steel sheet.
- [26] Specifically among them, Japanese Patent Publication No. Hei 2-294428 discloses a grain-oriented electrical steel sheet having a high magnetic flux density, wherein 0.0007 to 0.045% by weight of P is added to the grain-oriented electrical steel sheet. In addition, Japanese Patent Publication No. 2006-241503 discloses a method of manufacturing a silicon steel sheet having stable magnetic properties by adding 0.015 to 0.07% by weight of P together with other elements and further adding one or more of 0.005 to 0.2% by weight of Sb and 0.01 to 0.5% by weight of Sn, when necessary.
- [27] Japanese Patent Publication No. 2007-254829 discloses a method of manufacturing a grain-oriented electrical steel sheet having excellent magnetic properties by adding 0.02 to 0.30% by weight of one or more of Sn, Sb, and P, when necessary. In addition, Japanese Patent Publication No. 2007-051338 discloses a method of manufacturing a grain-oriented electrical steel sheet having superior magnetic properties in a 45-degree direction by adding 0.2% by weight or less of P and further adding one or more of 0.001 to 0.02% by weight of Sb and 0.002 to 0.1% by weight of Sn, when necessary.
- [28] Japanese Patent Publication No. Hei 11-335794 also discloses a method of manufacturing an electrical steel sheet by adding 0.0005 to 2.0% by weight of at least one element, selected from the group consisting of Sn, Sb, P, B, Bi, Mo, Te and Ge, to a component system of the electrical steel sheet.
- [29] While the addition of the elements such as Sn, Sb and P is disclosed in the above

patent literatures, it was disclosed that the above-mentioned elements is in a very wide content range. In addition, the patent literature simply discloses that one or more of the elements are included in a steel sheet. That is, although the conventional researches have found out that the addition of Sn, Sb and P can improve magnetic properties of an electrical steel sheet, they have failed to disclose the appropriate contents of the respective elements and a synergic effect that may be generated by the interaction between the elements. Thus, a specific alternative of improving magnetic properties of an electrical sheet by the addition of appropriate contents of the elements remains to be provided.

[30] The primary and secondary recrystallization behaviors of an electrical steel sheet including Sn, Sb and P are different from those of a convention electrical steel sheet including an inhibitor only. The prior arts, however, fail to provide solutions to this problem. That is, steel with the above elements has a smaller primarily recrystallized grain size and a stronger inhibitory effect on the secondary recrystallization than steel without the above elements. However, the prior arts do not disclose the context of controlling the annealing process in consideration of the above points of view.

[31] Apart from the above points, the secondary recrystallization occurs in the final annealing process among a series of the processes of the method for manufacturing an electrical steel sheet, such as slab hot rolling, annealing of hot rolled steel sheet, cold rolling, decarburization annealing, and final annealing. When the initiation temperature is excessively increased and maintained for a long time so as to conduct the secondary recrystallization, the productivity maybe be deteriorated.

[32] That is, since the final annealing is performed by heating coiled steel sheets to a high temperature, the coiled steel sheets may adhere to each other. Thus, a surface of each coiled steel sheet is coated with an annealing separator, which mainly contains MgO, before the final annealing. Here, since the surface of each coiled steel sheet is coated with MgO together with moisture, i.e., in the form of paste, the each coiled steel sheet is subject to a two-step soaking process. The two-step soaking process is divided into a first soaking process in which moisture in a steel sheet is removed from paste and a second soaking process in which the steel sheet is maintained at an appropriate temperature after being heated to the secondary recrystallization temperature after the first soaking process.

[33] In the first soaking process, moisture that coexists with MgO is removed, and Si contained in the steel sheet takes part in the reaction to form an MgO-SiO_2 composite oxide film on a surface of the steel sheet.

- [34] As described above, the orientation of grains that grow preferentially is determined by the secondary recrystallization temperature. Thus, the secondary recrystallization temperature must be precisely controlled. That is, the secondary recrystallization occurs when the inhibitor such as MnS or AlN is redissolved in a steel sheet. Thus, it is most desirable to abruptly remove the inhibitor within as narrow temperature range as possible. When the temperature is sharply increased, the inhibitor may be removed in a wide temperature range. In this case, grains having various orientations may also grow. Thus, it is difficult to obtain a grain-oriented electrical steel sheet having excellent magnetic properties and including a preferentially larger number of grains whose orientations are close to the Goss orientation. For this reason, in the prior art, a steel sheet is heated very slowly to the secondary recrystallization temperature, particularly at a rate of 10 to 17°C. However, when a steel sheet is heated at such slow rate, an excessive amount of time is required to heat the steel sheet to the temperature for the second soaking process, which leads to the low productivity.
- [35] Furthermore, although AlN and MnS that have been used as the inhibitors are useful for increasing a fraction of grains having the Goss orientation during secondary recrystallization, they are harmful to magnetic properties of a final grain-oriented electrical steel sheet. Therefore, it is desirable to remove the inhibitors after secondary recrystallization. When the electrical steel sheet is maintained at a high temperature in a controlled atmosphere, the elements can be removed. Thus, the second soaking process is performed at a high temperature. The second soaking process is very useful since the N and S elements and island grains are reduced. In most electrical steel sheets, however, the primary and secondary recrystallization processes are performed after large amounts of N and S are dissolved into the steel sheet, in order to form large amounts of the inhibitors, i.e. AlN and MnS. Therefore, too much time is required to perform the second soaking process to remove the large amounts of N and S, which leads to the poor productivity.

[36]

Disclosure of Invention

Technical Problem

- [37] The present invention is designed to solve the problems of the prior art, and therefore it is an aspect of the present invention to provide a grain-oriented electrical steel sheet having further improved magnetic properties by adjusting contents of the Sn, Sb and P to suitable ranges, optimizing the correlation between the elements and adding an

additional magnetism-improving element.

[38] Also, it is another aspect of the present invention to provide a method for manufacturing a grain-oriented electrical steel sheet, which solves the problem associated with the poor productivity that is easily caused in the manufacture of the electrical steel sheet having the excellent properties according to one exemplary embodiment of the present invention.

[39] It is still another aspect of the present invention to provide a method for manufacturing a grain-oriented electrical steel sheet having a heating pattern that is suitable for the component system.

[40]

Technical Solution

[41] According to an aspect of the present invention, there is provided a grain-oriented electrical steel sheet essentially including 0.03 to 0.07% by weight of Sn, 0.01 to 0.05% by weight of Sb, and 0.01 to 0.05% by weight of P.

[42] In this case, the P+0.5Sb may be in range of 0.0370 to 0.0630 (wherein P and S represents contents (% by weight) of corresponding elements, respectively).

[43] Also, the grain-oriented electrical steel sheet may further include one or more of 1.40% by weight or less of As, 0.50% by weight or less of Cu, 0.1% by weight or less of Bi, 1.40% by weight or less of Te, 1.40% by weight or less of Ni, 0.35% by weight or less of Cr, 1.40% by weight or less of Pb, and 1.40% by weight or less of the sum of at least one element selected from the group of Mo, B, Ge, Nb, Ti, and Zn.

[44] In addition, the grain-oriented electrical steel sheet may further include 2.0 to 4.0% by weight of Si, 0.020 to 0.040% by weight of acid-soluble Al and 0.01 to 0.20% by weight of Mn.

[45] Additionally, the crystal orientation of the electrical steel sheet may deviate from the Goss orientation by less than 3 degrees.

[46] Furthermore, the grain-oriented electrical steel sheet may be manufactured from a steel slab further comprising 0.04 to 0.07% by weight of C, 10 to 55 ppm of N and 0.0010 to 0.0055% by weight of S.

[47] Also, there is provided a method of manufacturing an electrical steel sheet. Here, the method include: manufacturing a steel sheet by hot-rolling, annealing and cold-rolling a steel slab, wherein the steel slab essentially comprises 0.03 to 0.07% by weight of Sn, 0.01 to 0.05% by weight of Sb and 0.01 to 0.05% by weight of P; subjecting the cold-rolled steel sheet to decarburization and nitriding annealing processes within a temperature range of 800 to 950°C; and finally annealing the annealed steel sheet,

wherein, when the final annealing operation comprises first soaking, heating, and second soaking operations, the heating temperature is increased at a heating rate of 18 to 75°C/hr at the beginning, and then increased at a rate of 10 to 15°C/hr within the range of 900 to 1020°C.

- [48] In this case, the P+0.5Sb may be in range of 0.0370 to 0.0630 (wherein P and S represents contents (% by weight) of corresponding elements, respectively).
- [49] Also, the steel slab may further include one or more of 1.40% by weight or less of As, 0.50% by weight or less of Cu, 0.1% by weight or less of Bi, 1.40% by weight or less of Te, 1.40% by weight or less of Ni, 0.35% by weight or less of Cr, 1.40% by weight or less of Pb, and 1.40% by weight or less of the sum of at least one element selected from the group of Mo, B, Ge, Nb, Ti, and Zn.
- [50] In addition, the steel slab may further include 2.0 to 4.0% by weight of Si, 0.020 to 0.040% by weight of acid-soluble Al, 0.01 to 0.20% by weight of Mn, 0.04 to 0.07% by weight of C, 10 to 55 ppm of N and 0.0010 to 0.0055% by weight of S.
- [51] Additionally, the operation of reheating a steel slab may include: controlling the heating temperature so a content of re-dissolved N can be in a range of 10 to 40 ppm.
- [52] Also, the heating temperature of the steel slab may be in a range of 1050 to 1250°C.
- [53] Furthermore, the second soaking temperature is in a range of 1150 to 1250°C.

Advantageous Effects

- [54] According to the present invention, the grain-oriented electrical steel sheet having excellent magnetic properties may be manufactured by optimizing the contents of the added elements and making the maximum use of the synergetic effect among the elements, and it is possible to solve the problem associated with the poor productivity that is easily caused in the manufacture of the grain-oriented electrical steel sheet.
- [55]

Brief Description of Drawings

- [56] FIG. 1 is a graph illustrating the changes in iron loss according to a deviation (an angle β as shown in FIG. 2) of the crystal orientation of a steel sheet from the Goss orientation.
- [57] FIG. 2 is a conceptual view illustrating a deviation from the Goss orientation, which is represented by angles α , β and γ .
- [58] FIG. 3 is a graph illustrating that the improvement of iron loss goes beyond limits, which have been expected in the art, when Sn, Sb and P are added within pre-determined content ranges.

[59] FIG. 4 is a graph illustrating the improvement of iron loss with fixed contents of Sb and P and an increased content of Sn.

[60] FIG. 5 is a graph illustrating the improvement of iron loss with fixed contents of Sn and P and an increased content of Sb.

[61] FIG. 6 is a graph illustrating the improvement of iron loss with fixed contents of Sn and Sb and an increased content of P.

[62] FIG. 7 is a graph illustrating the improvement of iron loss with a fixed content of Sn and increased contents of P and Sb.

[63] FIG. 8 is a graph illustrating the results of FIG. 7 using Equation of $P+0.5Sb$.

[64]

Best Mode for Carrying out the Invention

[65] Hereinafter, exemplary embodiments of the present invention will be described in detail.

[66] The present inventors have conducted in-depth research into the contents of Sn, Sb, and P in component systems of conventional electrical steel sheets including Sn, Sb, and P, and the effect on the improvement of magnetic properties of the electrical steel sheets, which may be exerted by controlling the above elements. In the in-depth research, the present inventors have found that a far excellent threshold effect than expected previously can be achieved by appropriately controlling the content ranges of the elements, controlling the relationship between the elements, and further adding As in addition to Sn, Sb and P. Therefore, the present invention was achieved on the basis of the above facts.

[67] The concept of the present invention is shown in FIG. 3. Specifically, FIG. 3 is graph conceptually illustrating the variation in iron loss of an electrical steel sheet with respect to the content of Sn, Sb, or P. In FIG. 3, the horizontal axis represents the content of Sn, Sb, or P, and the vertical axis represents iron loss.

[68] Referring to FIG. 3, when the content of Sn, Sb, or P falls within the conventional content range, it has been known that the variation in iron loss forms a continuous line having a local minimum point within an appropriate range. However, when a certain condition is provided within the conventional content range according to one exemplary embodiment of the present invention, a significant reduction in iron loss may be achieved. That is, when the content of Sn, Sb, or P falls in the conventional content range as shown in FIG. 3, it may be expected that the variation in iron loss forms a continuous line with no remarkable change in iron loss. However, the results of experiments conducted by the present inventors show that a remarkable effect on

the improvement of iron loss, which has been unexpected in the prior art, may be achieved when the contents of the elements fall within predetermined ranges.

[69] Controlling the contents of the corresponding elements to fall within a predetermined content range is not enough to achieve the effect on the improvement of iron loss. The effect on the improvement of iron loss may be achieved when the three elements are simultaneously added. That is, even when the content of Sb is changed within the conventional content range thereof, the remarkable effect on the improvement of iron loss as shown in FIG. 3 may not be obtained. The effect may be obtained only when Sn and P are added in appropriate amounts at the same time. For this reason, the three elements must be added simultaneously, and their content ranges must be simultaneously controlled to appropriate contents. In this case, it is possible to obtain the critical effect pursued by the present invention. These experimental results support this point. That is, according to the experimental results, small grains were locally detected when Sb and P were added without the use of Sn. The locally detected, small grains are considered to be traces of grains having orientations other than the Goss orientation, and thus may deteriorate magnetic properties of an electrical steel sheet. When Sn, Sb and P were added at the same time, however, uniform secondarily recrystallized grains may be obtained, and an RD//[001] texture may strongly develop into a primarily recrystallized steel sheet.

