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(54) LEAN METHOD FOR SECONDARY RECRYSTALLIZATION OF GRAIN ORIENTED ELECTRICAL STEEL IN A CONTINUOUS PROCESSING LINE

(57) The present invention relates to a process for the production of grain-oriented electrical steel sheet, to a grain-oriented steel strip prepared by the process and to its use in electric transformers, in electric motors or in electric devices, preferably where magnetic flux has to be channeled or contained.

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Description

[0001] The present invention relates to a process for the production of grain-oriented electrical steel, to a grain-oriented steel strip prepared by the process, to a grain-oriented steel strip having a Peak Magnetic Polarization for the peak magnetic field strength of 800 A/m at 50 Hz of 1.85 to 1.98 T, and to the use in electric transformers, in electric motors or in electric devices, preferably where magnetic flux has to be channeled or contained.

[0002] Grain Oriented Electrical Steel (GOES) is a soft magnetic material preferably containing high silicon content providing high permeability to the magnetic field, easily magnetizing and demagnetizing. For example, GOES is the steel sheet used for manufacturing electric transformer cores with a minimum specific loss and a high achievable working induction, for example up to 1.85 T for a wide range of thicknesses like 0.23 to 0.35 mm.

[0003] According to Wuppermann et al., Electrical Steel, Stahl-Informations-Zentrum, Düsseldorf, Ed. 2005, pages 5 and 6, the iron crystal axis is an axis of easy magnetization of the body-centered cubic iron crystal. This axis, oriented closely to the rolling direction, gives excellent magnetic properties to the GOES in this direction of the steel strip. These are the orientation grains called "Goss grains" which provide a strongly anisotropic behaviour and reduce the power loss. The Goss texture makes it very difficult to orient the magnetic moments out of the plane of the sheet and in the direction perpendicular to the direction of rolling.

[0004] According to N. Chen et al., Acta Materialia 51 (2003), pages 1755 to 1765 and K. Günther et al., Journal of Magnetism and Magnetic Materials 320 (2008), 2411 to 2422 the manufacturing of GOES is in general performed according to different technologies across the world. To achieve the highly oriented Goss texture, the metallurgical process is highly complex and may consist in the following manufacturing steps: steel melting via a blast furnace and basic oxygen converter or an electric arc furnace, steel metallurgy refining via a vacuum degassing vessel, casting to slab via continuous casting or thin slab or thin strip, slab reheating or direct slab rolling on a hot rolling mill to get a hot rolled coil, coil surface preparation, hot strip annealing and pickling, cold rolling in one or two stages down to a final thickness, decarburization annealing and optionally a surface nitridation, providing a MgO coating of the strip surface, high temperature box annealing where the cold rolled decarburized coils are stacked, heat flattening and insulation coating and optionally a magnetic domain refinement.

[0005] According to the so called "High Heating" technology, the casting and the high temperature slab reheating conditions to about 1400 °C make it possible to have a well-developed inhibition system comprising particles of AlN, MnS and other compounds in the iron matrix, even before the cold process, which promotes abnormal grain growth. However, in low heating technology, with the low temperature in the slab heating process, the inhibition system is absent or weak, therefore low heating technology requires a nitridation treatment of the strip surface after the decarburization annealing stage to build a required inhibition system.

[0006] Therefore, the primary recrystallization (PRX), occurring during this decarburization anneal will control and prepare the secondary grain growth. However, due to the large number of metallurgical phenomena competing during this stage like carbon removal, formation of the oxide layer, primary grain growth, this process is unstable but fundamental for obtaining an efficient nitridation, a high-quality glass film, and many Goss germs in the matrix. Indeed it is known that a dense oxide layer, produced during the beginning of annealing, can be favorable to a good surface aspect, but may become a barrier to decarburization and nitration.

[0007] According to the prior art, the next metallurgical step is to hold the steel strip in a high temperature annealing cycle either in a batch annealing furnace or a rotary batch annealing furnace, where secondary recrystallization (SRX) occurs and where the main objectives are to develop abnormal grain growth to obtain a Goss texture with the inhibitors previously formed, to eliminate all elements as sulphur or nitrogen when SRX is finished and to form a coating layer named glass film containing Mg_2SiO_4 to ensure electric insulation and surface tension.

[0008] Problems that may occur with the processes according to the prior art are that all these mechanisms require thermal energy and time, in particular due to the large mass of coil to be heated in batch to allow diffusion and grain growth, which constitutes a high time and cost consumption in the current GOES manufacturing. In including safety steps and possible intermediate soakings the total process lead time lasts about 6 days. Moreover the coil windings require the use of a layer of MgO to isolate the steel surface and then avoiding the surface stickiness of the windings in the long and high temperature box annealing. Furthermore in a coil batch annealing, the thermic treatment is heterogeneous. At a certain time, the temperature is different at any strip position in width and length. In case of a continuous strip annealing treatment the temperature is homogenate and therefore the SRX strip temperature can be optimized and controlled.

[0009] As iron-silicon alloy is an electrical conductive media, induced currents develop over the sheet thickness under the effect of a magnetic flux variation over time; they are called the eddy currents. The reduction of the thickness as well as the increase of the electrical resistivity by addition of alloy elements as for example silicon, are the main two factors able to reduce significantly the losses induced by the eddy currents. Indeed a 10% thickness decrease results in a reduction by ca 20% in Eddy current losses at the same 50 Hz induction level. Whereas a 0.5% increase Silicon content results in a reduction by ca 12% in Eddy current losses at the same 50 Hz induction level. However, the issues in the conventional GOES manufacturing are that thinner thickness and more silicon content make the material more brittle, more difficult to cold roll and more difficult to reach a stable secondary recrystallization SRX particularly for material having a final thickness gauge lower than 0.22 mm.

