



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.11.2023 Bulletin 2023/45

(21) Application number: **23171590.5**

(22) Date of filing: **04.05.2023**

(51) International Patent Classification (IPC):

C21D 8/12 (2006.01)	C21D 9/46 (2006.01)
C22C 38/02 (2006.01)	H01F 1/147 (2006.01)
H01F 1/16 (2006.01)	C23C 22/08 (2006.01)
C23C 22/74 (2006.01)	C21D 1/68 (2006.01)
H01F 1/18 (2006.01)	C22C 38/04 (2006.01)
C22C 38/06 (2006.01)	C22C 38/08 (2006.01)
C22C 38/10 (2006.01)	C22C 38/12 (2006.01)
C22C 38/14 (2006.01)	C22C 38/16 (2006.01)
C22C 38/18 (2006.01)	

(52) Cooperative Patent Classification (CPC):

C22C 38/02; C21D 1/68; C21D 8/1222;
C21D 8/1255; C21D 8/1272; C21D 8/1283;
C21D 9/46; H01F 1/14783; H01F 1/18;
C21D 8/1233; C21D 8/1294; C21D 9/663;
C21D 2201/05; C22C 38/04; C22C 38/06; (Cont.)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **04.05.2022 EP 22171629**

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(54) **METHOD FOR PRODUCING A GRAIN-ORIENTED ELECTRICAL STEEL STRIP AND GRAIN-ORIENTED ELECTRICAL STEEL STRIP**

(57) The invention relates to a method of producing a grain-oriented electrical steel strip, the method comprising: a) providing a hot strip having a composition comprising 2.0-4.0% by weight Si, 0.010-0.100% by weight C, up to 0.065% by weight Al, up to 0.02% by weight N, optionally up to 0.5% by weight Cu; optionally up to 0.060% by weight S; and optionally up to 0.3% by weight Cr, Mn, Ni, Mo, P, As, Sn, Sb, Se, Nb, Sr, Co, Zn, Y, Yt, Ti, Pb, Te, B or Bi, the balance being iron, and unavoidable impurities; b) optionally coiling and annealing the hot strip; c) cold rolling the hot strip to give a cold strip; d) decarburization annealing the cold strip, wherein this step optionally comprises a nitriding treatment and wherein a surface of the cold strip includes an oxide layer after the decarburization annealing; e) applying an annealing separator layer to the surface of the cold strip that includes the oxide layer, wherein the annealing separator comprises at least 50% by weight MgO based on the total dry weight of the annealing separator, 0.1 to

2.0% by weight chloride ions based on the total weight of MgO in the annealing separator and 4.5 to 45% by weight of SiO₂, preferably 10 to 20 %, based on the total weight of MgO in the annealing separator; f) high-temperature annealing the cold strip coated with the annealing separator layer at a temperature of 1000°C to 1250°C to form a forsterite layer on the surface of the calcined cold strip; g) optionally applying an insulation layer to the surface of the cold strip having the forsterite layer; and h) annealing the cold strip. The invention further relates to a grain-oriented electrical steel strip comprising a forsterite layer disposed on a cold-rolled steel substrate comprised of a steel comprising: 2.0-4.0% by weight Si, up to 0.005% by weight C, up to 0.065% by weight Al, up to 0.020% by weight N, optionally up to 0.5% by weight Cu; optionally up to 0.060% by weight S; and optionally up to 0.3% by weight Cr, Mn, Ni, Mo, P, As, Sn, Sb, Se, Nb, Sr, Co, Zn, Y, Yt, Ti, Pb, Te, B or Bi, the balance being iron, and unavoidable impurities, wherein the for-

sterite layer has a thickness of 0.1 to 0.5 μm and the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels is < 15%.

(52) Cooperative Patent Classification (CPC): (Cont.)

C22C 38/08; C22C 38/10; C22C 38/12;

C22C 38/14; C22C 38/16; C22C 38/18

Description

[0001] The invention relates to a method of producing a grain-oriented electrical steel strip and to a grain-oriented electrical steel strip.

[0002] When the present application refers to "electrical steel strips", this means electrical steel sheets and electrical steel strips produced by rolling steels of suitable composition, and circuit boards or blanks that have been divided therefrom, which are intended for the production of parts for electrical engineering applications.

[0003] Grain-oriented electrical steel strips are especially suitable for uses in which the emphasis is on a particularly low cyclic magnetization loss and high demands are made on permeability or polarization. Such demands exist especially in the case of parts for power transformers, distribution transformers and higher-quality small transformers.

[0004] As elucidated specifically, for example, in EP 1025 268 B1, in the course of the production of electrical steel strips, generally a steel comprising (in % by weight) typically 2.5% to 4.0% Si, 0.010% to 0.100% C, up to 0.150% Mn, up to 0.065% Al and up to 0.0150% N, and in each case optionally 0.010% to 0.3% Cu, to 0.060% S, to 0.100% P, and to in each case 0.2% As, Sn, Sb, Te and Bi, the balance being iron and unavoidable impurities, is first cast to give a preliminary material, such as a slab, thin slab or a cast strip. The preliminary material is then, if required, subjected to an annealing treatment and then hot-rolled to give a hot strip.