[70] In addition, when the respective content ranges of P and Sb are controlled simultaneously, another critical synergic effect may be generated. Therefore, the contents of P and Sb need to be controlled under a single Equation.

[71] Therefore, in the present invention, the contents of Sn, Sb, and P among the elements of an electrical steel sheet are controlled as follows, and the relationship between the contents of P and Sb, as defined by the following Equation, is controlled within an appropriate range.

[72] 1) Sn: 0.03 to 0.07% by weight

[73] 2) Sb: 0.01 to 0.05% by weight

[74] 3) P: 0.01 to 0.05% by weight

[75] 4) $P+0.5Sb$: 0.0370 to 0.0630 (wherein P and S represents contents (% by weight) of corresponding elements, respectively).

[76] The content of each element was determined as shown above for the following reasons.

[77] Sn: 0.03 to 0.07% by weight

[78] Sn functions to reduce the size of secondarily recrystallized grains by increasing the

number of secondary nuclei having the $\{110\}<001>$ orientation. Thus, the addition of Sn leads to the improved iron loss properties. Also, Sn plays an important role in inhibiting the grain growth through segregation in grain boundaries, and compensates for the reduction of the effect to inhibit the grain growth as AlN particles are made coarse and content of Si is increased. Therefore, the secondarily recrystallized textures having the $\{110\}<001>$ orientation may be successfully formed even with a relatively higher content of Si. That is, the Si content may be increased without any adverse effect on the accomplishment of the secondarily recrystallized textures having the $\{110\}<001>$ orientation, and it is also possible to reduce the final thickness. As described above, the Sn content is preferably in a range of 0.03 to 0.07% by weight when the contents of other elements are adjusted to appropriate ranges. That is, when the content of Sn is controlled to fall within the range of 0.03 to 0.07% by weight as described above, discontinuous and dramatic reductions in iron loss, which has been unexpected in the prior art, may be achieved. Therefore, the content of Sn is preferably controlled to fall within the above range. In addition, when the Sn content is excessively high, brittle properties may be increasingly caused. However, when the content of Sn is controlled within the above range, brittle properties may be reduced.

[79]

[80] Sb: 0.01 to 0.05 % by weight

[81] Sb functions to inhibit the excessive growth of primarily recrystallized grains through segregation in grain boundaries. Since Sb is added to inhibit the growth of grains during primary recrystallization, the non-uniformity in the size of the primarily recrystallized grains in a thickness direction of a steel sheet is removed, and, at the same time, secondarily recrystallized grains can be formed in a stable manner. As a result, it is possible to manufacture a grain-oriented electrical steel sheet having more superior magnetic properties. In particular, when the content of Sb is in a range of 0.01 to 0.5% by weight, the effect of Sb may be improved to such an extent that was unexpected in the prior art. As described above, Sb functions to inhibit the excessive growth of primarily recrystallized grains through segregation in grain boundaries. However, when Sb is added in an amount of 0.01% by weight or less, it may not function properly. When Sb is added in an amount of 0.05% by weight or more, primarily recrystallized grains become excessively small in size. Accordingly, the initiation temperature of secondary recrystallization may be low, thereby degrading the magnetic properties, or the inhibitory effect on the growth of grains may become excessively high, thereby preventing the formation of the secondarily recrystallized

grains.

[82]

[83] P: 0.01 to 0.5% by weight

[84] P functions to promote the growth of primarily recrystallized grains in a low-temperature-heated, grain-oriented electrical steel sheet. Hence, P increases the temperature of secondary recrystallization and thus increases the integration density of {110}<001>-oriented grains in final products. When the primarily recrystallized grains are too large, secondary recrystallization becomes unstable. However, as long as the secondary recrystallization occurs, large primarily recrystallized grains are more advantageous in increasing the secondary recrystallization temperature. Meanwhile, P not only reduces the iron loss of final products by increasing the number of grains with {110}<001> orientation in primarily recrystallized sheets, but also increases the integration density of {110}<001>-oriented grains in final products by strongly developing the {111}<112> texture in the primarily recrystallized sheets, thus to increase the magnetic flux density of the final products. Also, P functions to segregate in grain boundaries even at a high temperature of approximately 1000°C during secondary recrystallization annealing thus to retard the decomposition of precipitates so as to enhance the inhibitory effect. When the content of P is limited to 0.01 to 0.05% by weight, a remarkable effect on the improvement of iron loss, which has been unexpected in the prior art, may be achieved. In order to present the functions of P sufficiently, P needs to be added in an amount of 0.01% by weight or more. However, when P is added in an amount of 0.05% by weight or more, the size of primarily recrystallized grains may be reduced instead of being increased. Therefore, secondary recrystallization may be unstably performed, and the cold rolling properties of steel may be deteriorated with an increase in the brittleness of steel.

[85]

[86] P+0.5Sb: 0.0370 to 0.0630 (wherein P and S represent contents (% by weight) of corresponding elements, respectively)

[87] According to the results of experiments conducted by the present inventors, iron loss properties were improved greatly when the content of P+0.5Sb was controlled to fall within the above range, as well as when each of the elements was added. This is because the addition of the above elements causes a synergic effect, and the synergic effect is discontinuously maximized when the contents of the elements satisfy the above range of the Equation, compared to the other numeral ranges of the elements. Therefore, it is more desirable to control the content of P+0.5Sb to fall within the

above range as well as controlling the content range of each element.

[88] When the content of each element of an electrical steel sheet is limited to the above range, the orientation of the steel sheet becomes close to the Goss orientation, thereby greatly improving the magnetic properties of the steel sheet. Hence, an electrical steel sheet having advantageous effects according to the present invention essentially includes 0.03 to 0.07% by weight of Sn, 0.01 to 0.5% by weight of Sb, and 0.01 to 0.05% by weight of P. In addition to limiting the contents of the elements to the above corresponding ranges, the content of $P+0.5Sb$ (wherein, P and S represent contents of corresponding elements, respectively) may be limited to 0.0370 to 0.0630.

[89] In addition to controlling the content of each of Sn, Sb, and P as described above, when at least one selected from the group consisting of As, Cu, Bi, Te, Ni, Cr, Pb, Mo, B, Ge, Nb, Ti and Zn may be added in an appropriate amount, the magnetic properties of a steel sheet may be further improved due to the advantageous effects, for example, such as controlling the secondary recrystallization temperature and making the size of grains uniform. The reasons for the addition of each of the elements are described in more detail, as follows.

[90]

[91] As: 1.40% by weight or less

[92] According to the researches by the present inventors, As is an element that further enhances magnetic properties by assisting the functions of the inhibitors such as P, Sb and Sn. When As is added, the temperature of initiation of secondary recrystallization may be increased, and thus secondary recrystallization may occur in a stable manner at a temperature that is advantageous for the growth of grains having the Goss orientation. However, when As is added in an amount of more than 1.40% by weight, the deterioration of a film, which is formed during annealing of a steel sheet, and the deterioration of magnetic properties are unavoidable. Thus, the content of As is limited to 1.40% by weight. Even when the content of As is insufficient, magnetic properties are not deteriorated compared to when As is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of As. Thus, it is more desirable to add As in an amount of 0.003% by weight or more in order to obtain the advantageous effects.

[93]

[94] Cu: 0.50% by weight or less

[95] Cu may precipitate in the form of fine particles during hot rolling, which are used as an inhibitor of the growth of primarily recrystallized grains. In particular, the effect of

Cu is distinguished when decarburization is performed at the same time as the nitriding process. However, when the decarburization is performed at the same time as the nitriding process, the size of primarily recrystallized grains become more non-uniform than when the nitriding process is performed after the decarburization. When the size of the primarily recrystallized grains becomes more non-uniform, excessively grown grains are secondarily recrystallized due to their size advantage, which leads to the deteriorated magnetic properties of final products. This problem may be solved by adding Cu, which is a sulfide-forming element, in an appropriate amount. That is, when Cu is added in a very small amount, fine sulfides may be formed, and be increased in number. In other words, Cu finely precipitates into sulfides during hot rolling and inhibits the excessive growth of the primary recrystallized grains. Accordingly, the size of grains may be made uniform, and thus only Goss grains may be participated selectively during the secondary recrystallization. As a result, it is possible to manufacture a grain-oriented electrical steel sheet having superior magnetic properties. When Cu is added in an amount of more than 0.50% by weight, the primarily recrystallized grains become excessively small in size. Accordingly, the temperature of initiation of secondary recrystallization may be lowered, which, in turn, deteriorates the magnetic properties. Thus, the content of Cu may be limited to 0.50% by weight. Even when the content of Cu is insufficient, magnetic properties are not deteriorated, compared to when Cu is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of Cu. Thus, it is more desirable to add Cu in an amount of 0.05% by weight or more in order to obtain the advantageous effects.

[96]

[97] Bi: 0.1% by weight or less

[98] In the present invention, Bi may be added in an amount of 0.1% by weight or less in addition to the desirable composition. The present inventors researches suggest that Bi functions as an auxiliary inhibitor to increase the initiation temperature of secondary recrystallization and to make the secondary recrystallization stable. Thus, the addition of Bi allows the production of a grain-oriented electrical steel sheet having excellent magnetic properties. When Bi is added in an amount of more than 0.1% by weight, the deterioration of a film, which is formed during annealing of a steel sheet, and the deterioration of magnetic properties are unavoidable. Thus, the content of Bi is limited to 0.1%. Even when the content of Bi is insufficient, magnetic properties are not deteriorated compared to when Bi is not added at all. In this case, however, it is difficult

to obtain advantageous effects by the addition of Bi. Thus, it is more desirable to add Bi in an amount of 0.005% by weight or more in order to obtain the advantageous effects.

[99]

[100] Te: 1.40% by weight or less

[101] According to the researches by the prevent inventors, Te is an element that further enhances the magnetic properties by assisting the functions of the inhibitors such as P, Sb and Sn. When Te is added, the initiation temperature of secondary recrystallization is increased, and thus the secondary recrystallization occurs stably at a temperature that is advantageous for the growth of grains having the Goss orientation. However, when Te is added in an amount of more than 1.40% by weight, the deterioration of a film, which is formed during annealing of a steel sheet, and the deterioration of magnetic properties are unavoidable. Thus, the content of Te is limited to 1.40% by weight. Even when the content of Te is insufficient, magnetic properties are not deteriorated compared to when Te is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of Te. Thus, it is more desirable to add Te in an amount of 0.01% by weight or more in order to obtain the advantageous effects.

[102]

[103] Ni: 1.40% by weight or less

[104] According to the researches by the present inventors, Ni improves the structure of a hot-rolled steel sheet, and functions as an auxiliary inhibitor to increase the initiation temperature of secondary recrystallization, and to make the secondary recrystallization stable. Thus, when Ni is added, a grain-oriented electrical steel sheet having excellent magnetic properties may be produced. When Ni is added in an amount of more than 1.40% by weight, the deterioration of a film, which is formed during annealing of a steel sheet, and the deterioration of magnetic properties are unavoidable. Thus, the content of Ni is limited to 1.40% by weight. Even when the content of Ni is insufficient, magnetic properties are not deteriorated compared to when Ni is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of Ni. Thus, it is more desirable to add Ni in an amount of 0.01% by weight or more in order to obtain the advantageous effects.

[105]

[106] Cr: 0.35% by weight or less

[107] Cr is a ferrite-forming element that grows primarily recrystallized grains and

increases the number of grains having an {110}<001> orientation in primarily re-crystallized sheets. Thus, when Cr is added, a grain-oriented electrical steel sheet having a low iron loss and a high magnetic flux density may be produced. Here, when Cr is added in an amount of more than 0.35% by weight, it will form a compact oxide layer on a surface of a steel sheet during the simultaneous decarburization and nitriding annealing processes, thus to prevent nitrifying. Accordingly, the content of Cr is limited to 0.35% by weight. Even when the content of Cr is insufficient, magnetic properties are not deteriorated compared to when Cr is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of Cr. Thus, it is more desirable to add Cr in an amount of 0.02% by weight or more in order to obtain the advantageous effects.

[108]

[109] Pb: 1.4 % by weight or less

[110] In the present invention, Pb may be added in an amount of 1.40% by weight or less in addition to the desirable contents of the elements. The present inventors researches suggest that Pb functions as an auxiliary inhibitor to increase the initiation temperature of secondary recrystallization, and to make secondary recrystallization stable. Thus, when Pb is added, a grain-oriented electrical steel sheet having excellent magnetic properties may be produced. When Pb is added in an amount of more than 1.40% by weight, the deterioration of a film, which is formed during annealing of a steel sheet, and the deterioration of magnetic properties are unavoidable. Thus, the content of Pb is limited to 1.40% by weight. Even when the content of Pb is insufficient, magnetic properties are not deteriorated compared to when Pb is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of Pb. Thus, it is more desirable to add Pb in an amount of 0.005% by weight or more in order to obtain the advantageous effects.