[0010] The object of the present invention is therefore to provide an improved process for the preparation of grain oriented electrical steel which does not comprise the problems of the known processes as mentioned above, in particular SRX shall be optimized. Further, a more efficient way of handling energy during the production should be found and a new manufacturing method allowing to process thin GOES gauges with high silicon content except the known conventional cold processing treatment are wanted.

[0011] These objects are solved by the process according to the present invention for the production of grain-oriented electrical steel sheet at least comprising the following steps:

(A) providing a hot rolled steel strip based on a steel comprising, beside Fe and unavoidable impurities (all amounts are % by weight):

1 to 8% Si,
less than 0.010% S + Se, and
less than 3% C + Mn + Cu + Cr + Sn + Al + N + Ti + B,

(B) at least one cold rolling step of the hot strip of step (A) to obtain a cold strip,
(C) a primary recrystallization annealing of the cold strip obtained in step (B) optionally including a nitriding treatment,
(D) a secondary recrystallization annealing treatment by heating to a temperature OTAG2 with a heating rate of at least 40 K/s to obtain the grain-oriented electrical steel sheet,

wherein the temperature OTAG2 is set according to the following equation (I):

$$1420K - DP \times PGS \times \rho HAGB / \log((S+\Delta N) \times HRSRX / 20) < OTAG2 < 1420K \quad (I),$$

wherein OTAG2, HRSRX, PGS, ΔN, DP, S and pHAGB have the following meanings:

OTAG2	Optimum Temperature of Abnormal Grain Growth in K,
HRSRX	Heating Rate to Secondary Recrystallization Treatment in K/s,
PGS	Average Primary Grain Size in μm,
ΔN	Nitriding Degree in ppm, calculated by Nitrogen Degree in ppm before SRX annealing (D) minus Nitrogen Degree in ppm before primary recrystallization annealing (C)
DP	Atmosphere Dew Point during heating rate in K,
S	sum of Sulphur content and Selenium content in ppm,
ρHAGB	High Angle (> 15°) primary Grain Boundary average density in μm^{-1}.

[0012] Unless explicitly stated otherwise, in the present text and the claims, the contents of particular alloy elements are each reported in % by weight.

[0013] The above mentioned objects are further solved by a grain-oriented steel strip prepared by the process according to the present invention, by a grain-oriented steel strip having a Peak Magnetic Polarization for the peak magnetic field strength of 800 A/m at 50 Hz of 1.85 to 1.98 T. and by the use of a steel strip according to the present invention in electric transformers, in electric motors or in any electric device where magnetic flux has to be channeled or contained.

[0014] The process according to the present invention and its single steps are explained in detail in the following:
Step (A) of the process according to the present invention comprises providing a hot rolled steel strip based on a steel comprising, beside Fe and unavoidable impurities (all amounts are % by weight) 1 to 8% Si, less than 0.010% S + Se, and less than 3% C + Mn + Cu + Cr + Sn + Al + N + Ti + B.

[0015] According to the present invention, the amount of Si present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is 1 to 8% Si, preferably 2 to 5% Si.

[0016] According to the present invention, the amount of C present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is preferably 0.001% to 1.0% C, particularly preferably 0.01% to 0.1% C.

[0017] According to the present invention, the amount of Mn present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is preferably 0.001% to 3.0% Mn, particularly preferably 0.01% to 0.3% Mn.

[0018] According to the present invention, the amount of S and Se present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is preferably 0.0001% to 0.01% S and Se, particularly preferably 0.001% to 0.01%

S and Se.

[0019] According to the present invention, the amount of Cu present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is preferably 0.001% to 3.0% Cu, particularly preferably 0.01% to 0.3% Cu.

[0020] According to the present invention, the amount of Al present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is preferably 0.001% to 2.0% Al, particularly preferably 0.01% to 1.0% Al.

[0021] According to the present invention, the amount of N present in the steel that is the basis of the hot rolled steel strip that is provided in step (A) is preferably 0.0001% to 0.10% N, particularly preferably 0.001% to 0.01% N.

[0022] According to the present invention, the amount of Cr and Sn and Ti and B in sum present in the steel is less than 3%, particularly preferably less than 1%.

[0023] The present invention preferably relates to the process according to the present invention, wherein the hot rolled steel strip is based on a steel comprising, beside Fe and unavoidable impurities (all amounts are % by weight) 2 to 5 Si, 0.01 to 0.1 C, 0.01 to 0.3 Mn, 0.001 to 0.01 S, 0.01 t 0.3 Cu, 0.01 to 1.0 Al and 0.001 to 0.01 N.

[0024] In general, the step of providing a hot rolled steel strip based on a steel as defined above is known to the skilled artisan and is, for example, described in DE 19745455 C2 and EP 1752 549 B1.