[0005] The resultant hot strip is coiled to give a coil and can then, if required, be subjected to annealing and to a likewise optionally executed descaling or pickling treatment.

[0006] Then a cold strip is rolled from the hot strip in one or more stages, with performance of intermediate annealing if required between the cold rolling steps in a multistage cold rolling Operation effected in multiple steps.

[0007] The resultant cold strip then typically undergoes a decarburization anneal, in order to minimize the carbon content of the cold strip for avoidance of magnetic aging. After the decarburization anneal, an annealing separator is applied to the strip surfaces, which typically comprises MgO. The annealing separator prevents the windings of a coil wound from the cold strip from being welded to one another in a subsequently conducted high-temperature anneal.

[0008] During the high-temperature anneal, which is typically conducted in a bell furnace under protective gas, a microstructure texture that makes a significant contribution to the magnetic properties forms in the cold strip as a result of selective grain growth. At the same time, a forsterite layer forms on the strip surfaces during the high-temperature anneal, often also referred to in the technical literature as "glass film". In addition, the steel material is cleaned by diffusion processes that proceed during the high-temperature anneal.

[0009] Subsequent to the high-temperature anneal, the flat steel product having the forsterite layer which is obtained in this way is coated with an insulation layer, thermally aligned and subjected to stress-relief annealing in a concluding "final anneal". This final anneal can be effected before or after the finishing of the flat steel product produced in the manner described above to give the blanks required for further processing. By means of a final anneal which is conducted after the blanks have been divided off, the additional stresses that have arisen in the course of the dividing Operation can be dissipated. Electrical steel strips produced in such a way generally have a thickness of 0.15 mm to 0.5 mm.

[0010] As further elucidated in WO 03/000951 A1, it is likewise prior art that the domain structure can additionally be improved by the application of an insulation layer which exerts a permanent tensile stress on the sheet substrate, and additionally also that by a treatment in which lines of local stresses are generated transverse or oblique to the rolling direction in the flat steel product, the magnetic properties of grain-oriented electrical steel strips can be further improved. Surface structures of this kind can be generated, for example, by local mechanical deformations (EP 0 409 389 A2), laser or electron beam treatments (EP 0 008 385 B1; EP 0 100 638 B1; EP 0 571 705 A2) or etching of trenches (EP 0 539 236 B1).

[0011] For example, it is additionally known from EP 0 225 619 B1 that the forsterite layer also has an important influence on essential use properties of electrical steel strips. The losses, the noise characteristics in the transformer or else the bond strength of the insulation are affected by the forsterite layer between the magnetically active base material and the insulation layer.

[0012] The forsterite layer in low loss high performance grain-oriented electrical steel (GOES) is usually optimized for the use in transformers. To ensure electrical resistance the density of the forsterite layer is controlled, the tensile stress that the forsterite layer exerts on the base material is optimized to minimize magnetostrictive effects on transformer noise, and the adhesion of the forsterite layer to the base material is controlled to inhibit removal of surface layers during mechanical treatment of the GOES such as stamping of parts from a GOES sheet.

[0013] For some applications of grain-oriented electrical steel, such as for use in stator and rotor teeth for axial flux motors, the insulation properties as well as the magnetostriction properties of the GOES are not of primary importance. In these applications, stacks of the GOES sheets are laminated together via a backlack type resin, which results in an overall higher importance of the adherence properties of the forsterite layer to the base material for these GOES sheets compared to GOES sheets used in transformer applications.

[0014] EP 3 653 754 A1 suggests that the adherence of the forsterite layer could be influenced by the adherence of SiO₄ tetrahedrons not sharing oxygen with Mg but building local SiO₂ structures. In addition, during the formation of the

forsterite layer de- and re-nitriding phenomena appear to play an important role in particular regarding the formation, dissolution and transformation of the so-called inhibitor particles or Goss particles that dominate the final magnetic properties of the GOES. In this regard EP 3 048 180 B2 suggest to use TiO₂ in addition to MgO to control the de-nitriding. EP 2 623 621 B1 suggests a penetration of the oxide composition during forsterite formation by nitrogen.

[0015] Apart from a good adherence of the forsterite layer for these types of applications a major issue is that stamping of backlax laminated stacks of GOES results in extremely high tool wear. While for small transformers stamping of GOES is already linked to a high tool wear, but the tool wear can be improved by the use of stamping oils, the stamping of backlax laminated stacks of GOES cannot be carried out with the aid of a stamping oil, as the backlax resin decomposes in the presence of the stamping oil.

[0016] To solve this issue several prior art documents such as EP 0 607 440 B1, EP 0 565 029 B1 or EP 3 760 758 A1 suggest the creation of forsterite layer free materials. These teachings have in common that the removal of the forsterite layer is carried out after its formation during high temperature annealing using additional process steps such as pickling and chemical polishing that entail the risk of nonuniform removal.