[111] The sum of at least one selected from the group consisting of Mo, B, Ge, Nb, Ti, and Zn: 1.40% by weight or less

[112] In the present invention, the sum of at least one selected from the group consisting of Mo, B, Ge, Nb, Ti, and Zn is also preferably added in an amount of 1.40% by weight or less in addition to the above desirable elements. According to the researches by the present inventors, the elements further enhance magnetic properties by assisting the functions of the inhibitors such as P, Sb, and Sn. When the elements are added, the initiation temperature of secondary recrystallization is increased, and thus the secondary recrystallization may occur stably at a temperature that is advantageous for

the growth of grains having the Goss orientation. However, when the sum of the elements is added in an amount of more than 1.40% by weight, the deterioration of a film, which is formed during annealing of a steel sheet, and the deterioration of magnetic properties are unavoidable. Thus, the sum of the contents of the elements is limited to 1.40% by weight. Even when the content of each of the elements is insufficient, magnetic properties are not deteriorated compared to when each of the elements is not added at all. In this case, however, it is difficult to obtain advantageous effects by the addition of the elements. Thus, it is more desirable to add the sum of the elements in an amount of 0.003% by weight or more in order to obtain the advantageous effects.

[113] In this regard, an electrical steel sheet according to the present invention preferably essentially include 0.03 to 0.07% by weight of Sn, 0.01 to 0.05% by weight of Sb, and 0.01 to 0.05% by weight of P. When necessary, the electrical steel sheet may further include one or more of 1.40% by weight or less of As, 0.50% by weight or less of Cu, 0.1% by weight or less of Bi, 1.40% by weight or less of Te, 1.40% by weight or less of Ni, 0.35% by weight or less of Cr, 1.40% by weight or less of Pb, and 1.40% by weight or less of the sum of at least one element selected from the group of Mo, B, Ge, Nb, Ti, and Zn. In addition that the contents of the respective elements is limited to the corresponding ranges thereof, it is more desirable to the content of P+0.5Sb to the range of 0.0370 to 0.0630 (wherein, represent contents (% by weight) of corresponding elements, respectively).

[114] According to the researches by the prevent inventors, the crystal orientation of an electrical steel sheet composed of the above elements according to the present invention must deviate from the Goss orientation by less than 3 degrees so as to secure superior iron loss properties.

[115] In addition to the above elements, additional elements (such as Si, Mn and Al) typically used in electrical steel sheets and other unavoidable impurities are added to an electrical steel sheet. However, these additional elements can be applied to the electrical steel sheet according to the present invention by easily deriving contents of the additional elements from the components and their contents used in the conventional electrical steel sheets. Thus, there is no need to limit the content range of each of the additional elements. That is, it is important to address the content of the Sn, Sb, and P element and the relationship between them and limit the contents of the optionally added additional elements to the above corresponding ranges.

[116] However, more preferred examples of the additional elements (such as Si, Mn, and

Al) which are suitable for the component system of the present invention will be provided below and described in brief.

[117] Si: 2.0 to 4.0% by weight

[118] Si is used as a basic element of an electrical steel sheet and increases the specific resistance of materials to reduce the core loss. When the content of Si is less than 2.0% by weight, the specific resistance of materials may decrease, and core loss properties may be consequently deteriorated. On the other hand, when the content of Si is more than 4.0% by weight, the brittleness of steel will be increased, in which case cold rolling becomes very difficult, and the formation of secondarily recrystallized grains becomes unstable. For this reason, the content of Si is limited to 2.0 to 4.0% by weight.

[119]

[120] Acid soluble Al: 0.020 to 0.040% by weight

[121] Al ends in the formation of nitrides, such as AlN, (Al,Si)N, (Al,Si,Mn)N, which act as inhibitors. When the content of Al is less than 0.02%, its effect of the inhibitors may not be sufficiently achieved. When the content of Al is excessively high, Al-based nitrides precipitate and grow too coarsely, and thus the effect of Al as an inhibitor is insufficient. For this reason, the content of Al is limited to the range of 0.020 to 0.040% by weight.

[122]

[123] Manganese (Mn): 0.01 to 0.20% by weight

[124] Mn is an element that functions to increase the specific resistance of materials to reduce iron loss in the same manner as in Si. Also, Mn functions to react with nitrogen, which is introduced together with Si by nitriding treatment, to form a precipitate of (Al,Si,Mn)N. Accordingly, Mn inhibits the growth of primarily recrystallized grains, thus to facilitate the secondary recrystallization. However, when Mn is added in an amount of more than 0.20% by weight, Mn may promote austenite phase transformation during hot rolling. As a result, the size of primarily recrystallized grains may be reduced, thus making the secondary recrystallization unstable. Hence, the content of Mn is limited to 0.20% by weight or less. In addition, Mn is an austenite-forming element that functions to increase an austenite fraction during reheating of a hot rolled steel sheet and thus increase the amount of precipitates, and also functions to prevent primarily recrystallized grains from growing excessively through the refinement of precipitates and the formation of MnS. Therefore, Mn should be added in an amount of 0.01% by weight or more. Therefore, the content of Mn is limited to 0.01 to 0.2% by

weight

[125] C is removed during decarburization annealing performed after cold rolling. N and S should be removed to amounts as low as possible under an atmosphere control during second soaking treatment. Thus, N and S are regarded as impurities in the component system of an electrical steel sheet. However, since these elements exist in the electrical steel sheet for various reasons until they are cold-rolled, these elements may be comprised in a predetermined content range in a steel slab, a hot-rolled steel sheet, and a cold-rolled steel sheet (i.e., a steel sheet right immediately after the cold rolling process), which are used to manufacture electrical steel sheets. In the present invention, it is more desirable to control the content of these elements to fall within the following range.

[126]

[127] C : 0.04 to 0.07% by weight

[128] C is an element that does not greatly contribute to improving the magnetic properties of a grain-oriented electrical steel sheet according to the present invention. Thus, C should be removed to an amount as low as possible. However, when C is contained in a content greater than a predetermined amount, C promotes the austenite phase transformation of steel during the rolling process, thus to make a structure of a hot-rolled structure fine during hot rolling and assist in the formation of a uniform fine structure of the hot-rolled structure. For this reason, C is preferably added in a content of 0.04% by weight or more. However, when C is used in an excessively high content, coarse carbides may be deposited and cannot be easily removed during decarburization. Accordingly, C is preferably added within the above range at the beginning.

[129]

[130] N : 10 to 55 ppm

[131] N is an element which induces the refinement of grains by reacting with Al, etc. When these elements are distributed properly, a structure after cold rolling may be made fine appropriately, which contributes to securing an appropriate primarily recrystallized grain size. However, when N content is excessively high, the primary recrystallized grains become too fine, which, in turn, increases the driving force of facilitating the growth of grains during secondary recrystallization. As a result, grains having undesired orientations may also grow. Furthermore, when N content is too high, it takes a lot of time to remove N during the final annealing process. Therefore, N content is set to an upper limit of 55 ppm. As will be described later, the content of N dissolved during the reheating of slab may be 10 ppm or more. Thus, N content is

set to a lower limit of 10 ppm in consideration of a content rate of N which may be redissolved.

[132]

[133] S : 0.0010 to 0.0055%

[134] When S is contained in a slab in an amount of more than 0.0055%, S is redissolved and precipitated during the reheating of a hot-rolled slab. Thus, primarily recrystallized grains will be reduced in size, which leads to a decrease in the initiation temperature of secondary recrystallization, and thus to degrade the magnetic properties of steel. In addition, since a lot of time is required to remove dissolved S in a second soaking section of the final annealing process, the productivity of a grain-oriented electrical steel sheet is low. On the other hand, when the content of S is 0.0055% or less, the size of initial grains before cold rolling may be made coarse, and thus grains having the {110}<001> orientation whose nucleus is created in a transformed band in the primary recrystallization process may be increased in number. Accordingly, the secondarily recrystallized grains may be reduced in size, which leads to the improved magnetic properties of final products. For this reason, S content is set to 0.0055% or less. Since S somewhat affects the size of primarily recrystallized grains by the formation of MnS, S may be added in a content of 0.001% by weight or more. Therefore, S content is limited to 0.0010 to 0.0055 % by weight.

[135] It will be understood by those of ordinary skill in the art that various elements contained in grain-oriented electrical steel sheets may also be contained as alloy elements in an electrical steel sheet according to the present invention in addition to the above-mentioned elements. It is apparent that combinations and applications of conventional known elements are made within the scope of the present invention.

[136] The electrical steel sheet according to the present invention may be manufactured by using one of the conventional methods of manufacturing an electrical steel sheet, which are widely known in the art. However, it is more desirable to manufacture the electrical steel sheet by using the following method. Hereinafter, more preferred methods will be described in detail. However, it should be understood that conditions unspecified below are in accordance with the widely known conditions.

[137] A conventional manufacturing method is used until a cold-rolled steel sheet is manufactured. That is, a method, which includes: hot-rolling a steel slab, annealing the hot-rolled steel slab and cold-rolling the annealed steel slab, may be selected from one of the conventional methods widely known to those skilled in the art, or a modifications thereof may be used, when necessary. In addition, additional processes (i.e. pickling)

required for hot rolling and cold rolling of an electrical steel sheet may also be included and used accordingly.

[138] When a steel slab is reheated for hot rolling, the reheating temperature is preferably adjusted to such a range that N and S are incompletely dissolved. In particular, the content of N is preferably controlled to be in a range of 10 to 40 ppm. That is, the researches by the present inventors suggest that it is important to control an amount of nitrides which is redissolved during reheating and precipitated during cooling, but not to control the total N content to be within a suitable range. Thus, the content of N, which is remelted during reheating, is controlled to be within an appropriate range. That is, the refinement of grains is determined according to the amount of the precipitated nitride. When the grains are made too fine, grains having orientations different from the Goss orientation may grow. On the contrary, when the grains are made too coarse, undesirable grains may not be removed during the secondary recrystallization. Hence, it is desirable to limit the content of the dissolved N to 10 to 40 ppm. The slab-reheating temperature used to control the content of the dissolved N may be determined based on the content of Al contained in steel. When the content of Al that may preferably included in the present invention is taken into consideration, the reheating temperature is more preferably in a range of 1050 to 1250°C.

[139] Since processes prior to the cold-rolling process may be suitably selected from one of the conventional methods as described above, detailed descriptions thereof will be omitted for clarity. However, when a steel sheet is used to manufacture a grain-oriented electrical steel sheet, a thickness of a hot-rolled steel sheet is generally in a range of 1.8 to 3.5 mm and a thickness of a cold-rolled steel sheet is generally in a range of 0.18 to 0.35 mm. Here, the annealing of the hot-rolled steel sheet is carried out by heating a steel sheet to 1000 to 1200°C, subjecting the heated steel sheet to soaking treatment at a temperature of 850 to 950°C and cooling the steel sheet. When going through the above-mentioned processes, the average size of precipitates is in a range of 300 to 3000 after the hot rolling or annealing of the hot-rolled steel sheet.

[140] Then, the cold-rolled steel sheet goes through decarburization annealing and recrystallization annealing, which will now be described in detail.

[141] The cold-rolled steel sheet goes through decarburization and nitriding annealing processes in an atmosphere of a mixed gas of ammonia, hydrogen and nitrogen. The above decarburization and nitriding annealing processes may be easily applied by the use of a conventional nitriding method. The nitriding annealing may be performed at the same time as or after the decarburization annealing. When decarburization is

performed before nitriding annealing, precipitates such as Si_3N_4 or $(\text{Si}, \text{Mn})\text{N}$, are formed. These precipitates are thermally unstable and thus easily decomposed. Therefore, since such precipitates cannot properly function as inhibitors, they should be maintained at a high temperature for a long time, so that they can be converted into precipitates such as AlN or $(\text{Al}, \text{Si}, \text{Mn})\text{N}$. When the decarburization and nitriding annealing processes are performed simultaneously, a long processing time is not required since AlN and $(\text{Al}, \text{Si})\text{N}$ are formed at the same time. Thus, it is more desirable to perform the decarburization and nitriding annealing processes at the same time. However, it should be noted that the decarburization before the nitriding annealing may also be effectively used to manufacture an electrical steel sheet having advantageous properties according to the present invention. That is, the simultaneous decarburization and nitriding annealing processes are easier and useful to manufacture an electrical steel sheet according to the present invention, but the present invention is not limited thereto.

- [142] According to the researches by the present inventors, when the contents of Sn, Sb, and P are controlled to fall within the ranges suggested by the present invention, the size of grains is highly different from those of the conventional component system. Thus, it is more desirable to consider this point. That is, when the contents of the elements are controlled respectively to fall within the ranges, the size of primarily recrystallized grains is made fine, and secondary recrystallization may easily occur under the same primary recrystallization condition. When primarily recrystallized grains are made fine, secondary recrystallization occurs easily. However, these elements have an effect to prevent the secondary recrystallization from occurring easily with the primary recrystallized grains of the same size. Thus, it is necessary to determine whether the secondary recrystallization of the present invention occurs more easily or less easily than the conventional case according to which of the effects works more predominantly, followed by employing the determination results under the decarburization annealing conditions. According to the researches by the present inventors, since the driving force of facilitating the secondary recrystallization is greatly increased as the primarily recrystallized grains get finer, it is desirable to control the decarburization annealing temperature (that is, primary recrystallization temperature) to such an extent that the primarily recrystallized structure cannot become too fine when the elements are added. The decarburization annealing temperature may be set to 800 to 950°C which is 10 to 30°C higher than in the typical cases. When the decarburization annealing temperature is low, the decarburization can not be sufficiently

achieved, and the formed grains remain fine. Consequently, grains having undesired orientations may grow during the secondary recrystallization. Conversely, when the decarburization annealing temperature is too high, the primary recrystallized grains may grow excessively. In the composition system according to the present invention, a desirable size of the primarily recrystallized grains is in a range of approximately 18 to 25 μ m. A dew point of the composition system according to the present invention may be set to 50 to 70°C which is 2 to 4°C lower than that of a composition system, which does not contain Sn, Sb, and P, which is more desirable in better managing an oxide layer, controlling the orientation of grains of the final products, and improving the iron loss characteristics.