[0025] In particular, step (A) of the process according to the present invention comprises a steelmaking to obtain a steel having the above mentioned composition. The step of steelmaking is also known to the skilled artisan and is described in the documents mentioned above. Afterwards the steel is preferably processed in a hot melt casting to obtain bars of steel. More preferably, the bars obtained accordingly are hot rolled into hot band strips which preferably undergo a hot strip annealing and pickling. The hot band strips that are obtained in step (A) of the process according to the present invention preferably have a thickness of 0.5 to 3.5 mm, more preferably 1.0 to 3.0 mm.

[0026] After step (A) hot band strips having the above mentioned composition and thickness are obtained. These hot band strips are preferably directly introduced into step (B) of the process according to the present invention.

[0027] Step (B) of the process according to the present invention comprises at least one cold rolling step of the hot strip of step (A) to obtain a cold strip. Cold rolling which is done in step (B) of the process according to the present invention is in general known to the skilled artisan and is, for example, described in WO 2007/014868 and WO 99/19521.

[0028] According to the present invention, in step (B) one, two or more cold rolling steps are conducted. Preferably, in step (B) of the process according to the present invention at least two cold rolling steps are conducted.

[0029] The present invention therefore preferably relates to the process according to the present invention, wherein in step (B) at least two cold rolling steps are conducted.

[0030] Further preferred, in step (B) of the process according to the present invention, a first cold rolling step is conducted, in which the hot rolled strip that is obtained from step (A) of the process according to the present invention is cold rolled down to a thickness of for example 0.05 to 2.00 mm, preferably 0.10 to 0.55 mm. Apparatuses in which cold rolling is conducted are in general known to the skilled artisan, for example mentioned in WO 2007/014868 and WO 99/19521.

[0031] Further preferred, the cold rolled strip that is obtained in this first cold rolling step is decarburized after the first cold rolling step. This can be done according to methods known to the skilled artisan, for example in an Intermediate Annealing stage at a temperature of 700 to 950 °C, preferably 800 to 900 °C. The Dew Point of the atmosphere which is present in this annealing stage can be 10 to 80 °C. Apparatuses in which this annealing is conducted are in general known to the skilled artisan, for example described in WO 2007/014868 and WO 99/19521. Annealing is preferably conducted to obtain a steel sheet or strip having a low carbon content, for example less than 30 ppm.

[0032] Preferably a pickling step is conducted after the annealing stage and the optional nitriding stage, which can be made according to methods known to the skilled artisan. For example, pickling can be conducted by using aqueous solutions of acids like phosphoric acid, sulfuric acid and/or hydrochloric acid. The present invention therefore preferably relates to the process according to the present invention, wherein a pickling step is conducted after step (C) and before step (D).

[0033] According to a preferred embodiment of the process according to the present invention, the steel sheet that is obtained after the first cold rolling step in step (B) of the process according to the present invention has a carbon content of less than 30 ppm before the final, preferably the second, cold rolling step in step (B).

[0034] The present invention therefore preferably relates to the process according to the present invention, wherein the steel sheet has a carbon content of less than 30 ppm before the final cold rolling step in step (B).

[0035] Further preferred, a second cold rolling step is conducted, in which the cold rolled strip obtained from the first cold rolling step, preferably after annealing and pickling, is further rolled down to a thickness of 0.05 to 0.35 mm, more preferably 0.10 to 0.22 mm.

[0036] The present invention preferably relates to the process according to the present invention, wherein the cold strip has a thickness of 0.05 to 0.35 mm, preferably 0.10 to 0.22 mm, after step (B).

[0037] Step (C) of the process according to the present invention comprises an annealing of the cold strip obtained in step (B) resulting in primary recrystallization and optionally a nitriding treatment.

[0038] This annealing is preferably conducted at a temperature of for example 400 to 950 °C, more preferably 600 to

900 °C. The optional nitriding treatment is further preferably conducted in an atmosphere comprising N_2 or N-comprising compounds, for example NH_3. Annealing and nitriding can be conducted separately in two successive steps, wherein annealing is conducted first. According to a second embodiment, annealing and nitriding can be conducted in one single step.

[0039] The annealing step (C) is preferably conducted to obtain a cold rolled strip having a nitriding degree, calculated by Nitrogen Degree in ppm before SRX annealing (D) minus Nitrogen Degree in ppm before primary recrystallization annealing (C), of 0 to 300 ppm, more preferably 20 to 250 ppm. Furthermore, the strip that is obtained after step (C) of the process according to the present invention has an average grain size of preferably 5 to 25μm, more preferably 5 to 20 pm. In addition, the strip that is obtained after step (C) of the process according to the present invention has preferably an average High Angle primary Grain Boundary density of 0.005 to 0.1 μm^{-1}, more preferably of 0.01 to 0.09 μm^{-1}.

[0040] Further details of step (C) of the process according to the present invention are known to the skilled artisan.

[0041] Step (D) of the process according to the present invention comprises a secondary recrystallization annealing treatment by heating to a temperature OTAG2 with a heating rate of at least 40 K/s to obtain the grain-oriented electrical steel sheet. According to the present invention, the temperature OTAG2 is set according to the following equation (I):

$$1420K - DP \times PGS \times \rho HAGB / \log((S+\Delta N) \times HRSRX / 20) < OTAG2 < 1420K \qquad (I),$$

wherein OTAG2, HRSRX, PGS, ΔN, DP, S and ρHAGB have the following meanings:

OTAG2	Optimum Temperature of Abnormal Grain Growth in K,
HRSRX	Heating Rate to Secondary Recrystallization Treatment in K/s,
PGS	Average Primary Grain Size in μm,
ΔN	Nitriding Degree in ppm, calculated by Nitrogen Degree in ppm before SRX annealing (D) minus Nitrogen Degree in ppm before primary recrystallization annealing (C)
DP	Atmosphere Dew Point during heating rate in K,
S	sum of Sulphur content and Selenium content in ppm,
ρHAGB	High Angle (> 15°) primary Grain Boundary average density in μm^{-1}.

