METHOD OF MANUFACTURING COLD-ROLLED NONORIENTED ELECTRO-MAGNETIC STEEL SHEET AND PRODUCT ELECTROMAGNETIC STEEL SHEET

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ATTORNEYS
METHOD OF MANUFACTURING COLD-ROLLED NONORIENTED ELECTRO-MAGNETIC STEEL SHEET AND PRODUCT ELECTROMAGNETIC STEEL SHEET

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20 Claims

ABSTRACT OF THE DISCLOSURE

In the method of manufacturing a cold-rolled non-oriented electromagnetic steel sheet comprising Si in an amount of 1.0–4.0% by weight, acid soluble Al in an amount of 0.1–3.0% by weight and the rest being iron, comprising the ordinary production steps of decarburization, at least one cold-rolling step, and a final heat-treatment subsequent to the final cold-rolling step (including skin pass or temper rolling), the improvement which comprises the decarburization treatment being carried out in the production steps before the final cold-rolling step, the inner oxidized layer present in the surface part of the steel being removed after the decarburization treatment but before the final cold-rolling step; all the heat-treatments after the removal of the inner oxidized layer being carried out in a non-oxidizing atmosphere which contains water and hydrogen in such amounts that the ratio of the partial pressure of steam formed during the heat-treatment steps to the partial pressure of hydrogen is less than 0.05 to avoid the re-forming of an inner oxidized layer.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to a method of manufacturing a cold-rolled non-oriented electromagnetic steel sheet, and more particularly to a method of manufacturing a cold-rolled non-oriented electromagnetic steel sheet excellent in characteristics at high magnetic field intensity and electromagnetic steel sheet products.

Description of the Prior Art

Electromagnetic steel sheets have been previously called silicon sheets or electric steel sheets and are widely used to form iron cores for electrical machinery and apparatus. There are a variety of electromagnetic steel sheets classified according to the various rolling methods, rolling orientations, configurations and other factors, such as hot-rolled silicon steel sheets, hot-rolled and welded non-oriented silicon steel sheets or strips, cold-rolled non-oriented silicon steel sheets or strips, and cold-rolled oriented, or anisotropic, silicon steel sheets or strips, which materials are all widely known.

Generally, these electromagnetic steel sheets are required to have various characteristics, among which the magnetic characteristics in particular should be excellent and which sheets are graded in terms of iron loss. In order to improve the magnetic characteristics, the iron loss must be reduced. Since the iron loss consists of the hysteresis loss and eddy current loss, it is necessary to decrease both of these losses. To provide a reduction in hysteresis loss, it is necessary to lessen certain defects in the steel sheets, such as recrystallized grain domains, impurity inclusions, and stresses exerted in the steel sheets during their manufacturing process. In addition, the aggregate structure of the crystals composing the steel sheet should possess a preferred orientation suitable for exhibiting magnetic characteristics.

On the other hand, in order to effect a decrease in eddy current loss, it is necessary to coat the steel sheet with an electric insulation film so that, when the steel sheet thus coated is used as material for a laminated iron core, the steel sheet components of the core are electrically insulated. Besides, the steel sheet must contain alloying elements which heighten the electrical resistance of steel sheet itself, such as silicon (Si) and aluminum (Al), and further the thickness of the steel sheet should be decreased.

For the production of a cold-rolled non-oriented electromagnetic steel sheet, which is a type of electromagnetic steel sheet, manufacturing processes have been devised in view of the above described factors as a matter of course so as to achieve the desired magnetic characteristics. For example, a well known fundamental method for producing cold-rolled non-oriented electromagnetic steel sheets employs the so-called "method in which hot-rolled coils formed by the rolling of slabs containing not more than 4.0% Si, 0.1 to 3.0% acid soluble aluminum (Sol. Al) and as small a percentage of other impurities as possible are annealed according to the necessity, cold-rolled to the desired sheet thickness and thereafter subjected to direct annealing or box annealing. Besides, where it is intended to obtain higher-class electromagnetic steel sheets containing larger crystal grains so as to have a lower iron loss, there is another conventional manufacturing method available which employs "the two-step cold rolling method" (the single cold rolling and skin pass rolling method) wherein the above-mentioned hot-rolled coils, after annealed as required, are cold-rolled to the desired thickness at two stages with an intermediate annealing stage in between and thereafter subjected to a bright continuous annealing or a box annealing. The cold-rolled non-oriented electromagnetic steel sheet manufactured by any of the above described prior methods fails to have any desirable iron loss value particularly at a high magnetic field intensity. This is related to the fact that the said steel sheet is graded in accordance with the Japanese Industrial Standards (JIS). However, the iron loss values for this grading are specified with regard to the products by the aforesaid conventional methods, so that W10/50 (the iron loss at a magnetic flux density of 10 kg. and a frequency of 50 Hz.), W20/50 (the iron loss at a magnetic flux density of 15 kg. and a frequency of 50 Hz.), W25/50 (the iron loss at a magnetic flux density of 25 kg. and a frequency of 50 Hz.) are the proof value while W15/50 (the iron loss at a magnetic flux density of 15 kg. and a frequency of 50 Hz.) is the reference value. At present, these iron loss values are set upon the basis of lower magnetic flux densities than those when the said electromagnetic steel sheet is put to practical use to form the iron cores for electrical machinery and apparatus, and particularly for rotary machines.