[143] As described above, a steel sheet after the decarburization annealing is coated with an annealing separator which contains MgO as a basic element, coiled, and finally annealed for a long time to manufacture an electrical steel sheet whose grains having the Goss orientation are predominately distributed. The specific processes include a first soaking process for removing moisture from the annealing separator coated on the coiled steel sheet, a temperature-raising process for raising temperature to secondarily recrystallize the primarily recrystallized steel sheet, and a second soaking process for removing impurities while proceeding with the recrystallization. Here, the reheating temperature was raised at a very low rate in order to make the inhibitors redissolve instantaneously in a narrow temperature range and to get rid of the hindrance to the growth of grains and initiate the secondary recrystallization in a narrow temperature range, and the second soaking time is set to a long time period in order to remove impurities. Since the above conventional method has problems associated with the poor productivity, the present inventors have made many attempts to find the clue to the problems, and have found that it is advantageous to divide the heating rate into two-stage heating rates after the first soaking process.

[144] That is, although the temperature is raised at a high rate, the secondary recrystallization does not occur below the temperature at which the inhibitors are dissolved. Therefore, when the temperature is raised at a high rate at the beginning, and then raised at a slow rate, which is similar to a heating rate used in the conventional method, from the temperature at which secondary recrystallization occurs, the secondary recrystallization may be obtained with the same level while the time required is reduced, thereby improving productivity. In the present invention, a reference temperature at which the heating rate is changed is set to 900 to 1020°C. That is, a steel sheet is heated at a high rate after the first soaking process, and then heated

at a low rate within the reference temperature range in consideration of the secondary recrystallization. In the present invention, a high heating rate in the initial heating section is set to 18 to 75°C/hr, and a low heating rate is set to 10 to 15°C/hr in consideration of the secondary recrystallization. In the present invention, when the amount of the redissolved nitrogen which acts as an inhibitor is limited to the range as described above, and the total content of S is limited to 0.0055% by weight or less, the time required to remove these elements may be reduced, compared to the conventional method.

- [145] Since the first and second soaking temperatures are adjusted to temperature ranges falling within the typical soaking temperature range, it is unnecessary to limit the first and second soaking temperatures to a certain range. However, the first soaking temperature may be in the range of 650 to 850°C, and the second soaking temperature may be in the range of 1150 to 1250°C. This temperature range may be slightly varied according to the composition of a steel sheet, or through the modification of insignificant features except for the major technical features of the present invention.
- [146] In summary, the method of manufacturing an electrical steel sheet according to the present invention includes: reheating a steel slab having the desirable composition of the present invention; manufacturing a steel sheet by hot-rolling the reheated steel slab, annealing the hot-rolled steel sheet and cold-rolling the annealed steel sheet; subjecting the cold-rolled steel sheet to decarburization and nitriding annealing processes within a temperature range of 800 to 950°C; and finally annealing the annealed steel sheet. In addition, the final annealing operation includes first soaking heating and second soaking operations. In the heating operation, a heating rate is set to 18 to 75°C/hr at the beginning and the heating temperature is then increased at a rate of 10 to 15°C/hr within the range of 900 to 1020°C.

[147]

Mode for the Invention

- [148] Hereinafter, embodiments of the present invention will be described in more detail with reference to the attached drawings. However, the description proposed herein is just a preferable example for the purpose of illustrations only, not intended to limit the scope of the invention, so it should be understood that other equivalents and modifications could be made thereto without departing from the spirit and scope of the invention.

[149]

- [150] EXAMPLES

[151] Variation in iron loss with respect to contents of added Sn, Sb and P

[152] A grain-oriented electrical steel sheet, which includes, by weight: 3.26% of Si, 0.055% of C, 0.12% of Mn, 0.026% of soluble Al, 0.0042% of N, 0.0045% of S, varying contents of Sn, Sb, and P as listed in the following Tables 1 to 4, and the balance of Fe and other unavoidable impurities, was used herein. Then, a slab of the electrical steel sheet was heated for 210 minutes at a temperature of 1170°C at which the re-dissolved N is present in a content of 25 ppm, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 920°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 63°C, and 1% dry ammonia into a furnace of 875°C and maintaining the cold-rolled steel sheet in the furnace for 180 seconds.

[153] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 950°C and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Tables 1 to 4.

[154] Table 1

[Table 1]

[Table]

Sn (wt%)	P(wt%)	Sb(wt %)	Magnetic flux density, B10[T]	Iron Loss W17/50 [W/kg]	[P+0.5Sb] (wt%)	Note
0	0	0	1.885	1.08	0	Comparative steel 1
0	0	0.005	1.878	1.07	0.0025	Comparative steel 2
0	0	0.015	1.901	1.05	0.0075	Comparative steel 3
0	0	0.025	1.903	1.04	0.0125	Comparative steel 4
0	0	0.035	1.908	1.04	0.0175	Comparative steel 5
0	0	0.045	1.91	1.04	0.0225	Comparative steel 6
0	0	0.055	1.893	1.06	0.0275	Comparative steel 7
0	0	0.075	1.882	1.08	0.0375	Comparative steel 8
0	0	0.1	1.873	1.1	0.05	Comparative steel 9
0	0.01	0	1.898	1.05	0.01	Comparative steel 10
0	0.02	0	1.903	1.03	0.02	Comparative steel 11
0	0.025	0	1.908	1.03	0.025	Comparative steel 12
0	0.03	0	1.91	1.02	0.03	Comparative steel 13

0	0.035	0	1.911	1.02	0.035	Comparative steel 14
0	0.035	0.005	1.917	1.01	0.0375	Comparative steel 15
0	0.035	0.015	1.918	0.99	0.0425	Comparative steel 16
0	0.035	0.025	1.923	0.99	0.0475	Comparative steel 17
0	0.035	0.035	1.925	0.99	0.0525	Comparative steel 18
0	0.035	0.045	1.922	0.99	0.0575	Comparative steel 19
0	0.035	0.055	1.91	1.01	0.0625	Comparative steel 20
0	0.035	0.075	1.906	1.03	0.0725	Comparative steel 21
0	0.035	0.1	1.905	1.04	0.085	Comparative steel 22
0	0.04	0	1.908	1.02	0.04	Comparative steel 23
0	0.04	0.025	1.923	0.99	0.0525	Comparative steel 24
0	0.045	0	1.913	1.02	0.045	Comparative steel 25
0	0.05	0	1.905	1.03	0.05	Comparative steel 26
0	0.075	0	1.9	1.05	0.075	Comparative steel 27
0.01	0	0	1.893	1.06	0	Comparative steel 28
0.01	0	0.025	1.915	1.02	0.0125	Comparative

						steel 29
0.01	0.035	0	1.912	1.02	0.035	Comparative steel 30
0.01	0.035	0.025	1.923	0.99	0.0475	Comparative steel 31
0.01	0.04	0	1.913	1.01	0.04	Comparative steel 32
0.01	0.04	0.025	1.921	0.985	0.0525	Comparative steel 33
0.02	0	0	1.903	1.05	0	Comparative steel 34
0.02	0	0.025	1.913	1.02	0.0125	Comparative steel 35
0.02	0.035	0	1.912	1.01	0.035	Comparative steel 36

[155] Table 2

[Table 2]

[Table]

Sn(wt%)	P(wt%)	Sb(wt%)	Magnetic flux density B10[T]	Iron loss W17/50 [W/kg]	[P+0.5Sb] (wt%)	Note
0.03	0	0	1.907	1.04	0	Comparative steel 37
0.03	0	0.025	1.917	1.01	0.0125	Comparative steel 38
0.03	0.035	0	1.91	1.01	0.035	Comparative steel 39
0.03	0.035	0.025	1.95	0.93	0.0475	Inventive steel 1
0.03	0.04	0	1.915	1.01	0.04	Comparative steel 40
0.03	0.04	0.025	1.943	0.95	0.0525	Inventive steel 2
0.04	0	0	1.91	1.03	0	Comparative steel 41
0.04	0	0.025	1.918	1	0.0125	Comparative steel 42
0.04	0.035	0	1.925	0.99	0.035	Comparative steel 43
0.04	0.035	0.025	1.95	0.92	0.0475	Inventive steel 3
0.04	0.04	0	1.92	0.985	0.04	Comparative steel 44
0.04	0.04	0.025	1.951	0.92	0.0525	Inventive steel 4
0.05	0	0	1.913	1.02	0	Comparative steel 45

0.05	0	0.005	1.911	1.02	0.0025	Comparative steel 46
0.05	0	0.015	1.913	1	0.0075	Comparative steel 47
0.05	0	0.025	1.923	0.99	0.0125	Comparative steel 48
0.05	0	0.035	1.925	0.99	0.0175	Comparative steel 49
0.05	0	0.045	1.917	1	0.0225	Comparative steel 50
0.05	0	0.055	1.917	1.01	0.0275	Comparative steel 51
0.05	0	0.075	1.91	1.02	0.0375	Comparative steel 52
0.05	0	0.1	1.905	1.05	0.05	Comparative steel 53
0.05	0	0.125	1.888	1.06	0.0625	Comparative steel 54
0.05	0.01	0	1.915	1.02	0.01	Comparative steel 55
0.05	0.01	0.025	1.925	0.99	0.0225	Comparative steel 56
0.05	0.01	0.035	1.922	0.99	0.0275	Comparative steel 57
0.05	0.01	0.055	1.914	1.01	0.0375	Comparative steel 58
0.05	0.02	0	1.917	1.01	0.02	Comparative steel 59
0.05	0.02	0.025	1.918	0.99	0.0325	Comparative steel 60
0.05	0.02	0.035	1.94	0.97	0.0375	Inventive steel

						5
0.05	0.02	0.055	1.918	0.99	0.0475	Comparative steel 61
0.05	0.025	0	1.916	1	0.025	Comparative steel 62
0.05	0.025	0.025	1.944	0.95	0.0375	Inventive steel 6
0.05	0.025	0.035	1.952	0.93	0.0425	Inventive steel 7
0.05	0.025	0.055	1.916	0.99	0.0525	Comparative steel 63
0.05	0.03	0	1.92	0.99	0.03	Comparative steel 64
0.05	0.03	0.025	1.948	0.93	0.0425	Inventive steel 8
0.05	0.03	0.035	1.945	0.93	0.0475	Inventive steel 9

[156] Table 3

[Table 3]

[Table]

Sn(wt%)	P(wt%)	Sb(wt%)	Magnetic flux density B10[T]	Iron loss W17/50 [W/kg]	[P+0.5Sb (wt%)]	Note
0.05	0.03	0.055	1.915	0.99	0.0575	Comparative steel 65
0.05	0.035	0	1.918	0.99	0.035	Comparative steel 66
0.05	0.035	0.005	1.922	0.99	0.0375	Comparative steel 67
0.05	0.035	0.015	1.955	0.91	0.0425	Inventive steel 10
0.05	0.035	0.025	1.962	0.9	0.0475	Inventive steel 11
0.05	0.035	0.035	1.961	0.9	0.0525	Inventive steel 12
0.05	0.035	0.045	1.949	0.93	0.0575	Inventive steel 13
0.05	0.035	0.055	1.923	0.99	0.0625	Comparative steel 68
0.05	0.035	0.075	1.918	1	0.0725	Comparative steel 69
0.05	0.035	0.1	1.908	1.02	0.085	Comparative steel 70
0.05	0.04	0	1.921	0.99	0.04	Comparative steel 71
0.05	0.04	0.005	1.923	0.99	0.0425	Comparative steel 72
0.05	0.04	0.015	1.953	0.91	0.0475	Inventive steel 14
0.05	0.04	0.025	1.958	0.9	0.0525	Inventive steel 15
0.05	0.04	0.035	1.954	0.91	0.0575	Inventive steel 16
0.05	0.04	0.045	1.956	0.93	0.0625	Inventive steel 17
0.05	0.04	0.055	1.925	0.99	0.0675	Comparative steel 73

0.05	0.04	0.075	1.926	0.99	0.0775	Comparative steel 74
0.05	0.04	0.1	1.92	1	0.09	Comparative steel 75
0.05	0.045	0	1.918	0.99	0.045	Comparative steel 76
0.05	0.045	0.025	1.947	0.93	0.0575	Inventive steel 18
0.05	0.045	0.035	1.944	0.97	0.0625	Inventive steel 19
0.05	0.045	0.055	1.918	1	0.0725	Comparative steel 77
0.05	0.05	0	1.915	1	0.05	Comparative steel 78
0.05	0.05	0.025	1.941	0.97	0.0625	Inventive steel 20
0.05	0.05	0.035	1.923	0.99	0.0675	Comparative steel 79
0.05	0.05	0.055	1.908	1.03	0.0775	Comparative steel 80
0.05	0.075	0	1.914	1.01	0.075	Comparative steel 81
0.05	0.075	0.025	1.92	1	0.0875	Comparative steel 82
0.05	0.075	0.035	1.915	1.01	0.0925	Comparative steel 83
0.05	0.075	0.055	1.895	1.06	0.1025	Comparative steel 84
0.06	0	0	1.908	1.02	0	Comparative steel 85
0.06	0	0.025	1.923	0.99	0.0125	Comparative steel 86
0.06	0.035	0	1.923	0.99	0.035	Comparative steel 87