[0042] The inventor of the present invention have found that particularly advantageous grain-oriented electrical steel sheets are obtained, if a secondary annealing treatment is conducted at a certain temperature OTAG2, which depends on Heating Rate to Secondary Recrystallization Treatment (HRSRX) in K/s, the Average Primary Grain Size (PGS) in pm, the Nitriding Degree (ΔN) in ppm, the Atmosphere Dew Point during heating rate (DP) in K, the sum of Sulphur content and Selenium content (S) in ppm and the High Angle (> 15°) primary Grain Boundary average density (pHAGB) in μm^{-1}.

[0043] If the secondary recrystallization annealing treatment in step (D) of the process according to the present invention is conducted by heating to a temperature OTAG2 with a heating rate of at least 40 K/s, preferably at least 50 K/s, a grain oriented steel sheet is obtained having a high peak magnetic polarization for the peak magnetic field strength of 800 A/m and a low specific total loss.

[0044] According to the present invention, the upper limit of OTAG2 is preferably 1420 K, particularly preferably 1415 K.

[0045] According to the present invention, the Heating Rate to Secondary Recrystallization Treatment is preferably 20 to 800 K/s, more preferably 50 to 750 K/s. The Heating Rate to Secondary Recrystallization Treatment is acquired with methods known to the skilled artisan, for example as described in EP 2 486157.

[0046] According to the present invention, the Average Primary Grain Size is preferably 5 to 25 μm, more preferably 5 to 20 μm. The Average Primary Grain Size is acquired with methods known to the skilled artisan, for example Grain size measured by EBSD analysis (OIM Analysis software).

[0047] According to the present invention, the Nitriding Degree, calculated by Nitrogen Degree in ppm before SRX annealing (D) minus Nitrogen Degree in ppm before primary recrystallization annealing (C), is preferably 0 to 300 ppm, more preferably 20 to 250 ppm. The Nitriding Degree is acquired with methods known to the skilled artisan, for example Nitrogen Elemental Analyzer of A36 LECO Corporation.

[0048] According to the present invention, the Atmosphere Dew Point during heating rate is preferably 223 to 273 K, more preferably 243 to 270 K. The Atmosphere Dew Point is acquired with methods known to the skilled artisan, for example as described in WO 2007/014868 and WO 99/19521.

[0049] According to the present invention, the sum of Sulphur content and Selenium content is preferably 1 to 100 ppm, more preferably 10 to 100 ppm. The sum of Sulphur content and Selenium is acquired with methods known to the skilled artisan, for example as described in WO 2007/014868 and WO 99/19521.

[0050] According to the present invention, the High Angle (> 15°) primary Grain Boundary average density is preferably

0.005 to 0.1 μm^{-1}, more preferably 0.01 to 0.09 μm^{-1}. The High Angle (> 15°) primary Grain Boundary average density is acquired with methods known to the skilled artisan, for example the Grain Boundary density is measured as primary grain boundary length per unit area and is provided directly by EBSD analysis (OIM Analysis software). The ρHAGB is the average of the values corresponding to misorientations higher than 15° (>15°).

[0051] One particularly essential feature of the present invention is that step (D) of the process according to the present invention is conducted at the above defined temperature OTAG2, wherein OTAG2 is calculated according formula (I).

[0052] The heating in step (D) of the process according to the present invention is conducted at a heating rate of at least 40 K/s. Preferably, the heating in step (D) of the process according to the present invention is conducted at a heating rate of at least 70 K/s, more preferably at least 100 K/s. This rapid heating can be conducted by any method known to the skilled artisan, for example by induction, by resistive heating, by conductive heating.

[0053] The heating in step (D) of the process according to the present invention is preferably conducted at a dew point of 223 to 273 K, particularly preferably 243 to 270 K.

[0054] In step (D) of the process according to the present invention the Secondary Recrystallization is performed so that a grain-oriented steel sheet according to the present invention is obtained.

[0055] In general, after step (D) of the process according to the present invention, a grain-oriented steel sheet having the advantageous properties as outlined above is obtained.

[0056] According to a preferred embodiment of the process according to the present invention, the cold strip that is introduced into step (D) does not comprise any annealing separators, preferably no MgO based coating.

[0057] Preferably, further process steps are conducted after step (D).

[0058] Preferably, the strip or sheet that is obtained after step (D) of the process according to the present invention is rapidly heated to a temperature of 1423 K or above. This heating step is preferably conducted under a protective gas atmosphere, for example comprising H_2. Particularly preferably, the soaking at a temperature of 1423 K or above is conducted in an atmosphere comprising 5 to 95 vol.-% H_2, balance nitrogen or any inert gas or mix gas with a DP of at least 10 °C. The soaking is preferably conducted to remove disturbing atoms, in particular to remove N and S. In a more preferable practice the soaking temperature above 1523K is chosen.