As a result, the prior cold-rolled non-oriented electromagnetic steel sheets have drawbacks in that the iron loss increases markedly as the magnetic flux density increases when the steel sheets are used as materials for iron cores in electrical machinery, especially for rotating machines. More particularly, the relation between magnetic flux density and iron loss is such that the iron loss is increased with increasing flux density. This phenomenon is especially remarkable when the flux density is above 15 kg.

For this reason, it has so far been extremely difficult to manufacture desirable cold-rolled non-oriented electromagnetic steel sheet suited to form iron cores for rotary electrical machinery.

SUMMARY OF THE INVENTION

An object of this invention is to provide cold-rolled non-oriented electromagnetic steel sheets with markedly re-
duced iron loss during heightened magnetic field intensity, by improving the conventional methods of manufacturing cold-rolled nonoriented electromagnetic steel sheets, and to provide an advantageous method for manufacturing such novel steel sheets.

Another object of the present invention is to provide a method for manufacturing a cold-rolled nonoriented electromagnetic steel sheet excellent in characteristics at high magnetic field intensity by improving the prior methods for producing cold-rolled nonoriented electromagnetic steel sheets, the improvement being applicable with effortless ease to any of the aforesaid prior basic methods so that the iron loss under a strong magnetic field is markedly lower.

These objects of the present invention are achieved by providing a method for manufacturing a cold-rolled non-oriented electromagnetic steel sheet excellent in characteristics at high magnetic field intensity which includes a decarburizing stage, a final cold rolling and a final heat treatment stage so as to produce a cold-rolled non-oriented electromagnetic steel sheet containing 1.0 to 4.0% silicon (Si), 0.1 to 3.0% acid-soluble aluminum (Sol. Al) and as small a percentage of other impurities as possible, which method is characterized by the improvement as providing the decarburizing treatment before at least one combination of cold rolling treatment, the inner oxidized layer extending in the surface portion of the steel sheet after said decarburizing treatment and prior to the cold rolling, and, after removing the inner oxidized layer, performing the heat treatment in an atmosphere wherein the partial pressure of steam divided by that of hydrogen is kept below 0.05 to prevent the formation of any inner oxidized layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, features and attendant advantages of this invention will be more fully appreciated as the same becomes better understood from the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 is a schematic sketch of the oxidized layers formed in the surface portion of the steel sheet at the hot rolling stage of the present invention.

FIG. 2 is a photograph showing a cross-sectional aspect corresponding to the sketch of FIG. 1.

FIG. 3 is a photograph illustrating a cross-sectional aspect immediately beneath the surface of a conventional electromagnetic steel sheet.

FIGS. 4 and 5 are respectively photographs showing cross-sectional aspect beneath the surface of electromagnetic steel sheets embodying the present invention.

FIG. 6 is a graph for comparison of iron loss curves of an electromagnetic steel sheet having an inner oxidized layer at each side and an electromagnetic steel sheet deprived of inner oxidized layers from both sides.

FIG. 7 is a graph showing the relationship between the thickness of the inner oxidized layer and the iron loss.

FIGS. 8 and 9(A)(B) are respectively work process diagrams based on the method of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be more fully understood by reference to the following detailed description of the preferred embodiments of the invention, which is given in conjunction with the accompanying drawings.

Generally regarding electromagnetic steel sheets, the carbon (C) existing in the steel hinders the growth of recrystallized grains, or the carbon existing in the forms of impurities and deposits in the steel, deteriorate the magnetic characteristics. Further, the carbon in the steel sheet fosters the phenomenon of magnetic aging when the sheet is used to form an iron core, thus causing the iron loss to increase. Therefore, in order to prevent magnetic aging in particular, it is necessary to lower the content of the carbon in electromagnetic steel sheet products, the content being preferably below 0.005%. A method generally adopted to lower the carbon content in the product electromagnetic steel sheet is to provide a decarburizing annealing stage adequately following the hot-rolling operation. Generally employed as such a decarburizing annealing method is the atmosphere decarburizing method in which annealing is effected in the so-called wet atmosphere which is composed of several tens percent hydrogen and the remaining percentage of nitrogen and steam with a dew point of several tens of degrees C. Besides, the scale decarburizing method which makes use of the mill scale of hot-rolled coils, or the vacuum decarburizing and refining method applicable to molten steel is now practically employed.