0.06	0.035	0.025	1.947	0.93	0.0475	Inventive steel 21
0.06	0.04	0	1.925	0.99	0.04	Comparative steel 88
0.06	0.04	0.025	1.944	0.94	0.0525	Inventive steel 22

[157] Table 4

[Table 4]

[Table]

Sn(wt%)	P(wt%)	Sb(wt %)	Magnetic flux density B10[T]	Iron loss W17/50 [W/kg]	[P+0.5Sb] (wt%)	Note
0.07	0	0	1.907	1.03	0	Comparative steel 89
0.07	0	0	1.908	1.03	0	Comparative steel 90
0.07	0	0.025	1.91	1.01	0.0125	Comparative steel 91
0.07	0.035	0	1.915	1.01	0.035	Comparative steel 92
0.07	0.035	0.025	1.946	0.93	0.0475	Inventive steel 23
0.07	0.04	0	1.915	1.01	0.04	Comparative steel 93
0.07	0.04	0.025	1.945	0.95	0.0525	Inventive steel 24
0.08	0	0	1.91	1.03	0	Comparative steel 94
0.08	0	0.025	1.913	1.02	0.0125	Comparative steel 95
0.08	0.035	0	1.915	1.02	0.035	Comparative steel 96
0.1	0	0	1.902	1.05	0	Comparative steel 97
0.1	0	0.025	1.912	1.02	0.0125	Comparative steel 98
0.1	0.035	0	1.913	1.02	0.035	Comparative steel 99

0.1	0.035	0.025	1.913	1	0.0475	Comparative steel 100
0.1	0.04	0	1.913	1.02	0.04	Comparative steel 101
0.1	0.04	0.025	1.918	1	0.0525	Comparative steel 102
0.15	0	0	1.873	1.1	0	Comparative steel 103
0.15	0	0.025	1.883	1.07	0.0125	Comparative steel 104
0.15	0.035	0	1.908	1.04	0.035	Comparative steel 105
0.15	0.035	0.025	1.903	1.03	0.0475	Comparative steel 106
0.15	0.04	0	1.891	1.06	0.04	Comparative steel 107
0.15	0.04	0.025	1.906	1.03	0.0525	Comparative steel 108

[158]

[159] In order to further study the experimental results as listed in Tables 1 to 4, the variations in iron loss measured by varying the content of each of Sn, Sb, and P while the contents of the other elements being fixed are as shown in FIGS. 4 to 6. In particular, FIG. 4 is a graph illustrating the results obtained by varying the content of Sn while the contents of Sb and P are fixed. As shown in FIG. 4, it was revealed that the iron loss exhibits successive behaviors without noticeable changes in threshold when S and P contents are out of the ranges as defined in the present invention. However, it was revealed that, when Sb and P were present in contents of 0.025% by weight and 0.035% by weight, and when Sn content was in a range of 0.03 to 0.07 % by weight together with 0.025% by weight of Sb and 0.035% by weight of P or 0.25% by weight of Sn and 0.04 by weight of P, a specific point at which iron loss is significantly improved was detected. Therefore, it was revealed that, when Sb content is adjusted to 0.03 to 0.7 % by weight under the conditions where Sb and P coexist, a

reduction in iron loss exceeds a critical level.

[160] FIG. 5 is a graph illustrating the variations in iron loss according to Sb content while Sn and P contents are fixed. When the Sn and P contents satisfy the ranges defined in the present invention, and the content of Sb was adjusted to 0.01 to 0.5 % by weight, a remarkable iron loss-reducing effect unexpected in the prior art was achieved.

[161] Also, FIG. 6 is graph illustrating the variations in iron loss according to P content while Sn and Sb contents are fixed. When the Sn and Sb contents satisfy their respective ranges, and the P content was adjusted to 0.01 to 0.05 % by weight, iron loss characteristics were improved discontinuously.

[162] Therefore, it was revealed that, when Sn, Sb, and P are controlled to fall within the respective ranges defined in the present invention, a significantly iron-loss reducing effect that was unexpected in the prior art was achieved.

[163] FIG. 7 is a graph illustrating the variations in iron loss according to the relationship between P and Sb while Sn content is fixed to 0.05 % by weight. In addition, FIG. 8 illustrates the improvement in iron loss when the relationship between P and Sb was substituted to Equation $P+0.5Sb$. It was revealed that iron loss was significantly improved when the Equation $P+0.5Sb$ was varied within the range of 0.0370 to 0.0630 defined in the present invention.

[164]

[165] Effect on control of the amount of dissolved nitrogen during slab reheating

[166] A grain-oriented steel sheet, which includes, by weight: 3.23% of Si, 0.058% of C, 0.12% of Mn, 0.025% of Al, 0.032% of P, 0.0053% of N, 0.0042% of S, 0.032% of Sb, 0.045% of Sn, 0.038% of P, and the balance of Fe and unavoidable impurities, was used herein. A slab of the steel sheet was reheated while varying the amount of re-dissolved N as listed in Table 5. Then, the slab is hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3mm. Then, the hot-rolled steel sheet was heated to 1100°C, maintained at 920°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 65°C, and 1% dry ammonia into a furnace of 875°C and maintaining the cold-rolled steel sheet in the furnace for 180 seconds.

[167] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In

addition, a heating rate was set to 45°C/hr in a heating range of 700 to 950°C and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained for 15 hours in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 5.

[168] Table 5

[Table 5]

[Table]

Amount of N re-dissolved during slab heating (wt%)	Magnetic flux density(B10, Tesla)	Iron loss(W17/50, W/kg)	Note
0.0004	1.758	1.32	Comparative steel 109
0.0015	1.949	0.94	Inventive steel 25
0.0027	1.942	0.95	Inventive steel 26
0.0037	1.939	0.96	Inventive steel 27
0.0048	1.915	1.02	Comparative steel 110

[169]

[170] As listed in Table 5, it was revealed that the Inventive steels 25 to 27, in which the content of N re-dissolved during the slab reheating satisfies the range defined in the present invention, show highly excellent magnetic properties, compared to the Comparative steels 109 and 110.

[171]

[172] Effect of thickness of a steel sheet on iron loss

[173] In order to study an effect of a thickness of a steel sheet on iron loss, an experiment was performed, as follows.

[174] A grain-oriented electrical steel sheet, which includes composition systems 1 and 2, was used herein. Here, the component system 1 includes, by weight: 3.23% of Si, 0.058% of C, 0.12% of Mn, 0.025% of soluble Al, 0.0050% of N, 0.0045% of S, 0.032% of Sb, 0.045% of Sn, 0.038% of P, and the balance of Fe and other unavoidable impurities, and the composition system 2 includes, by weight: 3.25% of Si, 0.054% of C, 0.11% of Mn, 0.025% of soluble Al, 0.0050% of N and 0.0045% of S,

and the balance of Fe and other unavoidable impurities without the use of Sn, Sb and P. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1150°C at which the re-dissolved N is present in a content of 23 ppm, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1100°C, maintained at 920°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce cold-rolled steel sheets having thicknesses of 0.35 mm, 0.30 mm, 0.27 mm and 0.23 mm, respectively. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 63°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

- [175] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 950°C and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained for 15 hours in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 6.

- [176] Table 6

[Table 6]

[Table]

	Thickness of cold-rolled steel sheet	Magnetic flux density (B10, Tesla)	Iron loss(W17/50, W/kg)	Note
component system 1	0.35	1.758	1.01	Inventive steel 28
component system 1	0.30	1.949	0.94	Inventive steel 29
component system 1	0.27	1.942	0.88	Inventive steel 30
component system 1	0.23	1.939	0.79	Inventive steel 31
component system 1	0.20	1.915	0.77	Inventive steel 32
component system 2	0.35	1.758	1.10	Comparative steel 111
component system 2	0.30	1.949	1.03	Comparative steel 112
component system 2	0.27	1.942	0.98	Comparative steel 113
component system 2	0.23	1.939	0.90	Comparative steel 114
component system 2	0.20	1.915	0.87	Comparative steel 115

[177]

[178]

As listed in Table 6, it was revealed that the component system 1 including Sb, Sn and P has highly improved iron loss, compared to the component system 2 which is free from the Sb, Sn and P components. Also, it was seen that the electrical steel sheets has more improved iron loss, regardless of the component systems, as a thickness of each steel sheet gets thinner. From this result, the iron loss in the Inventive steels, which include the component systems defined in the present invention, may be

expected according to the thickness of steel sheets, and a theoretical value of the iron loss according to the thickness of steel sheets may be calculated as represented by the following Equation 1.

[179] Equation 1

[180] Iron loss [W/kg] $\leq 0.46679 + 1.71622 * \text{thickness } [\mu\text{m}]$

[181]

[182] Determination of crystal orientation

[183] A grain-oriented steel sheet, which includes, by weight: 3.18% of Si, 0.0556% of C, 0.11% of Mn, 0.026% of soluble Al, 0.0046% of N, 0.0045% of S, 0.028% of Sb, 0.046% of Sn, 0.037% of P, and the balance of Fe and unavoidable impurities, was used herein. A slab of the grain-oriented electrical steel sheet having the above composition was heated for 210 minutes at a temperature of 1150°C at which the re-dissolved N is present in a content of 21 ppm, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1100°C, maintained at 920°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 63°C, and 1% dry ammonia into a furnace of 875°C and maintaining the cold-rolled steel sheet in the furnace for 180 seconds.

[184] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 950°C and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained for 15 hours in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics, and area-weight average of angles β (angles between [001] orientation and RD in respect to the TD axis) measured under each condition are listed in the following Table 7.

[185] Table 7

[Table 7]

[Table]

Sn (wt%)	P (wt%)	Sb (wt%)	Magnetic flux density B10[T]	Iron loss W17/50 [W/kg]	[P+0.5Sb] (wt%)	Angle	Note
0.03	0.035	0.025	1.951	0.93	0.0475	2.1	Inventive steel 33
0.03	0.04	0.025	1.942	0.95	0.0525	2.3	Inventive steel 34
0.04	0	0.026	1.917	1	0.0125	3.1	Comparat ive steel 116
0.05	0	0.024	1.924	1	0.0125	3.2	Comparat ive steel 117
0.05	0.025	0.029	1.945	0.94	0.0375	2.2	Inventive steel 35
0.05	0.03	0.028	1.947	0.93	0.0425	2.2	Inventive steel 36
0.05	0.035	0.031	1.963	0.91	0.0475	2.1	Inventive steel 37
0.05	0.075	0.025	1.923	1.01	0.0875	3.6	Comparat ive steel 118

[186]

[187] As listed in Table 7, it was revealed that the Inventive steels whose Sb, Sn and P contents is controlled to fall within the ranges defined in the present invention show a crystal orientation deviating from the Goss orientation by less than 3 degrees, and thus have superior magnetic properties. That is, it was confirmed that the electrical steel sheet according to one exemplary embodiment of the present invention may be produced into a grain-oriented electrical steel sheet having superior magnetic

properties by controlling the orientation of the secondarily recrystallized grains.

[188]

[189] Modified primary recrystallization method

[190] In order to verify an effect on iron loss during nitriding annealing after decarburization, but not during simultaneous decarburization and nitriding annealing, which is a more preferred method according to the present invention, an experiment was performed, as follows.

[191] A grain-oriented electrical steel sheet, which includes, by weight: 3.23% of Si, 0.058% of C, 0.12% of Mn, 0.025% of soluble Al, 0.0050% of N, 0.0045% of S, 0.045% of Sn, 0.038% of P, an varying content (0, 0.005, 0.025, 0.035 and 0.060%) of Sb, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C at which the re-dissolved N is present in a content of 27 ppm, re-heated, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 920°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The cold-rolled steel sheet was subject to a decarburization annealing process in a furnace of 860°C under a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C. Then, the cold-rolled steel sheet was subject to a nitriding process to contain 200±20 ppm of N. Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing, a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 15°C/hr over the entire heating temperature range. Also, the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained for 15 hours in a 100% hydrogen atmosphere, and then cooled in the furnace. Then, the finally annealed steel sheet was subject to general tension coating and overcoat processes. Magnetic characteristics measured under each condition are listed in the following Table 8.

[192] Table 8

[Table 8]

[Table]

Sb (wt%)	Magnetic flux density (B10, Tesla)	Iron loss (W17/50, W/kg)	Note
0	1.758	1.03	Comparative steel 119
0.005	1.904	0.99	Inventive steel 38
0.025	1.945	0.93	Inventive steel 39
0.035	1.939	0.94	Inventive steel 40
0.055	1.911	1.00	Comparative steel 120

[193]

[194] As listed in Table 8, it was revealed that the Inventive steels (component system 1) including suitable contents of Sb, Sn and P has highly improved iron loss, compared to the Comparative steels (component system 2) which is free from the Sb, Sn and P components. Also, it was seen that the iron loss of the electrical steel sheets is critically improved within the content ranges of the elements defined in the present invention when grains are primarily recrystallized in the decarburization before the nitriding process.

[195]

[196] Variation in iron loss by addition of As

[197] A grain-oriented electrical steel sheet, which includes, by weight: 3.15% of Si, 0.058% of C, 0.1% of Mn, 0.03% of soluble Al, 0.0049% of N, 0.004% of S, 0.05% of Sn, 0.032% of Sb, 0.04% of P, an varying content of As as listed in the following Table 9, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[198] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator,

and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 9.