[0017] EP 3 533 885 A1 and EP 2 322 674 B1 suggest to add zirconia ceramic fine powder, alumina fine powder, silicon dioxide fine powder or calcium compounds to the annealing separator before final annealing, whereby no glass layer or a monticellite layer is formed. The formation of monticellite is, however, similar disadvantageous with regard to the tool wear as the formation of the forsterite layer. In addition, the use of additives such as zirconia fine powder is uneconomical. In cases where the formation of a glass layer (forsterite layer) is completely suppressed during high temperature annealing the problem exists that no secondary recrystallization, i.e. no selected grain growth of so called Goss grains, takes place during high temperature annealing, which results in unusable magnetic properties of the resulting grain-oriented electrical steel.

[0018] Against the background of the aforementioned prior art, the problem to be solved by the present invention can be seen in the provision of a simple and cost-efficient method of producing grain-oriented electrical steel strips, especially for use in stator and rotor teeth for axial flux motors, with improved stampability, good adherence properties and good magnetic properties.

[0019] The invention has solved this problem by following the procedure of the method specified in claim 1 in the production of grain-oriented electrical steel strips.

[0020] Advantageous embodiments of the invention are specified in the dependent claims and are elucidated specifically hereinafter, as is the general concept of the invention. According to the invention, in the production of grain-oriented electrical steel strips, the steps that are typically envisaged for this purpose in the prior art are implemented. These include

a) providing a hot strip having the composition (in % by weight) of 2.0-4.0% Si, preferably 2.7 -3.7% Si, 0.010-0.100% C, preferably 0.020 to 0.080% C, up to 0.065% Al, preferably up to 0.055% Al, and up to 0.020% N, and in each case optionally up to 0.5% Cu, up to 0.060% S and likewise optionally in each case up to 0.3% Cr, Mn, Ni, Mo, P, As, Sn, Sb, Se, Te, B, Nb, Sr, Co, Zn, Y, Yt, Ti, Pb or Bi, the balance being iron and, preferably up to 0.350%, unavoidable impurities;

b) optionally coiling and annealing the hot strip;

c) cold rolling the hot strip in one or more cold rolling steps to give a cold strip;

d) decarburization annealing of the cold strip, wherein this step optionally comprises a nitriding treatment and wherein the cold strip after the decarburization anneal has an oxide layer on its surface;

e) applying an annealing separator layer to the surface of the cold strip having the oxide layer;

f) high-temperature annealing of the cold strip coated with the annealing separator to form a forsterite layer on the surface of the annealed cold strip;

g) optionally applying an insulation layer to the surface of the cold strip having the forsterite layer;

h) finally annealing the cold strip;

i) optionally laser-treating the cold strip.

[0021] It will be apparent that the method of the invention may comprise further steps, which are conducted in the conventional production of electrical steel strips in order to achieve optimized magnetic properties or properties that are important for practical use. These include, for example, smelting a steel melt having the composition described above, casting the steel melt to give a preliminary material, such as a slab, thin slab or cast strip, hot rolling the preliminary material to give a hot strip, reheating of the preliminary material obtained after the casting of the steel, descaling of the hot strip prior to the cold rolling or, in the case of the multistage performance of cold rolling, intermediate annealing conducted in a conventional manner between the cold rolling stages in each case.

[0022] Crucial factors here in achieving optimal effect in terms of the adherence properties of the electrical strip to be produced and its improved stampability are, in accordance with the invention, the application of an annealing separator layer to the surface of the cold strip that includes the oxide layer, wherein the annealing separator comprises MgO, 0.1 to 2.0% by weight chloride ions and 4.5 to 45% by weight SiO₂ based on the total weight of MgO in the annealing separator.

[0023] The invention proceeds here from the finding that the addition of 0.1 to 2.0% by weight of chloride ions based on the total weight of MgO to an annealing separator comprising MgO leads to the formation of a very thin low porous forsterite layer, in particular, a forsterite layer having a thickness between 0.1 and 0.5 μm , excellent adherence properties as well as good magnetic properties, during high-temperature annealing of the cold strip coated with the annealing separator. The low thickness of the forsterite layer results in a markedly improved stampability of the grain-oriented electrical steel sheet, which leads to less tool wear, while at the same time the adhesion of the thin forsterite layer is excellent and the magnetic properties remain unaffected compared to the state of the art product. The addition of 4.5 to 45% by weight SiO_2 as part of the annealing separator allows limiting the amount of channel like structures in the forsterite layer, which may otherwise have a negative impact on the final adhesion and magnetic properties of the forsterite layer. These channel-like structures may result during de-nitriding due to the fact that nitrogen has to pass through the SiO_2 layer, which is present on the steel surface. In other words, it was surprisingly found that the addition of SiO_2 to the annealing separator leads to an additional improvement in the adhesion and magnetic properties of the forsterite layer.

