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(54) **ANNEALING SEPARATION AGENT FOR PRODUCING GRAIN-ORIENTED SILICON STEEL
WITH SMOOTH SURFACE AND GOOD MAGNETIC PROPERTY**

(57) An annealing separator for manufacturing grain-oriented silicon steel with mirror-like surface having good magnetic performance consists of the composition of which is 77-98 by wt% of Al_2O_3 powder, 1-8 by wt% of alkaline earth powder, 1~15 by wt% of alkali metal chloride and/or alkaline earth metal chloride. The annealing separator of the invention can avoid forming a glass-film

undercoating on the surface of the steel sheet during high-temperature annealing, and at the same time, the oxide embedded at near-surface of the sheet is removed by means of corrosive reaction of the chloride, so that a produce with smooth surface and stable magnetic performance is obtained.

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Description**Field of the Invention**

5 **[0001]** The present invention relates to a method for manufacturing grain-oriented silicon steels, especially to an annealing separator for manufacturing grain-oriented silicon steels with mirror-like surface having excellent magnetic performance.

Description of the Prior Art

10 **[0002]** Grain-oriented silicon steel shall be subjected to decarburization annealing protected in a H_2 - N_2 atmosphere, after being subjected to processes of hot-rolling, normalizing and cold rolling, and accordingly the rolling stress is relieved and preliminary recrystallization is formed, and meanwhile, wet gas is introduced into a furnace for controlling a carbon content in the steel belt below 30ppm to prevent the final product from magnetic aging. The steel belt will be oxidized
15 when subjected to the decarburization annealing to form an oxide layer mainly consisting of SiO_2 and Fe_2SiO_4 , which will negatively affect the following decarburization. In the following high-temperature annealing process, the oxide layer undergoes chemical reaction with the annealing separator coated on surfaces of the steel belt, and produces a glass-film undercoating mainly consisting of Mg_2SiO_4 . The glass-film undercoating has the function of preventing the steel belt from bonding and purifying the steel during the high-temperature annealing.

20 **[0003]** The Mg_2SiO_4 glass-film undercoating on the surface of the grain-oriented silicon steel has relative high hardness, which results in a relative poor punching performance of the steel sheet, which is generally thousands of times; and, an embedded combination between the glass-film undercoating and a body of the steel sheet hinders magnetic domain wall movement, and increases magnetic hysteresis loss.

25 **[0004]** In order to improve the punching performance of the grain-oriented silicon steel and further improve the magnetic performance, Japanese develop a grain-oriented silicon steel without the glass-film undercoating. Japanese patent JP49096920 discloses a method that removes glass-film undercoating on the surface of the grain-oriented silicon steel by means of acid pickling. However, in order to completely wash out the glass-film undercoating with a thickness of $10\mu m$ (including the oxide embedded into the steel sheet), the steel shall be immersed in strong acid for a long period, which results in the problems of high cost, environmental pollution of the agent and the like.

30 **[0005]** Japanese patent JP05156362A discloses that Al_2O_3 is applied as a high-temperature annealing separator. Al_2O_3 does not react with the oxide layer or the body of steel sheet, so that the grain-oriented silicon steel without the glass film undercoating can be obtained directly. However, the method cannot remove the oxide layer or embedded oxide formed during decarburizing annealing, which is disadvantage in term of improving the magnetic performance.

35 **[0006]** To solve this problem, Japanese patent JP2003247024 relates to a method in which the ratio of PH_2O/PH_2 is controlled to form an atmosphere having a low degree of oxidizability, thus no Fe based oxide is formed, a separator mainly of Al_2O_3 then is coated to obtain grain-oriented steel with smooth surface. However, if the degree of oxidizability is too low during decarburizing, it will result in the difficulty of decarburization. In Japanese patent JP05156364A, after the decarburization annealing is completed, an oxide layer on the surface of the steel sheet is removed by means of acid pickling, and then a separator mainly of Al_2O_3 is coated.

40 **[0007]** In US patent US554719, $MgO+SiO_2$ is used as an annealing separator, which forms loose magnesium silicate on surfaces of a steel sheet during a secondary recrystallization annealing step, then the loose magnesium silicate is removed by brushing and washing, so that a product without glass-film undercoating is obtained.

45 **[0008]** In Japanese patent JP2000038615, magnesia and alumina added with chloride are used as an annealing separator, the formed glass film undercoating is removed by means of interfacial reaction of $(2/3)MC1_3 + Fe + (3/2)O_2 \rightarrow M_2O_3 + FeCl_2\uparrow$, so that a product without any glass-film undercoating is obtained.