[0059] According to a preferred embodiment of the process according to the present invention, the strip or sheet is heated in step (D) to a temperature of 1423 K or above. More preferably, the strip or sheet is heated in step (D) to a temperature of 1523 K or above.

[0060] Further preferred, the steel strip is cooled down afterwards, in particular by methods known to the skilled artisan, for example by natural cooling down to room temperature.

[0061] In addition, according to a preferred embodiment of the process according to the present invention, the steel strip is cleaned, and optionally pickled. Methods with which the steel strip is pickled are known to the skilled artisan. Preferably, the steel strip is treated with an aqueous acidic solution. Suitable acids are for example phosphoric acid, sulfuric acid and/or hydrochloric acid. According to the present invention, the grain oriented electrical steel sheets can be prepared in any format, like steel strips that are provided as coils, or cut steel pieces that are provided by cutting these steel pieces from the steel strips. Methods to provide coils or cut steel pieces are known to the skilled artisan.

[0062] The present invention provides a process for the preparation of grain-oriented electrical steel sheets comprising a continuous strip annealing treatment for which the temperature is homogeneous and therefore the SRX strip temperature can be optimized and better controlled each portion of the strip. The present invention therefore provides an improved process for the preparation of grain oriented electrical steel which does not comprise the problems of the known processes as mentioned above, in particular SRX shall be optimized. Further, a more efficient way of handling energy during the production should be found.

[0063] The present invention further relates to a grain-oriented steel strip prepared by the process according to the present invention. The grain-oriented steel strip prepared by the process according to the present comprises a very advantageous magnetic characteristics, in particular Peak Magnetic Polarization for the peak magnetic field strength of 800 A/m at 50 Hz of 1.85 to 1.98 T, which is essentially obtained due to the specific heat treatment in step (D) of the process.

[0064] The grain-oriented steel strip prepared by the process according to the present invention preferably has a thickness of 0.05 to 0.35 mm, more preferably 0.10 to 0.22 mm.

[0065] The grain-oriented steel strip prepared by the process according to the present invention preferably has an Average Primary Grain Size of 5 to 25 μm.

[0066] The grain-oriented steel strip prepared by the process according to the present invention preferably has a High Angle (> 15°) primary Grain Boundary average density of 0.005 to 0.1 μm^{-1}.

[0067] The grain-oriented steel strip prepared by the process according to the present invention preferably has a Content of Sulphur and/or Selenium of 0.0001 to 0.01 % by weight.

[0068] The grain-oriented steel strip prepared by the process according to the present invention preferably has a Nitriding Degree of 0 to 300 ppm.

[0069] The grain-oriented steel strip prepared by the process according to the present invention preferably has a Peak Magnetic Polarization for the peak magnetic field strength of 800 A/m at 50 Hz of 1.85 to 1.98 T.

[0070] The present invention therefore further relates to a grain-oriented steel strip having a Peak Magnetic Polarization for the peak magnetic field strength of 800 A/m at 50 Hz of 1.85 to 1.98 T. Preferably this grain-oriented steel strip comprises one further characteristic feature like thickness, Average Primary Grain Size, High Angle (> 15°) primary Grain Boundary average density, Content of Sulphur and/or Selenium and/or Nitriding Degree as mentioned above. The present invention also relates to the use of a steel strip according to the present invention in electric transformers, in electric motors or in electric devices, preferably where magnetic flux has to be channeled or contained.

[0071] The present invention is described on the basis of the following examples:

Example 1:

[0072] A steel with the composition of 3.15% by weight Si, 0.052% by weight C, 0.149% by weight Mn, 0.005% by weight S, 0.207% by weight Cu, 0.030% by weight Al, 0.008% by weight N undergoes a steelmaking and a hot melt casting. The bars are hot rolled into hot band strips which undergo a hot strip annealing and pickling, all processing steps in accordance with DE 19745455 C1 and EP 1 752 549 B1.

[0073] The strip is cold rolled in a first cold rolling step down to an intermediate thickness of 0.50 mm and then decarburized at an Intermediate Annealing stage (840 °C in wet atmosphere with Dew Point of 58 °C) and pickled with Sulfuric acid (68°C for 30 s). The second cold rolling is performed to reach a final thickness of 0.18 mm. Afterwards the final strip undergoes a fast annealing nitriding treatment leading to a Nitriding Degree, delta N of 150 ppm, measured with a Nitrogen Elemental Analyzer of A36 LECO Corporation. The primary recrystallized material is characterized by an average grain size of 19 μm, which is measured with a Grain size measured by EBSD analysis (OIM Analysis software) and being the average grain size, and an average High Angle primary Grain Boundary density of 0.071 μm^{-1}, which is measured with a Grain Boundary density is measured as primary grain boundary length per unit area and is provided directly by EBSD analysis (OIM Analysis software). The pHAGB is the average of the values corresponding to misorientations higher than 15° (>15°).

[0074] The final secondary recrystallization treatment is done according to following conditions; a single sample is placed inside an oven and undergoes an ultra-rapid heating rate of 250 K/s under dry N_2 protective gas atmosphere (Dew Point 243 K) up to a 1350 K soaking temperature under a dry mixture of H_{22}, N_2 and Ar as protective gas atmosphere to perform the Secondary Recrystallization.

[0075] Afterwards the strip is rapidly heated up to 1500 K temperature to perform a purification soaking under a slightly wet (DP is 288 K) H_2 protective gas atmosphere, in order to remove N and S. Finally the strip sample is cooled down, cleaned and slightly pickled before magnetic property measurements. Finally the sample is pickled with hydrochloric acid 37% at 60°C for 15s to observe the grain macrostructure.