[0024] A "forsterite layer" as used herein is a layer, which comprises predominantly forsterite but may additionally comprise other magnesium silicates such as, e.g., magnesium pyroxenes or olivines.

[0025] If the amount of chloride ions in the annealing separator is below 0.1% by weight of based on the total weight of MgO in the annealing separator, the thickness of the forsterite layer will become higher than 0.5 μm and the stampability will become poor. In case the amount of chloride ions in the annealing separator exceeds 2% by weight based on the total weight of MgO in the annealing separator the forsterite layer will become highly porous, which will lead to insufficient adherence properties as well as to insufficient magnetic properties of the resulting grain-oriented electrical steel strips. Therefore, according to the invention the annealing separator comprises MgO and 0.1 to 2.0% by weight, preferably 0.2 to 1.8 % by weight, of chloride ions based on the total weight of MgO.

[0026] Suitable annealing separators for the purposes of the invention are especially those annealing separators, which comprise at least 50% by weight, preferably at least 60% by weight, of MgO based on the total dry weight of the annealing separator.

[0027] The source of the chloride ions used in the annealing separator for the purpose of the invention can be selected from known chlorides. Suitable chlorides are for example NaCl , CaCl_2 , BaCl_2 , ZnCl_2 , NH_4Cl , MgCl_2 , SbCl_3 or mixtures thereof. According to a preferred embodiment of the invention, the source of the chloride ions is selected from NH_4Cl , MgCl_2 , SbCl_3 or mixtures thereof.

[0028] According to the invention, the annealing separator comprises 4.5 to 45% by weight, preferably 5 to 20% by weight, of SiO_2 based on the total weight of the MgO in the annealing separator.

[0029] According to a preferred embodiment of the invention, the annealing separator is free of TiO_2 . "Free of TiO_2 " as used herein means that no TiO_2 is purposefully added to the annealing separator. According to the prior art TiO_2 is usually added to control the de-nitriding during the formation of the forsterite layer and avoid the formation of voids/channels in the forsterite layer by binding nitrogen evaporating from the steel during the high temperature annealing. However, in the present invention it was surprisingly found that by keeping the annealing separator free of TiO_2 the thickness of the resulting forsterite layer could be reduced even further, leading to a further improved stampability of the final grain-oriented electrical steel sheet.

[0030] The application of the annealing separator in the method of the invention (step e)) is carried out in a manner, which is known to the skilled person. Typically, the annealing separator is applied to the surface of the cold strip that includes the oxide layer as a homogeneous dispersion in water, whereby the dispersion comprises about 2 to 6 parts by weight of water based on 1 part by weight of MgO in the annealing separator.

[0031] In a practical implementation of the method of the invention, the hot strip is optionally subjected to a hot strip anneal (step b)) in a manner which is known, in order to ensure optimal cold rollability. A possible method for hot strip anneal is described in EP 0 539 858 A1 by Nippon Steel. This includes one- or stage-annealing where the maximum soaking temperature of the first stage is between 950 and 1150 $^{\circ}\text{C}$ and the second stage maximum temperature is between 750 and 1050 $^{\circ}\text{C}$. In case of one-stage anneal, the maximum temperature is set from 950 to 1150 $^{\circ}\text{C}$. In any case, the soaking is set to at least 15 sec and up to 180 sec and the strip is afterwards cooled to room temperature at a rate of at least 10 K/s.

[0032] Typically, in the method of the invention, the cold rolling (step c)) is conducted in at least three cold rolling steps, optionally with an intermediate anneal between the cold rolling steps, in a manner known per se. The at least three subsequent cold rolling steps lead to the elimination of cold solidifications that arise in each preceding cold rolling step and ensure rollability for the subsequent rolling step. The conditions used for the intermediate annealing may correspond to the conditions used in the hot strip anneal in step b). Installations with which such intermediate annealing can be performed are generally known and disclosed, for example, in WO 2007/014868 A1 and WO 99/19521 A1.

[0033] The decarburization anneal (step d)), in which the carbon content of the steel substrate is minimized, can be combined with a nitriding treatment, which is likewise optionally conducted in a manner known per se, which has the aim of increasing the nitrogen content of the steel substrate. The decarburization annealing is preferably carried out at

temperatures in the range of 400 to 950 °C, e.g. 600 to 900 °C. The duration of the decarburization annealing is at least 45 s, preferably 75 to 135 s. The decarburization anneal is preferably performed using an atmosphere with a dew point between 40 and 80°C, preferably between 40 and 65°C. If a nitriding treatment is to be performed the annealing can be carried out under an atmosphere which comprises N₂ or N-comprising compounds, for example NH₃. Annealing and nitriding can be conducted in two separate steps one after the other with the annealing being performed at first. As an alternative simultaneously annealing and nitriding can be performed. If nitriding is performed in working step d) the conditions of the nitriding treatment should be adjusted such that a nitriding degree of up to 300 ppm, preferably 20 to 250 ppm, is achieved. The nitriding degree is calculated as the difference between the nitrogen content of the steel strip before the high temperature annealing (step f)) minus the nitrogen content before the decarburization annealing (step d)). The nitrogen content can be determined by usual means, such as with the 736 analyzer offered by Leco Corporation, St. Joseph, USA.