In the aforesaid hot rolling, the atmosphere is wet air having a strong oxidizing property, so that the outer oxidized layer (O) consisting, as shown in the sketch of FIG. 1 and the photograph of FIG. 2, of FeO, Fe₃O₄, Fe₃C, SiO₂ and 2Fe₂O₃ for example, that is, a layer of scale is formed on the hot-rolled coil surface, while an inner oxidized layer (I) containing SiO₂, Al₂O₃ and iron oxides is formed beneath the outer oxidized layer (O) on the surface portion of the base iron. The outer oxidized layer (O), or the scale, can be removed by means of such an ordinary pickling treatment as dilute solutions of sulfuric acid or hydrochloric acid, whereas the inner oxidized layer (I) cannot be removed with such a solution.

Furthermore, the atmosphere for the decarburizing annealing operation, after the hot rolling, has a weak oxidizing quality as well as a decarburizing property. Thus, even if the surface of the decarburized steel sheet is bright, the decarburization is accompanied by the formation of the above described inner oxidized layer, as shown in FIG. 3, in the surface portion of the cold-rolled steel sheet which has no outer oxidized layer, that is, no scale layer. The inner oxidized layer formed in this case is usually as thick as several microns to several tens of microns, and cannot be removed by means of an ordinary pickling solution, just as in the aforesaid case.

After making various studies with a view to improve the characteristics at high magnetic field intensity of a cold-rolled nonoriented electromagnetic steel sheet, the present inventors have ascertained that the iron loss at high magnetic field intensity can be markedly decreased by removing the above described inner oxidized layer.

As an illustration of this fact, an example is cited hereinafter. A cold-rolled nonoriented electromagnetic steel sheet (A) having an inner oxidized layer of 5 microns in thickness and a final thickness of 0.35 mm, was produced by pickling a hot-rolled coil containing 0.025% C, 3.1% Si, 0.003% and 0.26% Sol. Al by a known method so as to remove the scale and practicing the two-step cold-rolling method (the single cold rolling and skin pass rolling method) with the use of a wet atmosphere for the intermediate annealing and the final annealing. Meanwhile, another cold-rolled nonoriented electromagnetic steel sheet (B) was manufactured by pickling the same hot-rolled coil having undergone the scale removal and the intermediate annealing, in a pickling solution composed of 6% nitric acid, 1% hydrofluoric acid and the remaining percentage of distilled water, thereby removing the inner oxidized layer, and thereafter carrying out the skin pass rolling to a final thickness of 0.35 mm., and the subsequent final annealing operation with the use of an annealing atmosphere wherein the PH₂O/PH₂ (the partial pressure of the steam in the atmosphere divided by that of the hydrogen therein) was set at optimum relation between the magnetic flux density (MF) and an iron loss (WL) of each of the steel sheets (A) and (B) thus produced is shown in FIG. 6. It will be apparent from FIG. 6 that, with the final product (B) deprived of the inner oxidized layer, the iron loss (WL) is remarkably lowered at high field intensity values.
In connection with the pickling of hot-rolled silicon steel sheet, there is known, for example, the method disclosed in the report entitled "Removal of Oxide Films of Silicon Steel Sheet and Its Effects" Journal of the Institute of Electrical Engineers of Japan, Vol. 61, No. 641, December 1941. However, the oxide films dealt with in this report are, as specified therein, "films separable during the production of machines and apparatus with the use of the steel sheet" and "films which can be easily rubbed off with a piece of polishing paper and can be removed also by means of a pair of tweezers," that is, they are identical with the iron oxide layer (scale) formed during hot rolling; thus, being entirely different from the inner oxidized layer to be removed by the present invention. Furthermore, such inner oxidized layer cannot be removed by the use of the "dilute sulfuric acid" (at a temperature of 60 to 80°C) having a concentration of about 10% which is introduced in the report, as will be clear from the foregoing description. The inner oxidized layer is not separated even by a high degree of cold rolling. Thus, the above cited report does not suggest anything concerning the removal of the inner oxidized layer.