[199] Table 9

[Table 9]

[Table]

As (wt%)	Iron loss (W17/50, W/kg)	Note
0.005	0.93	Inventive steel 41
0.24	0.93	Inventive steel 42
0.55	0.91	Inventive steel 43
1.60	0.96	Comparative steel 121

[200]

[201] As listed in Table 9, for convenience' sake, when an electrical steel sheet includes As whose content satisfies the content range defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes As whose content is out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 9, As was added within the content range defined in the present invention in the case of the Inventive steels 41 to 43, and As was added in an excessive content in the case of the Comparative steel 121. Here, it was revealed that the iron loss is reduced in the case of the Inventive steels as As is added in an increasing content. However, it was seen that the iron loss is rather increased in the case of the Comparative steel 121 whose As content is excessively high, which indicates that the excessively high As content adversely affects the improvement of iron loss.

[202] Therefore, it was seen that As is desirably added in a content of 1.40% by weight or less.

[203]

[204] Variation in iron loss by addition of Cu

[205] A grain-oriented electrical steel sheet, which includes, by weight: 3.0% of Si, 0.052% of C, 0.12% of Mn, 0.026% of soluble Al, 0.0042% of N, 0.0045% of S, 0.05% of Sn, 0.027% of Sb, 0.039% of P, an varying content of Cu as listed in the following Table 10, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C at which the re-dissolved N is present in a content of 25 ppm, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[206] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the soaking temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 10.

[207] Table 10

[Table 10]

[Table]

Cu (wt%)	Magnetic flux density(B10, Tesla)	Iron loss(W17/50, W/kg)	Note
0.02	1.929	0.93	Inventive steel 44
0.11	1.935	0.93	Inventive steel 45
0.23	1.939	0.91	Inventive steel 46
0.30	1.943	0.89	Inventive steel 47
0.45	1.940	0.91	Inventive steel 48
0.62	1.901	0.94	Comparative steel 122

[208]

[209] As listed in Table 10, for convenience' sake, when an electrical steel sheet includes components whose contents satisfy the content ranges defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes components whose contents are out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 10, Cu was added within the content range defined in the present invention in the case of the Inventive steels 44 to 48, and Cu was added in an excessive content in the case of the Comparative steel 122. In particular, each of the Inventive steels 44 to 48 includes Cu in the more desirable content defined in the present invention, that is, in a content of 0.05% by weight or more, and the Inventive steel 44 includes Cu in a lower content than the more desirable content. It was seen that the Inventive steel 44 having a relatively low Cu content has iron loss similar to the conventional component system that does not include Cu at all, but the iron loss is significantly reduced in the case of the Inventive steels 44 to 48 including an increasing content of Cu. However, it was revealed that the iron loss is rather increased in the case of the Comparative steel 122 including excessive Cu, which indicates that the excessively high Cu content adversely affects the improvement of iron loss.

[210] Therefore, it was seen that Cu is desirably added in a content of 0.50% by weight or less.

[211]

[212] Variation in iron loss by addition of Bi

[213] A grain-oriented electrical steel sheet, which includes, by weight: 3.15% of Si, 0.058% of C, 0.1% of Mn, 0.03% of soluble Al, 0.0049% of N, 0.004% of S, 0.05% of Sn, 0.032% of Sb, 0.04% of P, an varying content of Bi as listed in the following Table 11, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[214] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing, a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 11.

[215] Table 11

[Table 11]

[Table]

Bi (wt%)	Iron loss (W17/50, W/kg)	Note
0.002	0.93	Inventive steel 49
0.007	0.93	Inventive steel 50
0.015	0.91	Inventive steel 51
0.023	0.91	Inventive steel 52
0.200	0.96	Comparative steel 123

[216]

[217] As listed in Table 11, for convenience' sake, when an electrical steel sheet includes Bi whose content satisfies the content range defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes Bi whose content is out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 11, Bi was added within the content range defined in the present invention in the case of the Inventive steels 49 to 52, and Bi was added in an excessive content in the case of the Comparative steel 123. Here, it was revealed that the iron loss is reduced in the case of the Inventive steels as Bi is added in an increasing content. However, it was seen that the iron loss is rather increased in the case of the Comparative steel 123 whose Bi content is excessively high, which indicates that the excessively high Bi content adversely affects the improvement of iron loss.

[218] Therefore, it was seen that Bi is desirably added in a content of 0.1% by weight or less.

[219]

[220] Variation in iron loss by addition of Te

[221] A grain-oriented electrical steel sheet, which includes, by weight: 3.15% of Si, 0.058% of C, 0.1% of Mn, 0.03% of soluble Al, 0.0049% of N, 0.004% of S, 0.05% of Sn, 0.032% of Sb, 0.04% of P, an varying content of Te as listed in the following Table 12, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[222] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing, a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere

of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 12.

[223] Table 12

[Table 12]

[Table]

Te (wt%)	Iron loss (W17/50, W/kg)	Note
0.005	0.93	Inventive steel 53
0.24	0.93	Inventive steel 54
0.55	0.91	Inventive steel 55
1.05	0.91	Inventive steel 56
1.60	0.96	Comparative steel 124

[224]

[225] As listed in Table 12, for convenience' sake, when an electrical steel sheet includes components whose contents satisfy the content ranges defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes components whose contents are out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 12, Te was added within the content range defined in the present invention in the case of the Inventive steels 53 to 56, and Te was added in an excessive content in the case of the Comparative steel 124. Here, it was revealed that the iron loss is reduced in the case of the Inventive steels as Te is added in an increasing content. However, it was seen that the iron loss is rather increased in the case of the Comparative steel 124 whose Te content is excessively high, which indicates that the excessively high Te content adversely affects the improvement of iron loss.

[226] It was seen that the iron loss is significantly reduced in the case of the Inventive steels 44 to 48 including an increasing content of Cu. However, it was revealed that the iron loss is rather increased in the case of the Comparative steel 122 including excessive Cu, which indicates that the excessively high Cu content adversely affects the improvement of iron loss.

[227] Therefore, it was seen that Te is desirably added in a content of 1.40% by weight or less.

[228]

[229] Variation in iron loss by addition of Ni

[230] A grain-oriented electrical steel sheet, which includes, by weight: 3.1% of Si, 0.051% of C, 0.1% of Mn, 0.026% of soluble Al, 0.0041% of N, 0.005% of S, 0.045% of Sn, 0.028% of Sb, 0.038% of P, an varying content of Ni as listed in the following Table 13, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[231] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 13.

[232] Table 13

[Table 13]

[Table]

Ni (wt%)	Iron loss (W17/50, W/kg)	Note
0.005	0.93	Inventive steel 57
0.11	0.93	Inventive steel 58
0.41	0.91	Inventive steel 59
0.90	0.90	Inventive steel 60
1.55	0.96	Comparative steel 125

[233]

[234] As listed in Table 13, for convenience' sake, when an electrical steel sheet includes Ni whose content satisfies the content range defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes Ni whose content is out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 13, Ni was added within the content range defined in the present invention in the case of the Inventive steels 57 to 60, and Ni was added in an excessive content in the case of the Comparative steel 125. Here, it was revealed that the iron loss is reduced in the case of the Inventive steels as Ni is added in an increasing content. However, it was seen that the iron loss is rather increased in the case of the Comparative steel 125 whose Ni content is excessively high, which indicates that the excessively high Ni content adversely affects the improvement of iron loss.

[235] Therefore, it was seen that Ni is desirably added in a content of 1.40% by weight or less.

[236]

[237] Variation in iron loss by addition of Cr

[238] A grain-oriented electrical steel sheet, which includes, by weight: 3.105% of Si, 0.057% of C, 0.09% of Mn, 0.027% of soluble Al, 0.0051% of N, 0.005% of S, 0.05% of Sn, 0.031% of Sb, 0.037% of P, an varying content of Cr as listed in the following Table 14, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally

produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[239] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 14.

[240] Table 14

[Table 14]

[Table]

Cr (wt%)	Magnetic flux density(B10, Tesla)	Iron loss(W17/50, W/kg)	Note
0.01	1.929	0.93	Inventive steel 61
0.05	1.939	0.91	Inventive steel 62
0.13	1.935	0.91	Inventive steel 63
0.27	1.949	0.89	Inventive steel 64
0.32	1.931	0.91	Inventive steel 65
0.57	1.897	0.96	Comparative steel 126

[241]

[242] As listed in Table 14, for convenience' sake, when an electrical steel sheet includes components whose contents satisfy the content ranges defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes components whose contents are out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 14, Cr was added within the content range defined in the present invention in

the case of the Inventive steels 61 to 65, and Cr was added in an excessive content in the case of the Comparative steel 126. In particular, each of the Inventive steels 62 to 65 includes Cr in the more desirable content defined in the present invention, that is, in a content of 0.05% by weight or more, and the Inventive steel 61 includes Cr in a lower content than the more desirable content. It was seen that the Inventive steel 61 having a relatively low Cr content has iron loss similar to the conventional component system that does not include Cr at all, but the iron loss is significantly reduced in the case of the Inventive steels 62 to 65 including an increasing content of Cr. However, it was revealed that the iron loss is rather increased in the case of the Comparative steel 126 including excessive Cr, which indicates that the excessively high Cr content adversely affects the improvement of iron loss.

[243] Therefore, it was seen that Cr is desirably added in a content of 0.35% by weight or less.

[244]

[245] Variation in iron loss by addition of Pb

[246] A grain-oriented electrical steel sheet, which includes, by weight: 3.12% of Si, 0.055% of C, 0.11% of Mn, 0.029% of soluble Al, 0.0049% of N, 0.0045% of S, 0.05% of Sn, 0.031% of Sb, 0.039% of P, an varying content of Pb as listed in the following Table 15, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[247] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the

temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 15.

[248] Table 15

[Table 15]

[Table]

Pb (wt%)	Iron loss (W17/50, W/kg)	Note
0.002	0.93	Inventive steel 66
0.24	0.93	Inventive steel 67
0.55	0.91	Inventive steel 68
1.05	0.91	Inventive steel 69
1.60	0.96	Comparative steel 127

[249]

[250] As listed in Table 15, for convenience' sake, when an electrical steel sheet includes Pb whose content satisfies the content range defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes Pb whose content is out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 15, Pb was added within the content range defined in the present invention in the case of the Inventive steels 66 to 69, and Pb was added in an excessive content in the case of the Comparative steel 127. Here, it was revealed that the iron loss is reduced in the case of the Inventive steels as Pb is added in an increasing content. However, it was seen that the iron loss is rather increased in the case of the Comparative steel 127 whose Pb content is excessively high, which indicates that the excessively high Pb content adversely affects the improvement of iron loss.

[251] Therefore, it was seen that Pb is desirably added in a content of 1.40% by weight or less.

[252]

[253] Variation in iron loss by addition of at least one element out of Mo, B, Ge, Nb, Ti and Zn

[254] A grain-oriented electrical steel sheet, which includes, by weight: 3.15% of Si, 0.058% of C, 0.1% of Mn, 0.03% of soluble Al, 0.0049% of N, 0.004% of S, 0.05% of Sn, 0.032% of Sb, 0.04% of P, an varying content of one element selected from the

group consisting of Mo, B, Ge, Nb, Ti and Zn as listed in the following Table 16, and the balance of Fe and other unavoidable impurities, was used herein. Here, a slab of the grain-oriented electrical steel sheet was heated for 210 minutes at a temperature of 1170°C, and then hot-rolled to produce a hot-rolled steel sheet having a thickness of 2.3 mm. Then, the hot-rolled steel sheet was heated to 1120°C, maintained at 910°C for 90 seconds, quickly cooled in water, pickled and cold rolled to finally produce a cold-rolled steel sheet having a thickness of 0.30 mm. The decarburization and nitriding processes were simultaneously performed by simultaneously introducing a mixed gas of 75% hydrogen and 25% nitrogen, which has a dew point temperature of 62°C, and 1% dry ammonia into a furnace of 875°C and maintaining each of the cold-rolled steel sheets in the furnace for 180 seconds.

[255] Next, the hot-annealed steel sheet was coated with MgO, i.e., an annealing separator, and then finally annealed into a coil. During the final annealing a first soaking temperature was set to 700°C, and a second soaking temperature was set to 1200°C. In addition, a heating rate was set to 45°C/hr in a heating range of 700 to 45°C/hr and to 15°C/hr in a temperature range of 950 to 1200°C. Also, the soaking time at 1200°C was set to 15 hours, and the final annealing process was carried out in a mixed atmosphere of 25% nitrogen and 75% hydrogen until the temperature approaches 1200°C. After the temperature approaches 1200°C, the hot-annealed steel sheet was maintained in a 100% hydrogen atmosphere, and then cooled in the furnace. Magnetic characteristics measured under each condition are listed in the following Table 16.