[0034] In principle, it is conceivable to execute the high temperature anneal in a continuous run. However, a particularly advantageous high-temperature annealing method in relation to the desired optimization of the magnetic properties and the practical utility of electrical steel strips produced in accordance with the invention has been found to be a high-temperature anneal (step f)) conducted in the form of a bell anneal. The temperatures for the high-temperature anneal are in the temperature range of 1000-1250°C known per se for this purpose. Preferably the temperature range used in the high-temperature anneal is more than 1150° C to 1250°C. The high temperature anneal is preferably carried out under a protective gas atmosphere, which, for example, comprises H₂. Particularly preferably, the high temperature anneal at the respective annealing temperature is performed under an atmosphere which comprises 5 to 95 Vol.-% H₂, the remainder being nitrogen or any inert gas or a mix gas, the dew point of the atmosphere being at least 10 °C. The soaking time, during which the high temperature soaking is carried out in this way, can be determined in a common manner, which is well known to the expert. By the high annealing performed in this way atoms of elements are removed, which would deteriorate the properties of the grain-oriented steel sheet. These elements are in particular N and S. Preferably the high temperature anneal is carried out for 10 to 200 hours.

[0035] On the surface of the cold strip having the forsterite layer, which is obtained by the high temperature anneal (step f)) an insulation layer may be optionally applied (step g)). Suitable insulation layers are known to the skilled person.

[0036] According to the method of the invention the cold strip is finally annealed in a manner known to the skilled person in order to remove residual mechanical stresses in the steel (step h)). In practice, the final annealing is preferably carried out at temperatures of over 700°C, more preferably more than 800°C, and less than 950°C. The use of a continuous annealing line has proven to be particularly effective.

As an optional measure in the method of the invention the cold-strip can be laser treated (step i)). The laser treatment causes a thermal shock in the steel, which results in refinement of the magnetic domains therein.

[0037] In accordance with the above elucidations, a grain-oriented electrical steel strip of the invention comprises a cold-rolled steel substrate consisting of a steel comprising (in percent by weight) 2.0-4.0% Si, preferably 2.7 -3.7% Si, up to 0.005% C, preferably up to 0.002% C, up to 0.065% Al, preferably up to 0.055% Al, and up to 0.020% N, preferably up to 0.010% N, and in each case optionally up to 0.5% Cu, up to 0.060% S, preferably 0.030% S, and likewise optionally in each case up to 0.3% Cr, Mn, Ni, Mo, P, As, Sn, Sb, Se, Te, B, Nb, Sr, Co, Zn, Y, Yt, Ti, Pb or Bi, the balance being iron and, preferably up to 0.350%, unavoidable impurities, wherein a forsterite layer present on said steel substrate has a thickness of 0.1 to 0.5 µm and the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels is < 15%.

[0038] The composition of the final grain-oriented electrical steep strip differs from the composition of the hot-strip provided in the method of the invention in that it contains a significantly lower carbon content due to decarburization. In addition, the nitrogen and sulfur content may be lower.

[0039] The carbon content of the electrical steel strip having the characteristics of the invention is typically up to 0.005% C, preferably up to 0.002% C, as a result of the process steps implemented in the course of its production, especially as a result of the decarburization anneal.

[0040] An electrical steel strip of this kind can especially be produced by employing the method of the invention.

[0041] The thickness of the forsterite layer can be determined using a cross-sectional reflection electron micrograph. It has been found that a forsterite layer having a thickness between 0.1 and 0.5 µm allows for an optimal balance between improved stampability and good magnetic properties of the grain-oriented electrical steel sheet, that makes the GOES sheet especially suitable for use for use in stator and rotor teeth for axial flux motors.

[0042] The area of the channels in the forsterite layer and the total area of the forsterite layer including the channels, i.e. voids, respectively, is determined using a cross-sectional reflection electron micrograph over a width of at least 200 µm and over the entire thickness of the forsterite layer and from these areas the percentage of the area of the channels, i.e. voids, in the forsterite layer to the total area of the forsterite layer including the channels, i.e. voids, is calculated. As mentioned above, channel like structures may result during de-nitriding due to the fact that nitrogen has to pass through the SiO₂ layer, which is present on the steel surface. These channel-like structures while usually contacting the steel

surface with the surface of the forsterite layer are not exclusively oriented perpendicular to the steel surface but may also run partially horizontally to the steel surface or diagonally within the forsterite layer. Therefore, these channel-like structures are visible as voids in the cross-sectional reflection electron micrograph. Therefore, the terms "channels" "channel-like structures" and "voids" are used interchangeably in the context of the present invention.