[0076] The outputs of this experimentation were a completed secondary recrystallized macrostructure having an excellent magnetic polarization J800 of 1.92 T, measured according to IEC 60404-2

Example 2:

[0077] A steel with the composition of 3.10% by weight Si, 0.047% by weight C, 0.155% by weight Mn, 0.008% by weight S, 0.199% by weight Cu, 0.030% by weight Al, 0.009% by weight N undergoes a steelmaking and a hot melt casting. The bars are hot rolled into hot band strips which undergo a hot strip annealing and pickling, all processing steps in accordance with DE 19745455 C1 and EP 1 752 549 B1.

[0078] The strip is cold rolled in a first cold rolling step down to an intermediate thickness of 0.36 mm and then decarburized at Intermediate Annealing stage (840 °C in wet atmosphere with Dew Point: 58 °C) and pickled with Sulfuric acid (68°C for 30 s). The second cold rolling is performed to reach a final thickness of 0.18 mm. Afterwards the final strip undergoes a fast annealing nitriding treatment leading to a Nitriding Degree of delta N 152 ppm. The primary recrystallized material is characterized by an average grain size of 14 μm and an average High Angle primary Grain Boundary density of 0.010 μm^{-1}.

[0079] The final secondary recrystallization treatment is done according to following conditions; a single sample is placed inside an oven and undergoes a ultra-rapid heating rate of 15 K/s under dry N_2 protective gas atmosphere (DP 243 K) up to a 1250 K soaking temperature under a dry mixture of H_2, N_2 and Ar as protective gas atmosphere to perform the Secondary Recrystallization.

[0080] Afterwards the strip is rapidly heated up to a 1500 K temperature to perform a purification soaking under a slightly wet 288 K H_2 protective gas atmosphere, in order to remove N and S. Finally the strip sample is cooled down, cleaned and slightly pickled with Sulfuric acid (68 °C for 15 s) before magnetic property measurements. Finally the sample is pickled with hydrochloric acid 37% at 60 °C for 15s to observe the grain macrostructure.

[0081] The outputs of this experimentation were a not completed secondary recrystallized macrostructure having a poor magnetic polarization J800 of 1.45 T measured according to IEC 60404-2.

[0082] Further experiments according to the present invention have been conducted according to examples 1 and 2. The conditions and results of these experiments are shown in the following.

Table 1

No.	Heating rate in Secondary Recrystallization [K/s]	Dew Point during heating rate [K]	Soaking Temperature for SRX [K]	Average Primary Grain Size [μm]	High Angle (> 15°) Grain Boundary average density [μm^{-1}]	Content of Sulphur and/or Selenium [ppm]	Nitriding Degree [ppm]	Peak magnetic polarization for the peak magnetic field strength of 800 A/m at 50 Hz [T]	Secondary Recrystallization
1	75	243	1350	17	0.067	45	112	1.90	completed
2	75	253	1320	17	0.080	50	60	1.88	completed
3	75	263	1290	20	0.087	40	57	1.87	completed
4	125	243	1350	14	0.064	45	115	1.93	completed
5	125	253	1320	18	0.075	50	62	1.89	completed
6	125	263	1290	20	0.086	70	70	1.88	completed
7	250	243	1350	19	0.071	50	150	1.92	completed
8	250	253	1320	17	0.085	60	80	1.91	completed
9	250	263	1290	19	0.086	70	72	1.89	completed
10	500	243	1350	19	0.077	45	135	1.92	completed
11	500	253	1320	16	0.090	25	125	1.91	completed
12	500	263	1290	20	0.078	25	27	1.92	completed
13	50	263	1350	18	0.045	50	100	1.88	completed
14	150	263	1350	18	0.055	50	85	1.89	completed
15	300	253	141b	9	0.060	30	70	1.92	completed
16	500	263	1415	6	0.020	20	21	1.90	completed
17	600	263	1415	13	0.029	30	20	1.91	completed
18	700	243	1415	17	0.067	40	105	1.92	completed
C19	15	243	1250	18	0.070	25	99	1.63	not completed
C20	15	243	1250	14	0.010	80	152	1.45	not completed
C21	20	273	1250	15	0.088	90	63	1.66	not completed
C22	75	288	1250	22	0.044	30	110	1.49	not completed

(continued)

No.	Heating rate in Secondary Recrystallization [K/s]	Dew Point during heating rate [K]	Soaking Temperature for SRX [K]	Average Primary Grain Size [μm]	High Angle (> 15°) Grain Boundary average density [μm^{-1}]	Content of Sulphur and/or Selenium [ppm]	Nitriding Degree [ppm]	Peak magnetic polarization for the peak magnetic field strength of 800 A/m at 50 Hz [T]	Secondary Recrystallization
C23	250	253	1250	4	0.001	25	265	1.45	not completed
C24	350	243	1250	4	0.002	25	170	1.47	not completed
C25	500	273	1250	4	0.003	50	9	1.46	not completed
C26	800	243	1250	15	0.005	60	132	1.46	not completed
C: comparative example									