[256] Table 16

[Table 16]

[Table]

Steels	Elements added	Content(wt%)	Iron loss(W17/50, W/kg)
Inventive steel 70	Mo	0.002	0.93
Inventive steel 71	Mo	0.31	0.92
Inventive steel 72	Mo	0.52	0.91
Comparative steel 128	Mo	1.61	0.96
Inventive steel 73	B	0.002	0.94
Inventive steel 74	B	0.020	0.92
Inventive steel 75	B	0.45	0.91
Comparative steel 129	B	1.55	0.96
Inventive steel 76	Ge	0.002	0.93
Inventive steel 77	Ge	0.24	0.92
Inventive steel 78	Ge	0.55	0.91
Comparative steel 130	Ge	1.60	0.96
Inventive steel 79	<u>Zn</u>	<u>0.002</u>	<u>0.93</u>
Inventive steel 80	<u>Zn</u>	<u>0.11</u>	<u>0.92</u>
Inventive steel 81	<u>Zn</u>	<u>0.45</u>	<u>0.91</u>
Comparative steel 131	<u>Zn</u>	<u>1.47</u>	<u>0.96</u>
Inventive steel 82	Nb	0.002	0.93
Inventive steel 83	Nb	0.08	0.92
Inventive steel 84	Nb	0.62	0.91
Comparative steel 132	Nb	1.61	0.96
Inventive steel 85	Ti	0.002	0.93
Inventive steel 86	Ti	0.12	0.92
Inventive steel 87	Ti	0.35	0.91
Comparative steel 133	Ti	1.63	0.96

[257]

[258] As listed in Table 16, for convenience' sake, when an electrical steel sheet includes components whose contents satisfy the content ranges defined in the present invention, this electrical steel sheet is considered to be Inventive steel, and when an electrical steel sheet includes components whose contents are out of the content range defined in the present invention, this electrical steel sheet is considered to be Comparative steel. In Table 16, Mo was added within the content range defined in the present invention in the case of the Inventive steels 70 to 72, and Mo was added in an excessive content in the case of the Comparative steel 128. In particular, each of the Inventive steels 71 and 72 includes Mo in the more desirable content defined in the present invention, that is, in a content of 0.003% by weight or more, and the Inventive steel 70 includes Mo in a lower content than the more desirable content. It was seen that the Inventive steel 70 having a relatively low Mo content has iron loss similar to the conventional component system that does not include Mo at all, but the iron loss is significantly reduced in the case of the Inventive steels 71 and 72 including an increasing content of Mo. However, it was revealed that the iron loss is rather increased in the case of the Comparative steel 128 including excessive Mo, which indicates that the excessively high Mo content adversely affects the improvement of iron loss.

[259] The effects of B on the improvement of iron loss were determined in the case of the Inventive steels 73 to 75 and Comparative steel 129, the effects of Ge on the improvement of iron loss were determined in the case of the Inventive steels 76 to 78 and Comparative steel 130, the effects of Zn on the improvement of iron loss were determined in the case of the Inventive steels 79 to 81 and Comparative steel 131, the effects of Nb on the improvement of iron loss were determined in the case of the Inventive steels 82 to 84 and Comparative steel 131, and the effects of Ti on the improvement of iron loss were determined in the case of the Inventive steels 85 to 87 and Comparative steel 132. Here, it was revealed the there is slight difference in the reduction in iron loss between the steels, but all the Inventive steels and Comparative steels show similar effects in the reduction in iron loss.

[260] Therefore, it was seen that each of the additional elements is desirably added in a content of 1.40% by weight or less, and more desirably added in a content of 0.003% by weight in order to achieve the more reliable improvement of iron loss.

[261]

Claims

- [1] A grain-oriented electrical steel sheet, essentially comprising 0.03 to 0.07% by weight of Sn, 0.01 to 0.05% by weight of Sb, and 0.01 to 0.05% by weight of P.
- [2] The grain-oriented electrical steel sheet of claim 1, wherein the P+0.5Sb is in range of 0.0370 to 0.0630 (wherein P and S represents contents (% by weight) of corresponding elements, respectively).
- [3] The grain-oriented electrical steel sheet of claim 1 or 2, further comprising one or more of 1.40% by weight or less of As, 0.50% by weight or less of Cu, 0.1% by weight or less of Bi, 1.40% by weight or less of Te, 1.40% by weight or less of Ni, 0.35% by weight or less of Cr, 1.40% by weight or less of Pb, and 1.40% by weight or less of the sum of at least one element selected from the group of Mo, B, Ge, Nb, Ti, and Zn.
- [4] The grain-oriented electrical steel sheet of claim 1 or 2, further comprising 2.0 to 4.0% by weight of Si, 0.020 to 0.040% by weight of acid-soluble Al and 0.01 to 0.20% by weight of Mn.
- [5] The grain-oriented electrical steel sheet of claim 1 or 2, wherein an area-weight average calculated from the absolute values of β of orientation, which is a degree that the crystal orientation of the electrical steel sheet deviates from the Goss orientation, is less than 3°.
- [6] The grain-oriented electrical steel sheet of claim 1 or 2, wherein the grain-oriented electrical steel sheet is manufactured from a steel slab further comprising 0.04 to 0.07% by weight of C, 10 to 55 ppm of N and 0.0010 to 0.0055% by weight of S.
- [7] A method of manufacturing an electrical steel sheet, the method comprising:
manufacturing a steel sheet by hot-rolling, annealing and cold-rolling a steel slab, wherein the steel slab essentially comprises 0.03 to 0.07% by weight of Sn, 0.01 to 0.05% by weight of Sb and 0.01 to 0.05% by weight of P;
subjecting the cold-rolled steel sheet to decarburization and nitriding annealing processes within a temperature range of 800 to 450°C/hr ; and
finally annealing the annealed steel sheet,
wherein, when the final annealing operation comprises first soaking heating and second soaking operations, the heating temperature is increased at a heating rate of 18 to 75°C/hr at the beginning and then increased at a rate of 10 to 15°C/hr within the range of 900 to 1020°C.

- [8] The method of claim 7, wherein the $P+0.5Sb$ is in range of 0.0370 to 0.0630 (wherein P and S represents contents (% by weight) of corresponding elements, respectively).
- [9] The method of claim 7 or 8, wherein the steel slab further comprises one or more of 1.40% by weight or less of As, 0.50% by weight or less of Cu, 0.1% by weight or less of Bi, 1.40% by weight or less of Te, 1.40% by weight or less of Ni, 0.35% by weight or less of Cr, 1.40% by weight or less of Pb, and 1.40% by weight or less of the sum of at least one element selected from the group of Mo, B, Ge, Nb, Ti, and Zn.
- [10] The method of claim 7 or 8, wherein the steel slab further comprises 2.0 to 4.0% by weight of Si, 0.020 to 0.040% by weight of acid-soluble Al, 0.01 to 0.20% by weight of Mn, 0.04 to 0.07% by weight of C, 10 to 55 ppm of N and 0.0010 to 0.0055% by weight of S.
- [11] The method of claim 7 or 8, wherein the operation of reheating a steel slab comprises: controlling the heating temperature so a content of re-dissolved N is in a range of 10 to 40 ppm.
- [12] The method of claim 11, wherein the heating temperature of the steel slab is in a range of 1050 to 1250°C.
- [13] The method of claim 7 or 8, wherein the second soaking temperature is in a range of 1150 to 1250°C.

[Fig. 1]

1/8

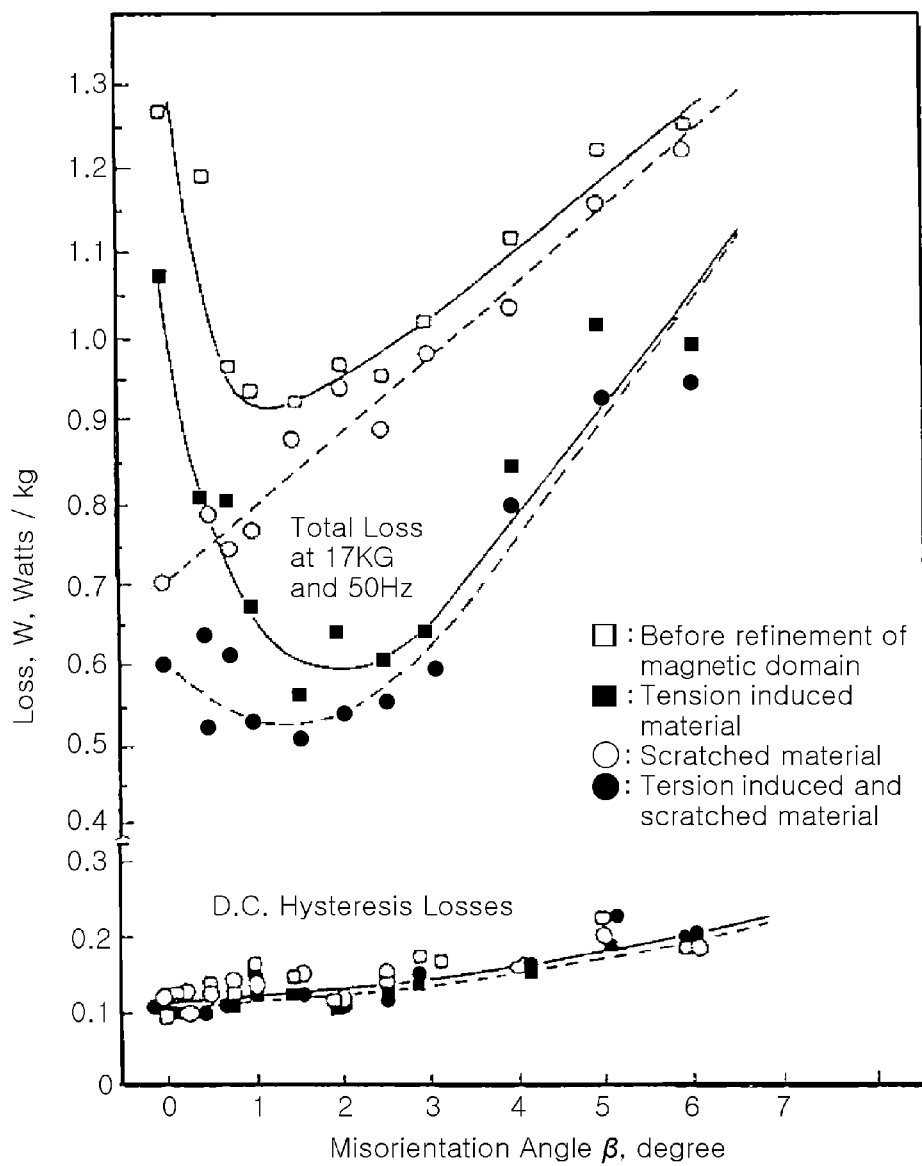


FIG. 1

[Fig. 2]

2/8

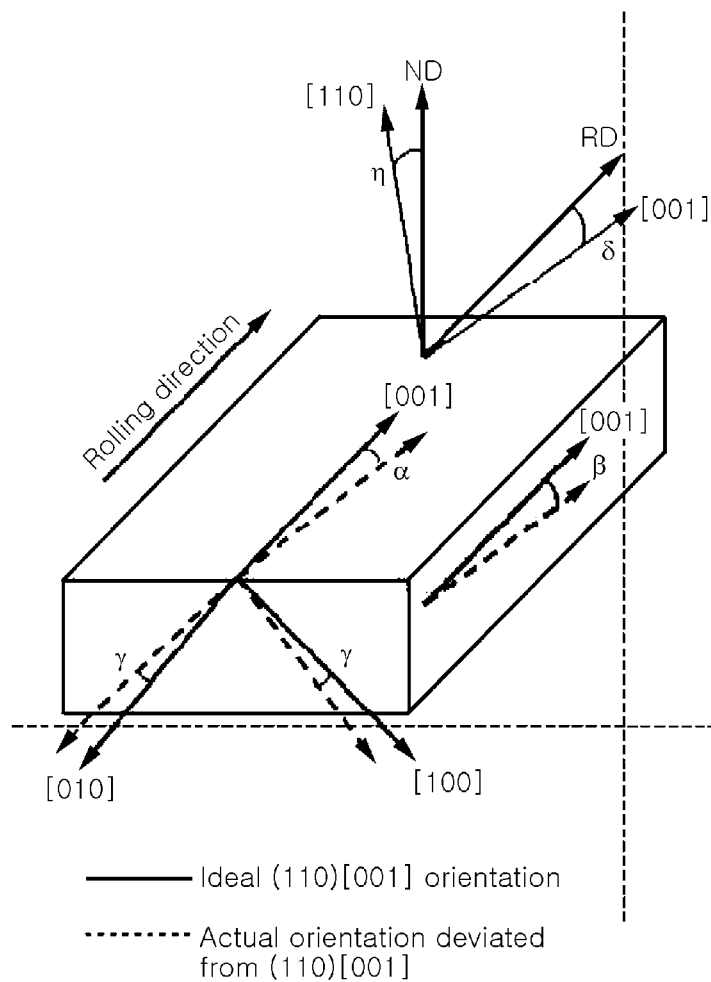


FIG. 2

[Fig. 3]

3/8

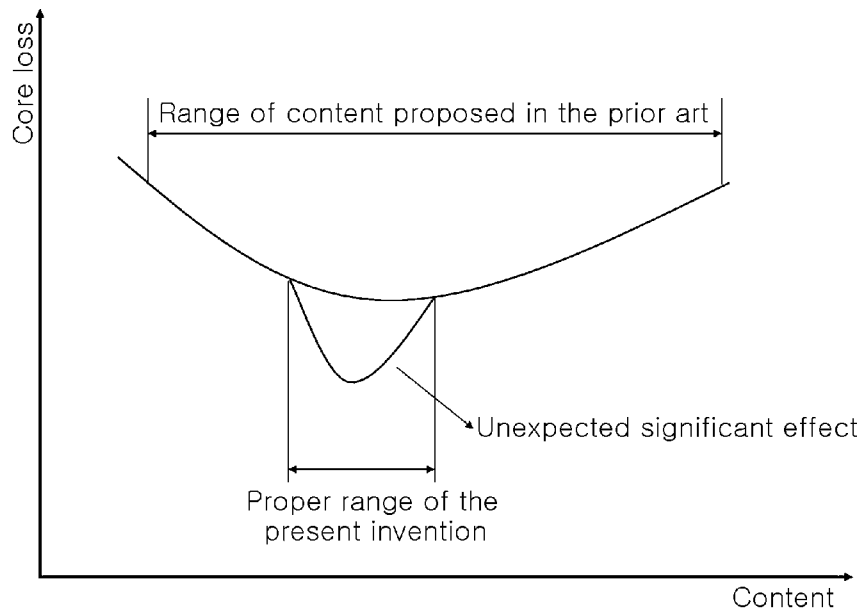


FIG. 3

[Fig. 4]