[0043] A percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the channels of < 15% results in excellent adhesion of the thin forsterite layer to the steel substrate, which is especially important if the material is to be used in stator and rotor teeth for axial flux motors, as in such a case the material is subsequently coated and laminated together with a backlack type resin, so that the interlayer adhesion between the single GOES sheets in the whole laminated stack of GOES sheets becomes strong. In contrast, a percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the channels of $\geq 15\%$ is detrimental, as the adhesion of the thin forsterite layer to the steel substrate becomes insufficient resulting in predetermined breaking points within the laminated stack of GOES sheets at each interface of the steel substrate to the thin forsterite layer.

[0044] The invention is elucidated in detail hereinafter by working examples and by Figure 1.

Figure 1 Schematic representation of a cross-sectional reflection electron micrograph of a grain-oriented electrical steel sheet comprising a forsterite layer

[0045] Figure 1 shows a schematic representation of a cross-sectional reflection electron micrograph of a grain-oriented electrical steel sheet 1 comprising a steel substrate 2 and a forsterite layer 3 formed thereon. The forsterite layer contains channel-like structures 4, which are either visible as channels 4 or voids 4 depending on their spatial orientation within the forsterite layer. When determining the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels, the area of the channels 4 in the cross-sectional reflection electron micrograph is determined and the area of the forsterite layer 3 including the area of the channels 4 in the cross-sectional reflection electron micrograph is determined, i.e. the total area of the forsterite layer including the area of the channels, which corresponds to the sum of the area of the forsterite layer 3 and the area of the channels 4 in the forsterite layer is determined. The determination of the respective areas is carried out over a width of at least 200 μm and over the entire thickness of the forsterite layer. The percentage is calculated by dividing the determined area of the channels in the forsterite layer by the determined total area of the forsterite layer including the area of the channels, i.e. by the sum of the area of the forsterite layer 3 and the area of the channels 4 in the forsterite layer and multiplying the result with 100. In other words, the total area of the forsterite layer including the area of the channels 4 is defined as being 100% and the respective percentage of the area of the channels 4 in the forsterite layer is determined using the rule of three.

Examples

[0046] A steel comprising (in % by weight) 3.5% Si, 0.075% C, 0.12% Mn, 0.05% Al, 0.009% N, 0.05% Cu, 0.011% S, 0.03% P, the balance being iron was first cast to give a thin slab. The thin slab was then subjected to an annealing treatment and then hot-rolled to give a hot strip.

[0047] The resultant hot strip was coiled to give a coil and then was subjected to annealing, descaling and pickling treatment. Thereafter a cold strip having a thickness of 0.167 mm was produced from the hot strip by cold-rolling in five stages.

[0048] The resulting cold strip underwent a decarburization anneal at 850°C under an oxidizing atmosphere with a dew point of 60 °C for 80 s. Directly after decarburization a nitriding treatment was carried out under a dry atmosphere and adding NH_3 to the atmosphere resulting in a nitriding degree of 150 ppm. After that, different annealing separator dispersions, which were comprised of the ingredients listed in Table 1, were applied one after the other along the length of the strip surface.

[0049] The material was then annealed in a bell furnace at 1200°C for 24 h at peak temperature. After this annealing residual powders, e.g., not adhering forsterite and other products, were removed using a smooth brush and water. The carbon content in the steel of the finished grain-oriented steel strip is below 0.003% by weight.

[0050] A metallographic cross section of the samples was performed and the thickness of the forsterite layer and the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels was determined using a cross-sectional reflection electron micrograph over a width of at least 200 μm and over the entire thickness of the forsterite layer. The results are documented in Table 1.

[0051] It can be seen that the prior art process (Example 1) leads to a dense and thick forsterite layer as is usually aimed for in a standard grain-oriented electrical steel product for use in transformers. The stampability of GOES with such a dense and thick forsterite layer is inferior compared to the inventive GOES due to a higher tool wear.

[0052] It can further be seen from the results in Table 1 that the addition of chloride ions to the annealing separator leads to a thin low porous forsterite layer. GOES with such a thin low porous forsterite layer show improved stampability

compared to prior art GOES with dense and thick forsterite layers. It is believed, that the addition of chlorine containing compounds results in a decomposition of the oxide layers present on the surface of the steel substrate and the oxides formed during the decarburization annealing treatment. The presence of chlorine containing compounds in the annealing separator therefore appears to hinder a reaction of the magnesia present in the annealing separator with the oxides present on the steel surface and therefore prevent the formation of a thick and dense forsterite layer during the high temperature annealing.