The secondary feature of the present invention lies in specifying the steel sheets having the thickness and composition as shown in the Table and the decarburizing method and also employing a specific atmosphere for the heat treatment following the stage of removing the inner oxidized layer, in the one-step cold-rolling method or the two-step cold-rolling method (the single rolling and skin pass rolling method) employed in conventional methods for manufacturing cold-rolled nonoriented electromagnetic steel sheet. Where the one-step cold-rolling method or the two-step cold-rolling method is to be practiced under conventional concepts, it will normally be considered to provide the stage of removing the inner oxidized layer after the completion of the final heat treatment. However, if the inner oxidized layer is removed after the final heat treatment, some drawbacks will appear. That is, when pickling or electropolishing is carried out under such severe conditions as removing the inner oxidized layer in a short time in the order of a few seconds or minutes, then, because the dissolving (polishing) speed varies greatly according to the orientation of the crystal grains composing the steel sheet and because the steel sheet contemplated in the invention is a high-class electromagnetic steel sheet with low iron loss which generally has coarse crystal grains, the steel sheet surface bears the effect of the magnetic flux concentrated at the surface portion of the steel sheet to a larger extent than by high field intensity. As will be understood from the foregoing description, the inner oxidized layer existing in the surface portion of cold-rolled nonoriented electromagnetic steel sheet has a great influence upon the iron loss at a high magnetic field intensity, and accordingly the removal of such an inner oxidized layer is the primary feature of the present invention.

The pickling prior to the cold rolling of hot-rolled coils is known in the art. The pickling solution is normally a dilute solution of sulfuric or hydrochloric acid. Moreover, the object of the conventional pickling is to remove the so-called scale composed of iron oxides (FeO, Fe₂O₃, Fe₃O₄, FeO, Fe₃O₄) thus not to remove the inner oxidized layer, as in the present invention. In fact, the inner oxidized layer is removed at all by means of such acid solutions as have been generally applied. Moreover, conventional acid solutions includes pickling depressors for preventing the dissolution of steel sheet (base iron).

On the other hand, to remove the inner oxidized layer according to the invention, it is essential to employ a means for removing the base iron. For example, a pickling solution capable of positively dissolving the base iron, an electrolytic pickling method, a mechanical removing method employing sand brushing or the like, or any other suitable means is adequately adopted for the said purpose.

Various studies made in the inventors have revealed that these demerits can be overcome by providing such improvement as comprises, in the one-step cold-rolling method or the two-step cold-rolling method (the single cold rolling and skin pass rolling method), removing the inner oxidized layer after the decarburizing treatment and, at the latest, before the final cold rolling and heat treatment, performed at all by means of such acid solutions as have been generally applied. Moreover, conventional acid solutions includes pickling depressors for preventing the dissolution of steel sheet (base iron).

That is to say, as the removal of the inner oxidized layer which has been formed by the hot-rolling and decarburization annealing, is carried out before the final recrystallization annealing, the crystal size of the layer is still not large at the time of removal, nor is the roughness of the surface of the steel sheet very pronounced.
which phenomenon may be caused by the chemical removal of the layer. Also as the cold-rolling step is provided after the removal of said inner oxidized layer, such roughness and scratches that may be produced by the mechanical removal of the layer, can be eliminated by cold-rolling; and the inside stress produced by the mechanical removal can be effectively put off by the heat treatment following the subsequent cold-rolling. However, if the atmosphere in which the heat treatment is carried out after the removal of the inner oxidized layer is an oxidizing atmosphere, such layer will be again produced. To avoid reforming this oxidizing layer, the heat treatment after the removal of the inner oxidized layer is carried out in an atmosphere of less than 0.05 in PH2O/PH2. Thus, there is obtained a cold-rolled, non-oriented electro-layer, and therefore has high magnetic field properties magnetic steel sheet which is free from the inner oxidized and a good surface.

Based on the above explanation, we can present Processes (I)-(15) as nine preferable processes of the present invention, provided, however, the present invention is not limited to these processes.

FIG. 8 shows a process diagram for the method of the present invention practised with the one-step cold rolling method.

FIG. 9(A), (B) shows a process diagram for the method of the present invention practised with the two-step cold-rolling method.

The explanation of the processes shown in FIG. 8 is as follows:

In order to meet conditions such that the cold-rolling step (4) and the heat treatment step (5) are required as the step subsequent to that for the removal of the inner oxidized layer and pickling step (3), it is necessary to remove the inner oxidized layer as well as the surface scale by using a pickling solution which is so strong as to dissolve the inner oxidized layer remaining and pickling step (3) before cold-rolling step (4). In this case, decarburization is carried out in the form of a hot rolled coil by the decarburizing annealing step (2) as shown in the process (1) or the vacuum degassing step (6) by the vacuum degassing treatment at the stage of molten steel as shown in the process (11). The atmosphere in which the final heat treatment step (5) is carried out is less than 0.05 in PH2O/PH2.

The explanation of the processes shown in FIGS. 9(A) and 9(B) is as follows:

The process (III) is represented by: Hot-rolling step (1) — pickling step (7) (for removing scale)—primary cold-rolling step (8)—intermediate heat-treatment and decarburizing annealing step (9)—the inner oxidized layer removal step (10)—secondary cold-rolling step (11) (skin pass or temper rolling)—final heat-treatment step (12) (dry annealing).