4/8

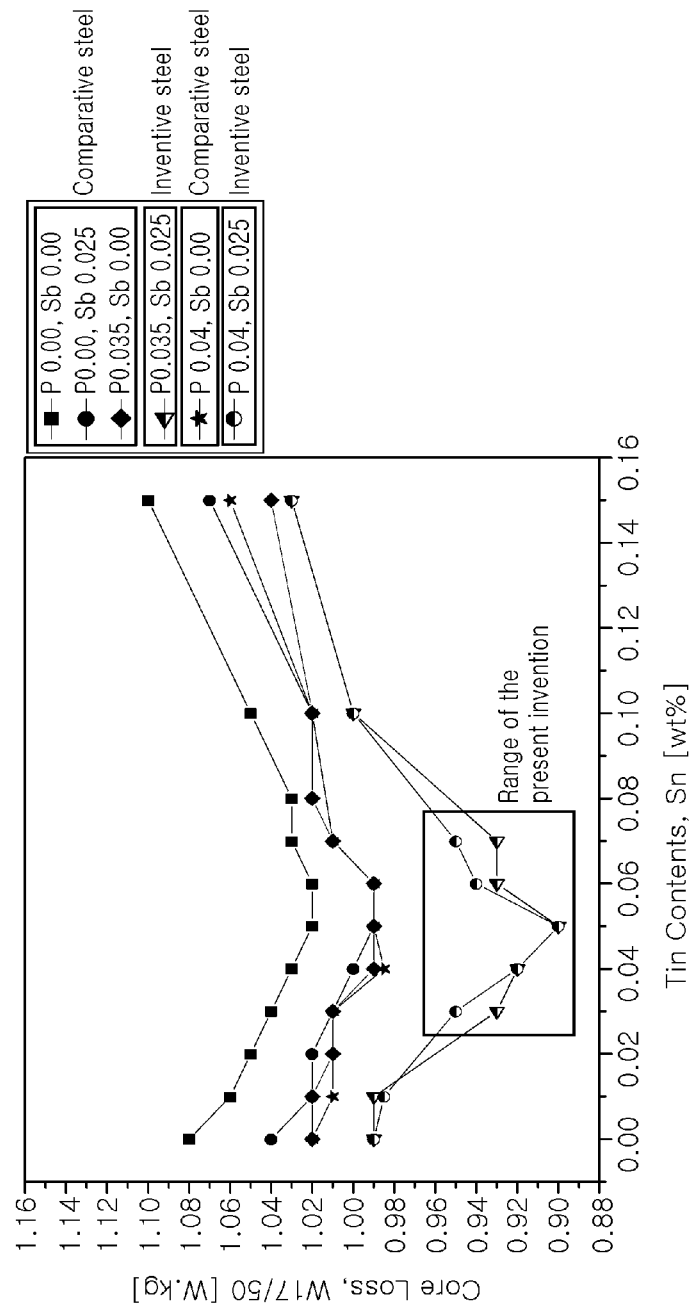


FIG. 4

[Fig. 5]

5/8

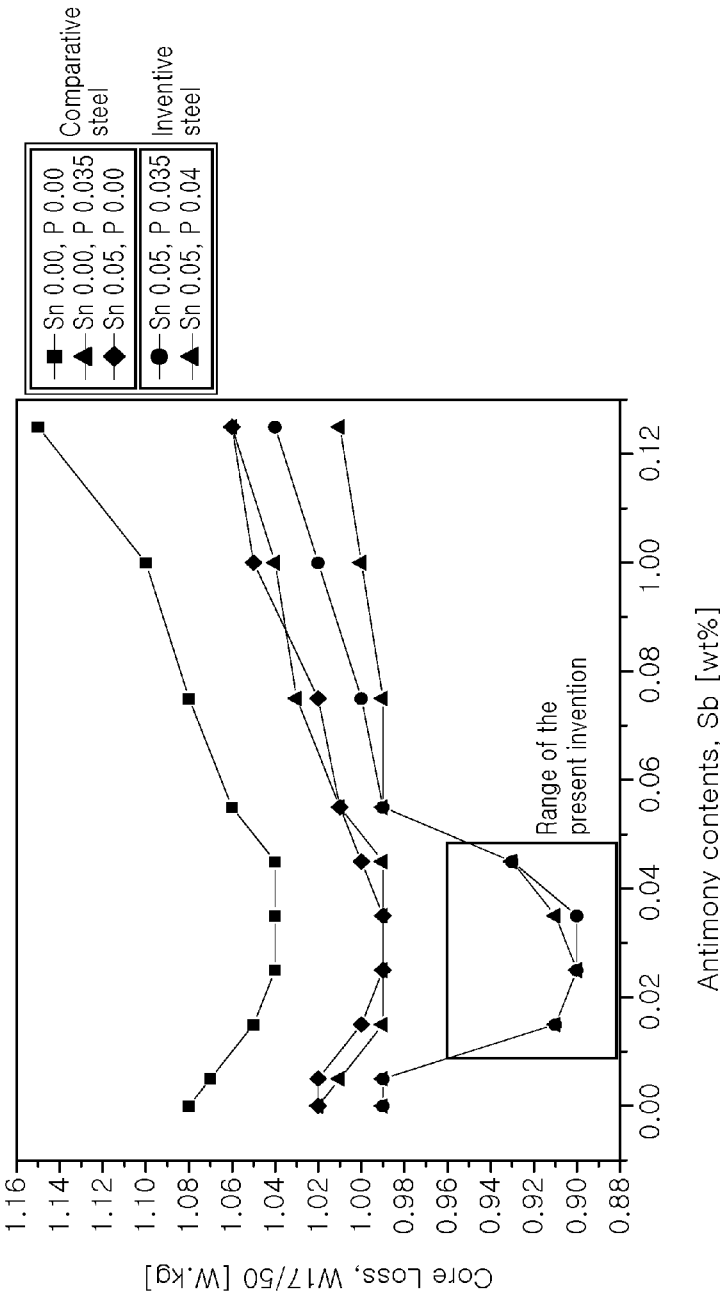


FIG. 5

[Fig. 6]

6/8

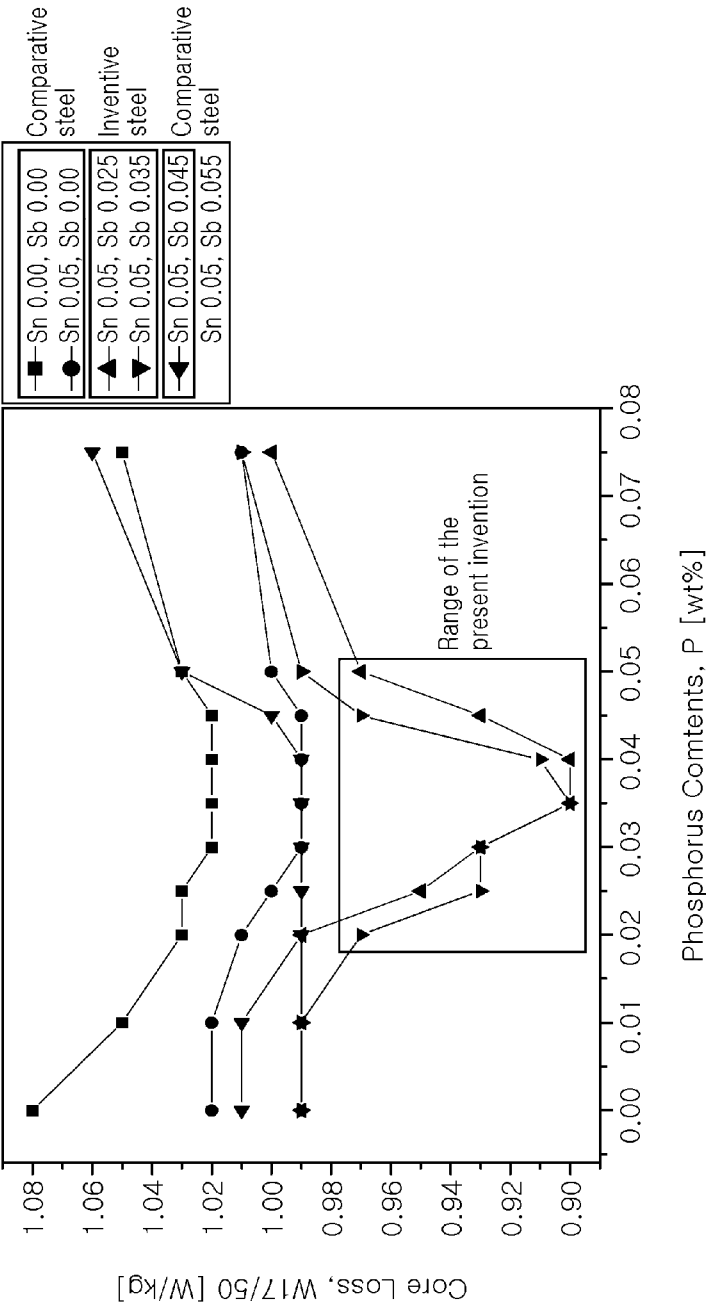


FIG. 6

[Fig. 7]

7/8

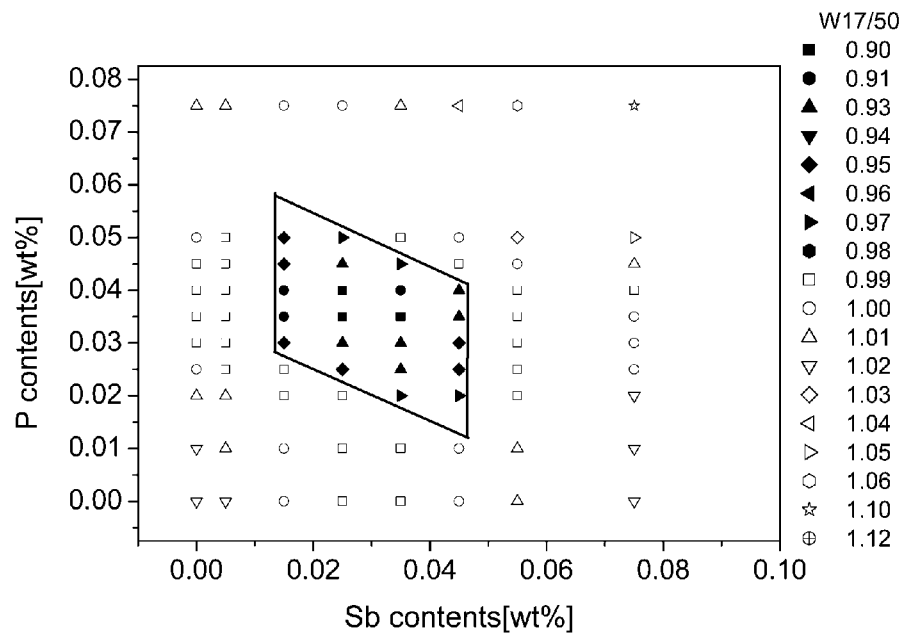


FIG. 7

[Fig. 8]

8/8

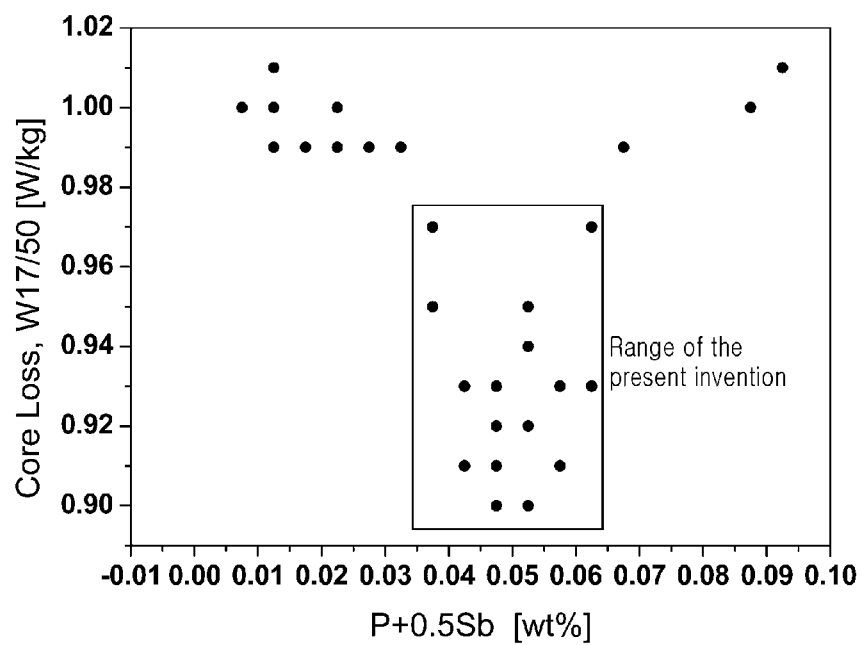


FIG. 8