[0053] However, the results in Table 1, especially Examples 9 and 16, also show that in case the chlorine ion concentration exceeds 2% by weight, the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels increases to values far above 15% and may even no longer be determinable due to the high porosity of the resulting thin forsterite layer. GOES with such highly porous thin forsterite layers, while showing improved stampability, have the drawback that the adhesion of the forsterite layer to the steel substrate is weak, which makes such GOES not suitable for use in backlack laminated GOES stacks, as the low adherence of the forsterite layer to the steel substrate results in predetermined breaking points within the laminated stack of GOES sheets at each interface of the steel substrate to the thin highly porous forsterite layer. In addition, the formation of a very thin layer of below 0.1 μm as in Example 16 results in insufficient magnetic properties as insufficient secondary recrystallization, i.e. insufficient selected grain growth of so called Goss grains, takes place during high temperature annealing.

[0054] The results in Table 1 further show that the addition of SiO_2 to the annealing separator results in a decrease of the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels (cf. Comparison of Examples 2 and 3). It is believed that the addition of SiO_2 to the annealing separator leads to a reaction of the magnesia with the SiO_2 and furthermore avoids the diffusion of Mg into the steel substrate. This results in the formation of a thin forsterite layer with reduced porosity despite the previous decomposition of the oxides present on the steel surface by the addition of a chlorine containing compound.

[0055] A comparison of Examples 2 and 18 shows that the omission of TiO_2 in the annealing separator in accordance with the method of the invention results in a thinner forsterite layer, thereby leading to an improved stampability of the final grain-oriented electrical steel sheet.

Table 1:

Example	MgO	TiO ₂	Colloidal silica (30% in water)	SiO ₂ particles	NH ₄ Cl	MgCl ₂	SbCl ₃	Film thickness (μ m)	Percentage channels/ forsterite layer (%)	Type
1	100	5				0.02		2.1	0	COMP
2	100		40		1.00			0.3	4	INV
3	100		150		1.00			0.2	1	INV
4	100		150			0.70		0.3	3	INV
5	100			12	1.00			0.3	2	INV
6	100	5		12				1.3	18	COMP
7	100		150			0.30		0.4	6	INV
8	100		50				2.50	0.3	4	INV
9	100		50				7.00	0.1	50	COMP
10	100			45	0.50			0.1	12	INV
11	100		120				0.12	0.4	0	INV
12	100		200			1.20		0.2	25	COMP
13	100			25			0.70	0.3	3	INV
14	100		15		0.20			0.5	8	INV
15	100			45		2.10		0.1	7	INV
16	100					2.10		< 0.1	not determinable	COMP
17	100					0.02		2.0	15	COMP
18	100	5	40		1.00			0.8	7	COMP
COMP: Comparative; INV: Inventive; all values in parts by weight if not otherwise designated										

Claims

1. A method of producing a grain-oriented electrical steel strip, the method comprising:

a) providing a hot strip having a composition comprising

2.0-4.0% by weight Si,
0.010-0.100% by weight C,
up to 0.065% by weight Al,
up to 0.02% by weight N,

optionally up to 0.5% by weight Cu;

optionally up to 0.060% by weight S; and

optionally up to 0.3% by weight Cr, Mn, Ni, Mo, P, As, Sn, Sb, Se, Nb, Sr, Co, Zn, Y, Yt, Ti, Pb, Te, B or Bi,
the balance being iron, and unavoidable impurities;

b) optionally coiling and annealing the hot strip;

c) cold rolling the hot strip to give a cold strip;

d) decarburization annealing the cold strip, wherein this step optionally comprises a nitriding treatment and wherein a surface of the cold strip includes an oxide layer after the decarburization annealing;

e) applying an annealing separator layer to the surface of the cold strip that includes the oxide layer, wherein the annealing separator comprises at least 50% by weight MgO based on the total dry weight of the annealing separator, 0.1 to 2.0% by weight chloride ions based on the total weight of MgO in the annealing separator and 4.5 to 45% by weight of SiO₂ based on the total weight of MgO in the annealing separator;

f) high-temperature annealing the cold strip coated with the annealing separator layer at a temperature of 1000°C to 1250°C to form a forsterite layer on the surface of the calcined cold strip;

g) optionally applying an insulation layer to the surface of the cold strip having the forsterite layer; and

h) annealing the cold strip.

2. The method of any one of the preceding claims, wherein the annealing separator applied in step e) is free of TiO₂.

3. The method of any one of the preceding claims, wherein the decarburization annealing comprises a nitriding treatment.

4. The method of any one of the preceding claims comprising laser-treating the cold strip after the cold strip is annealed in step h).

5. The method of any one of the preceding claims, wherein the cold rolling of the hot strip to give the cold strip in step c) is performed in at least three cold rolling steps.

6. The method of any one of the preceding claims comprising annealing the hot strip after coiling of the hot strip.

7. The method of any one of the preceding claims, wherein the high-temperature annealing in step f) is a bell anneal.

8. The method of claim 7, wherein the temperature in the high-temperature annealing in step f) is more than 1150°C to 1250°C.