The processes (IV), (V) and (VI) are featured by: Hot-rolling step (1) and the hot-rolled coil decarburizing annealing step (2), respectively; and the processes (VII), (VIII) and (IX) are featured by the vacuum degassing step (6) through the vacuum degassing treatment of molten steel and hot-rolling step (1), respectively. Any of the above-mentioned processes (IV), (V), (VI), (VII), (VIII) and (IX) may be represented as follows: The processes (IV) and (VII) involve the removal of the inner oxidized layer as well as scale by picking step (3)—primary cold-rolling step (8)—intermediate heat-treatment step (13) (dry annealing)—secondary cold-rolling step (11) (skin pass or temper rolling)—heat-treatment step (12) (dry annealing); the processes (V) and (VIII) involve the pickling step (7) (for removing scale)—primary cold-rolling step (8)—the inner oxidized layer removal step (10)—intermediate heat-treatment step (13) (dry annealing)—secondary cold-rolling step (11) (skin pass or temper rolling)—final heat-treatment step (12) (dry annealing); and the processes (VI) and (IX) involve the pickling step (7) (for removing scale)—primary cold-rolling step (8)—intermediate heat-treatment step (14) (wet annealing)—(or dry annealing)—the inner oxidized layer removal step (10)—secondary cold-rolling step (11) (skin pass or temper rolling) and the final heat-treatment step (12) (dry annealing).

As is clear from the above explanation, the method of the present invention is so constructed that an inner oxidized layer removal step is provided leaving at least one set of a cold-rolling and a heat treatment step, and a decarburizing step is provided as a step previous to said inner oxidized layer removal step; and the heat treatment subsequent to said inner oxidized layer removal step is carried out in an atmosphere incapable of producing an inner oxidized layer.

The reason why Si is limited to between 1.0-4.0% according to the present invention is that a steel sheet of less than 1.0% Si content is a low-grade product which does not especially require any iron loss (watt loss) in the magnetic field intensity, therefore, it is outside the scope of the present invention; and a steel sheet of more than 4.0% Si content is very brittle, making it difficult to subject it to cold-rolling without encountering difficulties.

On the other hand, Sol. Al is limited to 0.1-3.0%. The reason is that the Sol. Al content of less than 0.1% makes difficult the recrystallization at the heat treatment subsequent to the cold-rolling, and Sol. Al of more than 3.0% makes the steel sheet brittle, in combination with the Si content, making it difficult to subject it to cold-rolling without encountering difficulties.

In order to make the electromagnetic steel sheet non-annealing magnetically, it is desirable to reduce the carbon content to less than 0.005% by decarburization.

As mentioned above, the atmosphere at the heat treatment subsequent to the removal of the inner oxidized layer is limited to less than 0.05 in PH2O/PH2. If the partial pressure ratio is more than 0.05, an inner oxidized layer forms rapidly, making it impossible to achieve the object of the present invention.

Regarding the removal of said inner oxidized layer according to the present invention, the reduction of iron loss which is one of the objects of the present invention, can be achieved, even if such removal is not perfect, but involves an inner oxidized layer in a thickness of about 1μ. As shown in the photo of FIG. 5, that is, in the case of FIG. 5, the iron loss is W17/50 3.56 watt/kg, after removal (W17/50 3.43 watt/kg, after the perfect removal of inner oxidized layer 0μ), which has been lowered sufficiently from the iron loss of W17/50 4.09 watt/kg (thickness of inner oxidized layer 4μ) before removal as to nearly meet the purpose of removal.

Therefore, according to the present invention, the unremoved inner oxidized layer is permitted, provided that it is less than 1μ thick, because such thickness does not prevent the reduction of the iron loss.

The following are examples of the present invention:

Having generally described the invention, the following specific examples are provided for purposes of illustration only and are not intended to be limiting unless otherwise specified.

Example 1 (the one-step cold-rolling method)

Hot rolled coil annealing was carried out at 750°C for 8 hours with a hot rolled coil of 20 mm. thick containing carbon 0.035% by weight, silicon 2.3% by weight, Sol. Al 0.15% by weight and the rest being essentially iron with mill scale, so as to decarburize the carbon content to 0.0035%. Then, the following two methods were applied to the sample to be reduced to the final sheet product of 0.50 mm. thick by cold-
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rolling. Then, this was annealed at 925°C, for 3 minutes in a dry atmosphere consisting of 40% hydrogen and the rest being nitrogen (point: 0°C; PH₂/O₂=0). B (the present invention) shown in FIG. 8): After being pickled with a pickling solution consisting of 2% hydrochloric acid, 3% nitric acid, 1% hydrogen fluoride and the rest being water in the inner oxidized layer removal and pickling step (3), to remove scale and the inner oxidized layer, the sample was reduced to a final product of 0.50 mm thick in the cold-rolling step (4). Then, this was annealed in the same atmosphere as was used in the method A above, at 900°C, for 3 minutes in the final heat treatment step (5).