Table 2

No.	Peak magnetic polarization for the peak magnetic field strength of 800 A/m at 50 Hz [T]	Soaking Temperature for SRX [K]	calculated OTAG2	
			OTAG2 bottom limit [K]	OTAG2 upper limit [K]
1	1.90	1350	1320	1420
2	1.88	1320	1288	1420
3	1.87	1290	1241	1420
4	1.93	1350	1322	1420
5	1.89	1320	1300	1420
6	1.88	1290	1266	1420
7	1.92	1350	1324	1420
8	1.91	1320	1307	1420
9	1.89	1290	1288	1420
10	1.92	1350	1323	1420
11	1.91	1320	1318	1420
12	1.92	1290	1288	1420
13	1.88	1350	1337	1420
14	1.89	1350	1333	1420
15	1.92	1415	1377	1420
16	1.90	1415	1410	1420
17	1.91	1415	1389	1420
18	1.92	1415	1345	1420
C19	1.63	1250	1264	1420
C20	1.45	1250	1405	1420
C21	1.66	1250	1255	1420
C22	1.49	1250	1318	1420
C23	1.45	1250	1420	1420
C24	1.47	1250	1420	1420
C25	1.46	1250	1419	1420
C26	1.46	1250	1415	1420
C: comparative example				

[0083] OTAG2 has been calculated according to the following formula (I)

$$1420K - DP \times PGS \times \rho HAGB / \log((S+\Delta N) \times HRSRX / 20) < OTAG2 < 1420K \qquad (I),$$

wherein OTAG2, HRSRX, PGS, ΔN, DP, S and pHAGB have the following meanings:

OTAG2 Optimum Temperature of Abnormal Grain Growth in K,

HRSRX Heating Rate to Secondary Recrystallization Treatment in K/s,
PGS Average Primary Grain Size in μm,
ΔN Nitriding Degree in ppm, calculated by Nitrogen Degree in ppm before SRX annealing (D) minus Nitrogen Degree in ppm before primary recrystallization annealing (C),
DP Atmosphere Dew Point during heating rate in K,
S sum of Sulphur content and Selenium content in ppm,
pHAGB High Angle (> 15°) primary Grain Boundary average density in μm^{-1}.

[0084] The grain-oriented electrical steel sheet according to the present invention shows a very high Peak Magnetic Polarization and is therefore very useful in electric transformers, in electric motors or in electric devices, preferably where magnetic flux has to be channeled or contained.

Claims

1. A process according to the present invention for the production of grain-oriented electrical steel sheet at least comprising the following steps:

   (A) providing a hot rolled steel strip based on a steel comprising, beside Fe and unavoidable impurities (all amounts are % by weight):

   1 to 8 Si,
   less than 0.010 S + Se, and
   less than 3 C + Mn + Cu + Cr + Sn + Al + N + Ti + B,

   (B) at least one cold rolling step of the hot strip of step (A) to obtain a cold strip,
   (C) a primary recrystallization annealing of the cold strip obtained in step (B) optionally including a nitriding treatment,
   (D) a secondary recrystallization annealing treatment by heating to a temperature OTAG2 with a heating rate of at least 40 K/s to obtain the grain-oriented electrical steel sheet,

   wherein the temperature OTAG2 is set according to the following equation (I):

$$1420K - DP \times PGS \times \rho HAGB / \log((S+\Delta N) \times HRSRX / 20) < OTAG2 < 1420K \qquad (I),$$

   wherein OTAG2, HRSRX, PGS, ΔN, DP, S and pHAGB have the following meanings:

   OTAG2 Optimum Temperature of Abnormal Grain Growth in K,
   HRSRX Heating Rate to Secondary Recrystallization Treatment in K/s,
   PGS Average Primary Grain Size in μm,
   ΔN Nitriding Degree in ppm, calculated by Nitrogen Degree in ppm before SRX annealing (D) minus Nitrogen Degree in ppm before primary recrystallization annealing (C)
   DP Atmosphere Dew Point during heating rate in K,
   S sum of Sulphur content and Selenium content in ppm,
   pHAGB High Angle (> 15°) primary Grain Boundary average density in μm^{-1}.

2. The process according to claim 1, wherein the hot rolled steel strip is based on a steel comprising, beside Fe and unavoidable impurities (all amounts are % by weight) 2 to 5% Si, 0,01 to 0,1% C, 0,01 to 0,3% Mn, 0,001 to 0,01% S, 0,01 to 0,3% Cu, 0,01 to 1,0% Al and 0,001 to 0,01% N.

3. The process according to claims 1 or 2, wherein in step (B) at least two cold rolling steps are conducted.

4. The process according to any of claims 1 to 3, wherein the cold strip has a thickness of 0.05 to 0.35 mm, preferably 0.10 to 0.22 mm, after step (B).

5. The process according to any of claims 1 to 4, wherein the cold strip that is introduced into step (D) does not comprise

any annealing separators, preferably no MgO based coating.

6. The process according to any of claims 1 to 5, wherein the steel sheet has a carbon content of less than 30 ppm before the final cold rolling step in step (B).

7. The process according to any of claims 1 to 6, wherein a pickling step is conducted after step (C) and before step (D).

8. The process according to any of claims 1 to 7, wherein the strip or sheet is heated in step (D) to a temperature of 1423 K or above.

9. The process according to any of claims 1 to 8, wherein the strip or sheet is heated in step (D) to a temperature of 1523 K or above.