9. A grain-oriented electrical steel strip comprising a forsterite layer disposed on a cold-rolled steel substrate consisting of a steel comprising:

2.0-4.0% by weight Si,
up to 0.005% C by weight C,
up to 0.065% by weight Al,
up to 0.020% by weight N,

optionally up to 0.5% by weight Cu;

optionally up to 0.060% by weight S; and

optionally up to 0.3% by weight Cr, Mn, Ni, Mo, P, As, Sn, Sb, Se, Nb, Sr, Co, Zn, Y, Yt, Ti, Pb, Te, B or Bi
the balance being iron, and unavoidable impurities,

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wherein the forsterite layer has a thickness of 0.1 to 0.5 μm and the percentage of the area of the channels in the forsterite layer to the total area of the forsterite layer including the area of the channels is $< 15\%$.

5 **10.** The grain-oriented electrical steel strip of any one of the preceding claims comprising a carbon content of up to 0.002% by weight.

11. The grain-oriented electrical steel strip of claim 9 or 10 produced by the method of any one of claims 1 to 8.

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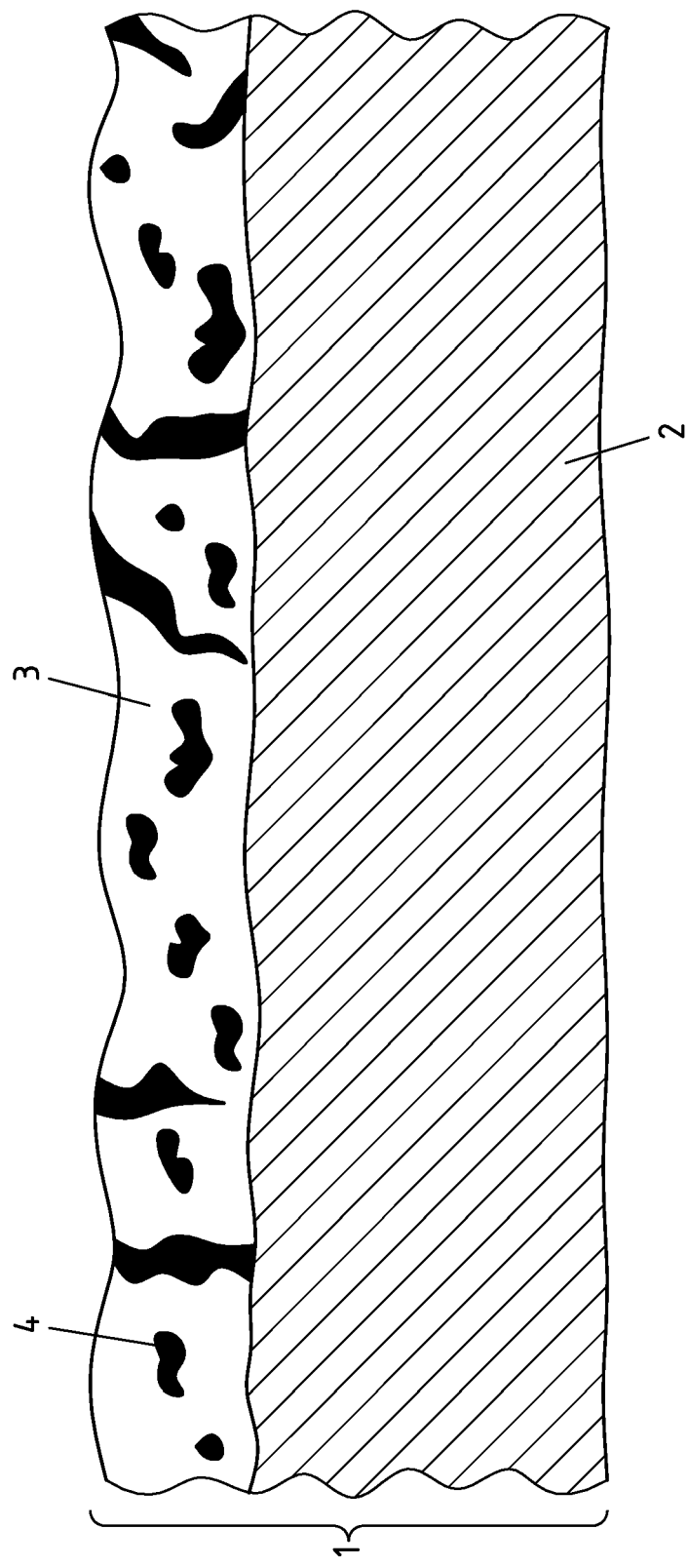


Fig.1



EUROPEAN SEARCH REPORT

Application Number

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A	EP 3 913 097 A1 (NIPPON STEEL CORP [JP]) 24 November 2021 (2021-11-24) * abstract * * claim 1 * * claim 5 * * table 9 * * table 10 * * table 11 * * paragraph [0236] - paragraph [0243] *	1-11	TECHNICAL FIELDS SEARCHED (IPC) C21D C22C H01F C23C
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Place of search The Hague		Date of completion of the search 23 August 2023	Examiner Vermeulen, Yves
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 23 August 2023	Examiner Vermeulen, Yves
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