The sheet samples respectively obtained by the above-mentioned methods were cut into Epstein test pieces; and the results of tests are shown in Table 1.

Example 2 (the two-step cold-rolling method)

After being pickled with a pickling solution consisting of 2% hydrochloric acid and the rest being water, to remove scale, a hot rolled coil of 2.5 mm thick, containing carbon 0.029% by weight, silicon 3.16% by weight, S 0.17% by weight and the rest being essentially iron, was reduced to an intermediate sheet of 0.39 mm thick by primary cold-rolling, and was subjected to decarburizing annealing to decarburize the carbon content to 0.0035% in a wet atmosphere consisting of 25% hydrogen and the rest being nitrogen and steam (Dew point: 40°C). Then, the sample was treated respectively by the following two methods.

A (the conventional method): After being reduced to a final product of 0.35 mm thick by secondary cold-rolling, the sample was annealed at 850°C, for 4 minutes in a dry atmosphere consisting of 25% hydrogen and the rest being nitrogen (PH₂/O₂=0.02) in the final heat treatment.

B (the present invention) as exemplified by the process III shown in FIG. 9(A): After the surface was ground with a sand brush, in the inner oxidized layer removal step (10), the sample was subjected to the same secondary cold rolling step (11) and final heat-treatment step (12) as was carried out in the method A above. The steel sheet samples respectively obtained by the above-mentioned methods were cut into Epstein test pieces; and the results are shown in Table 1.

Example 3 (the two-step cold-rolling method)

After being pickled with a pickling solution consisting of 2% hydrochloric acid and the rest being water to remove scale, a hot rolled coil of the same kind as was used in Example 2 above, was formed into a loose coil, and was subjected to hot rolled coil decarburizing annealing at 800°C; for 7 hours in the strongly decarburizing, wet atmosphere consisting of 88% hydrogen and 12% nitrogen and steam (Dew point: 53°C), to decarburize the carbon content to 0.0027%, and then again acid-washed with the pickling solution of the same kind as was used above.

The sample was treated respectively by the following 4 methods:

A (the conventional method): After being reduced to an intermediate sheet of 0.39 mm thick by primary cold-rolling, the sample was subjected to intermediate annealing in an atmosphere consisting of 20% hydrogen and the rest being nitrogen, and reduced to a final product of 0.35 mm thick by secondary cold-rolling and then annealed at 850°C for 4 minutes in the same atmosphere as was used in the method above.

B (the present invention, the process VI, shown in FIG. 9(B)): After the intermediate heat treatment step (14) (annealing) of the same treatment as was used in the method A above, the sample was removed by the inner oxidized layer removal step (10) with a chemical pickling solution consisting of 6% hydrogen peroxide, 2% hydrogen fluoride and the rest being water, and then reduced to the final sheet product of 0.35 mm. thick by secondary cold-rolling step (11) of the same as was used in the method A above, and annealed at 850°C, for 4 minutes in a dry atmosphere consisting of 25% hydrogen and the rest being nitrogen (PH₂/O₂=0.023) in the final heat treatment step (12). The cross-section of the so-obtained steel sheet is shown microscope-photographically in FIG. 4.

C (the present invention, or process V, shown in FIG. 9(B)): After the primary cold-rolling step (8), the same as used in method A above, the steel sheet was picked with a pickling solution preparing 5% hydrogen fluoride to concentrated hydrochloric acid in the inner oxidized layer removal step (10), the removal of the inner oxidized layer, subjected to intermediate annealing in the dry atmosphere consisting of 25% hydrogen and the rest being nitrogen (PH₂/O₂=0.05) in the intermediate heat-treatment step (13), and then reduced to the final sheet product of 0.35 mm thick in the secondary cold-rolling step (11) and annealed at 850°C for 4 minutes in the same dry atmosphere as was used in the above method in the final heat treatment step (12).

D (the present invention, or process IV, shown in FIG. 9(A)): The pickling subsequent to the decarburizing annealing of hot rolled coil was carried out in the same manner as mentioned above but with a pickling solution consisting of 2% hydrochloric acid, 5% hydrogen fluoride and the rest being water in the inner oxidized layer removal pickling step (3), to remove the annealing product and the inner oxidized layer. The so-treated sample was reduced to the intermediate sheet of 0.39 mm thick in the primary cold-rolling step (8), and subjected to intermediate annealing in the dry atmosphere consisting of 25% hydrogen and the rest being nitrogen (PH₂/O₂=0.025), in the intermediate heat-treatment step (13), and then reduced to the final sheet of 0.35 mm thick in the secondary cold-rolling step (11) and subjected to final annealing at 850°C, for 4 minutes in the same dry atmosphere as was used above in the final heat treatment step (12).