10. A grain-oriented steel strip prepared by the process according to any of claims 1 to 9.

11. A grain-oriented steel strip having a Peak Magnetic Polarization for the peak magnetic field strength of 800 A/m at 50 Hz of 1.85 to 1.98 T.

12. The use of a steel strip according to claim 10 or claim 11 in electric transformers in electric motors or in electric devices, preferably where magnetic flux has to be channeled or contained.

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EUROPEAN SEARCH REPORT

Application Number
EP 19 16 5239

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 6 488 784 B1 (FORTUNATI STEFANO [IT] ET AL) 3 December 2002 (2002-12-03) * column 7, lines 10-52; claims 1-14; example 3 * -----	1-12	INV. C21D8/12 H01F1/147
X A	US 2006/076086 A1 (TERASHIMA TAKASHI [JP] ET AL) 13 April 2006 (2006-04-13) * paragraph [0107]; claims 1-10; tables 1-3 * -----	11,12 1-10	
X A	US 2012/222777 A1 (FORTUNATI STEFANO [IT] ET AL) 6 September 2012 (2012-09-06) * paragraph [0039]; claims 1-14; example 3; table 3 * -----	11,12 1-10	
A	US 2003/116236 A1 (HAYAKAWA YASUYUKI [JP] ET AL) 26 June 2003 (2003-06-26) * paragraph [0113]; claims 1-31; tables 1-12 * -----	1-12	
A	US 2018/371571 A1 (HAN KYU-SEOK [KR] ET AL) 27 December 2018 (2018-12-27) * claims 1-19; tables 1-3 * -----	1-12	TECHNICAL FIELDS SEARCHED (IPC) C21D H01F
A	EP 2 743 358 A1 (JFE STEEL CORP [JP]) 18 June 2014 (2014-06-18) * claims 1-3; figures 1-5 * -----	1-12	

The present search report has been drawn up for all claims

3

Place of search	Date of completion of the search	Examiner
Munich	13 May 2019	Catana, Cosmin

CATEGORY OF CITED DOCUMENTS

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....
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EP 19 16 5239

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-05-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6488784 B1	03-12-2002	AT 218624 T	15-06-2002
		AU 3328899 A	27-09-1999
		BR 9908590 A	14-11-2000
		CN 1292832 A	25-04-2001
		CZ 20003023 A3	11-07-2001
		DE 69901692 T2	28-11-2002
		EP 1062371 A1	27-12-2000
		ES 2179635 T3	16-01-2003
		IT RM980149 A1	10-09-1999
		JP 2002506125 A	26-02-2002
		PL 343193 A1	30-07-2001
		RU 2218429 C2	10-12-2003
		SK 13342000 A3	09-04-2001
		US 6488784 B1	03-12-2002
		WO 9946413 A1	16-09-1999
US 2006076086 A1	13-04-2006	CN 1708594 A	14-12-2005
		CN 101311287 A	26-11-2008
		EP 1577405 A1	21-09-2005
		JP 4258349 B2	30-04-2009
		JP 2004169179 A	17-06-2004
		KR 20050065608 A	29-06-2005
		US 2006076086 A1	13-04-2006
		WO 2004040024 A1	13-05-2004
US 2012222777 A1	06-09-2012	CA 2781916 A1	03-06-2011
		CN 102686751 A	19-09-2012
		EP 2470679 A1	04-07-2012
		JP 5646643 B2	24-12-2014
		JP 2013512332 A	11-04-2013
		KR 20120096036 A	29-08-2012
		RU 2012126097 A	27-12-2013
		US 2012222777 A1	06-09-2012
		WO 2011063934 A1	03-06-2011
US 2003116236 A1	26-06-2003	CN 1400319 A	05-03-2003
		EP 1279747 A2	29-01-2003
		KR 20030010502 A	05-02-2003
		US 2003116236 A1	26-06-2003
US 2018371571 A1	27-12-2018	CN 108431244 A	21-08-2018
		EP 3395959 A1	31-10-2018
		JP 2019505671 A	28-02-2019
		KR 101675318 B1	11-11-2016
		US 2018371571 A1	27-12-2018
		WO 2017111432 A1	29-06-2017

EPO FORM P0459

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 19 16 5239

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13-05-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2743358 A1	18-06-2014	BR 112014002950 A2	01-03-2017
		CN 103703151 A	02-04-2014
		EP 2743358 A1	18-06-2014
		JP 5994981 B2	21-09-2016
		JP 2013057118 A	28-03-2013
		KR 20140022953 A	25-02-2014
		KR 20160046919 A	29-04-2016
		US 2014202599 A1	24-07-2014
		WO 2013024772 A1	21-02-2013

EPO FORM P0459

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- DE 19745455 C2 **[0024]**
- EP 1752549 B1 **[0024] [0072] [0077]**
- WO 2007014868 A **[0027] [0030] [0031] [0048] [0049]**
- WO 9919521 A **[0027] [0030] [0031] [0048] [0049]**
- EP 2486157 A **[0045]**
- DE 19745455 C1 **[0072] [0077]**

Non-patent literature cited in the description

- **WUPPERMANN et al.** Electrical Steel, Stahl-Informations-Zentrum. 2005, 5, , 6 **[0003]**
- **N. CHEN et al.** *Acta Materialia,* 2003, vol. 51, 1755-1765 **[0004]**
- **K. GÜNTHER et al.** *Journal of Magnetism and Magnetic Materials,* 2008, vol. 320, 2411-2422 **[0004]**