The samples obtained respectively by the above four methods were cut into Epstein test pieces, and the results of tests on these pieces are shown in Table 1.

<table>
<thead>
<tr>
<th>Number</th>
<th>Example method</th>
<th>Thickness of inner oxidized layer unremoved (mm)</th>
<th>Iron loss, watt/kg.</th>
<th>Magnetic flux density, kg.</th>
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<tbody>
<tr>
<td>1</td>
<td>(A) conventional</td>
<td>0.96  0.94  0.92</td>
<td>5.6  5.7  5.8</td>
<td>15.4  15.5  15.6</td>
</tr>
<tr>
<td></td>
<td>(B) present invention</td>
<td>1.05  1.08  1.02</td>
<td>5.6  5.7  5.8</td>
<td>15.4  16.4  16.5</td>
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<tr>
<td>2</td>
<td>(A) conventional</td>
<td>0.96  0.94  0.92</td>
<td>4.7  4.8  4.9</td>
<td>15.4  15.5  15.6</td>
</tr>
<tr>
<td></td>
<td>(B) present invention</td>
<td>1.05  1.08  1.02</td>
<td>4.7  4.8  4.9</td>
<td>15.4  16.4  16.5</td>
</tr>
<tr>
<td>3</td>
<td>(A) conventional</td>
<td>0.96  0.94  0.92</td>
<td>3.8  4.0  4.2</td>
<td>15.4  15.5  15.6</td>
</tr>
<tr>
<td></td>
<td>(B) present invention</td>
<td>1.05  1.08  1.02</td>
<td>3.8  4.0  4.2</td>
<td>15.4  16.4  16.5</td>
</tr>
</tbody>
</table>
The smoothness of the steel sheet obtained by the method of the present invention is excellent, therefore, its commercial value and the space factor are high.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit and scope of the claims.

What is claimed is:

1. A method of manufacturing a cold-rolled non-orient- ed electromagnetic steel sheet which has a greatly reduced iron loss when subjected to a high magnetic field, said steel sheet containing Si in an amount of 1.0–4.0% by weight, acid-soluble Al in an amount of 0.1–3.0% by weight and the rest being substantially iron, which comprises:
   (a) hot-rolling the steel material to form a steel sheet in an atmosphere of wet air having strong oxidizing properties,
   (b) annealing the steel sheet to decarburize it in an atmosphere having weak oxidizing properties,
   (c) cold-rolling the steel sheet in a wet atmosphere of strong oxidizing properties, such as steam having a partial pressure of steam formed during the heat-treating step to the partial pressure of hydrogen of less than 0.05 to avoid the re-forming of an inner oxidized layer,
   (d) removing the inner oxidized layer formed in the surface part of the steel sheet, which layer contains SiO₂, Al₂O₃ and oxides of iron to such an extent that it is present in an amount less than 1 μ in thickness,
   (e) cold-rolling the steel sheet, and
   (f) heat-treating the steel sheet in a non-oxidizing atmosphere which contains water and hydrogen in such amounts that the ratio of the partial pressure of steam formed during the heat-treating step to the partial pressure of hydrogen is less than 0.05 to avoid the re-forming of an inner oxidized layer.

2. The method according to claim 1, wherein the removal of said inner oxidized layer is carried out by pickling the steel sheet with a pickling solution consisting of hydrochloric acid 2%, nitric acid 3%, hydrogen fluoride 1% and the rest being water.

3. The method according to claim 1, wherein the removal of said inner oxidized layer is carried out by electrolytic pickling with a chemical pickling solution consisting of hydrogen peroxide 5%, hydrogen fluoride 2% and the rest being water.

4. The method according to claim 1, wherein the removal of said inner oxidized layer is carried out by pickling the steel sheet subsequent to the primary cold-rolling with a pickling solution made by adding 2% hydrogen fluoride to concentrated hydrochloric acid.

5. The method according to claim 1, wherein the removal of the inner oxidized layer is carried out by use of an electrolytic pickling method.

6. The method according to claim 1, wherein the removal of the inner oxidized layer is carried out by use of a sand-blasting method.

7. A method according to claim 1 wherein the steel sheet is pickled with a strong acid, capable of etching the iron in the steel sheet, to remove both the outer oxidized layer and the inner oxidized layer.

8. A process according to claim 1 wherein the inner oxidized layer is completely removed.

9. A cold-rolled non-oriented electromagnetic steel sheet of low iron loss at high magnetic field intensity consisting essentially of Si in an amount of 1.0–4.0% by weight and acid-soluble Al in an amount of 0.1–3.0% by weight, the rest being substantially iron, having an inner oxidized layer of less than 1 μ in thickness produced by the process of claim 1.

10. A method of manufacturing a cold-rolled, non-oriented electromagnetic steel sheet which has a greatly reduced iron loss when subjected to a high magnetic field, said steel sheet containing Si in an amount of 1.0–4.0% by weight, acid-soluble Al in an amount of 0.1–3.0% by weight and the rest being substantially iron, which comprises:
   (a) vacuum-degassing the steel material in the molten form to decarburize it,
   (b) hot-rolling the material to form a steel sheet in an atmosphere of wet air having strong oxidizing properties,
   (c) removing the inner oxidized layer formed in the surface part of the steel sheet, which layer contains SiO₂, Al₂O₃ and oxides of iron to such an extent that it is present in an amount less than 1 μ in thickness,
   (d) cold-rolling the steel sheet, and
   (e) heat-treating the steel sheet in a non-oxidizing atmosphere which contains water and hydrogen in such amounts that the ratio of the partial pressure of steam formed during the heat-treating step to the partial pressure of hydrogen is less than 0.05 to avoid the re-forming of an inner oxidized layer.

11. A process according to claim 10 wherein the inner oxidized layer is completely removed.

12. A method of manufacturing a cold-rolled, non-oriented electromagnetic steel sheet which has a greatly reduced iron loss when subjected to a high magnetic field, said steel sheet containing Si in an amount of 1.0–4.0% by weight, acid-soluble Al in an amount of 0.1–3.0% by weight and the rest being substantially iron, which comprises:
   (a) hot-rolling the steel to form a sheet in an atmosphere of wet air having strong oxidizing properties,
   (b) annealing the steel sheet to decarburize it in an atmosphere having weak oxidizing properties,
   (c) subjecting the steel sheet to a second cold-rolling step, and
   (d) removing the inner oxidized layer formed in the surface part of the steel sheet, which layer contains SiO₂, Al₂O₃ and oxides of iron to such an extent that it is present in an amount less than 1 μ in thickness,
   (e) subjecting the steel sheet to a second annealing step in an atmosphere having weak oxidizing properties,
   (f) subjecting the steel sheet to a second cold-rolling step, and
   (g) heat-treating the steel sheet in a non-oxidizing atmosphere which contains water and hydrogen in such amounts that the ratio of the partial pressure of steam formed during the heat-treating step to the partial pressure of hydrogen is less than 0.05 to avoid the re-forming of an inner oxidized layer.

13. The method according to claim 12, wherein said decarburization annealing and said second annealing are carried our simultaneously between the first cold-rolling step and said removal of the inner oxidized layer.

14. The method according to claim 12, wherein the removal of the inner oxidized layer is carried out between the decarburization annealing and said first cold-rolling step.

15. The method according to claim 12, wherein the secondary annealing step is carried out between the first cold-rolling and the removal of the inner oxidized layer.

16. A process according to claim 12 wherein the inner oxidized layer is completely removed.

17. A method of manufacturing a cold-rolled, non-oriented electromagnetic steel sheet which has a greatly reduced iron loss when subjected to a high magnetic field, said steel sheet containing Si in an amount of 1.0–4.0% by weight, acid-soluble Al in an amount of 0.1–3.0% by weight and the rest being substantially iron, which comprises:
   (a) vacuum-degassing the steel material in the molten state to decarburize it,
   (b) hot-rolling the steel to form a sheet in an atmosphere of wet air having strong oxidizing properties,
   (c) removing the inner oxidized layer formed in the surface part of the steel sheet, which layer contains SiO₂, Al₂O₃ and oxides of iron to such an extent that it is present in an amount less than about 1 μ in thickness, and oxide of iron,
(d) subjecting the steel sheet to a first cold-rolling step,
(e) subjecting the steel sheet to an annealing step in an atmosphere having weak oxidizing properties,
(f) subjecting the steel sheet to a second cold-rolling step, and
(g) heat-treating the steel sheet in a non-oxidizing atmosphere which contains water and hydrogen in such amounts that the ratio of the partial pressure of steam formed during the heat-treating step to the partial pressure of hydrogen is less than 0.05 to avoid the reforming of an inner oxidized layer.

18. The method according to claim 17, wherein the removal of the inner oxidized layer is carried out between the first cold-rolling and the annealing step (e).

19. The method according to claim 17, wherein the removal of the inner oxidized layer is carried out between said annealing step (e) and the second cold-rolling step.

20. A process according to claim 17 wherein the inner oxidized layer is completely removed.

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