50 **[0009]** JFE, a Japanese company, uses Al_2O_3 and the like, which does not react with the surface of the steel sheet, as a high-temperature annealing separator to directly obtain a grain-oriented silicon steel without any glass-film undercoating. In such a method, in order to completely eliminate near-surface oxide impurity of the steel sheet, the dew point for decarburizing shall be so strictly controlled that no Fe based oxide is formed on the surface of the steel sheet. However, this will inevitably cause the problem of decarburization and nitridation.

55 **[0010]** Armco company (now AK company), a US company, uses magnesia, which is added with SiO_2 , as an annealing separator, wherein the loose magnesium silicate formed on the steel sheet during a secondary recrystallization annealing step will benefit in introducing annealing protection gas into interlayer portion of the steel sheet for purifying the steel. However, generally, such a method cannot completely wash out the magnesium silicate on the surface, and cannot completely remove the embedded oxide at the near surface of the iron sheet, either, which restricts the effect of lowering iron core loss.

[0011] NSC, which is a Japanese company, uses magnesia, which is added with chloride, as an annealing separator. However, adding large amount of chloride will result in certain corrosion to the surface of the steel sheet during a

secondary recrystallization annealing, which will affect surface inhibitor, the secondary recrystallization will be unstable.

Table 1

	Main composition of the separator	fundamental
US3785882	100% by weight of Gross Al_2O_3	No undercoating reaction occurs
US554719	(35-85% by weight) MgO + (15-65% by weight) SiO_2	Loose undercoating, which can be easily removed, is formed on the steel sheet surface
JP08269560 A	$\text{MgO} + \text{Cl}^-$ An amount of Cl added is controlled at 0.05-0.5% by weight	The undercoating is removed by interfacial reaction of $(\text{CaCl}_2 + \text{Fe} (1/2)\text{O}_2 \rightarrow \text{CaO} + \text{FeCl}_2 \uparrow)$

Summary of the Invention

[0012] The object of the present invention is to provide an annealing separator for manufacturing grain-oriented silicon steel with mirror-like surface having good magnetic performance, which can prevent the glass-film undercoating from forming on the steel sheet, meanwhile the embedded oxide at the near-surface of sheet can be removed by means of corrosion reaction with the chloride, so that a product with smooth surface and stable magnetic performance can be obtained.

[0013] In order to obtain the above-described object, the technical solution of the present invention is that:

[0014] An annealing separator for manufacturing grain-oriented silicon steel with mirror-like surface having good magnetic performance consists of a composition as follows: 77~98% by weight of Al_2O_3 powder, 1~8% by weight of alkaline earth metal oxide powder, 1~15% by weight of alkali metal chloride and/or alkaline earth metal chloride.

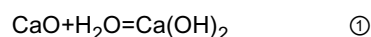
[0015] Further, the alkaline earth metal oxide comprises BeO , MgO , CaO , SrO , or BaO .

[0016] In addition, the alkali metal chloride comprises LiCl , NaCl , KCl , or RbCl .

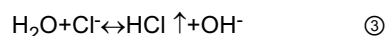
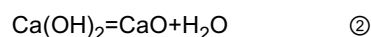
[0017] alkaline earth metal chloride comprises BeCl_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 or ZnCl_2 .

[0018] It is found by experiment that it will be effective for removing the oxide layer at the near-surface of sheet by applying a substance that does not react with the oxide layer of the sheet as the annealing separator during high-temperature annealing, the substance is added with a few amount of alkaline earth metal oxide for introducing moisture not higher than 2.5wt%, and a certain amount of chloride is also added, so that the moisture reacts with the chloride ion contained in the chloride additive to form corrosive solution with acidity, which is good advantageous for removing oxide layer at the near-surface of sheet.

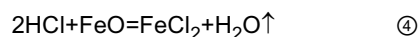
[0019] By adding and stirring water, the annealing separator for the grain-oriented silicon steel with mirror-like surface of the invention forms a coating liquid having a certain concentration, then coating on the surface of the decarburized sheet is carried out. After the completion of coating, the product is baked under a temperature not higher than 300°C for more than 30s, so as to expel free moisture in the separator. At this time, the separator forms a substance having micropores, and the main composition of the substance is a mixture of Al_2O_3 , $\text{Ca}(\text{OH})_2$ and one or more kinds of chloride, which has good permeability. The primary chemical reaction during the hydrolysis is

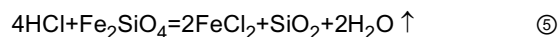


[0020] In a preliminary phase of the high-temperature annealing, $\text{Ca}(\text{OH})_2$ is subjected to a decomposition reaction and again produces CaO and releases moisture when the temperature is higher than 580°C . The presence of the moisture at one hand provides some solution, and at the other hand reacts with the chlorine ion to form an acid substance of HCl , which has a certain corrosion function. Chemical reactions occurred in subsequence during the high annealing are as follows:



[0021] HCl in gas phase penetrates through the separator, reacts with the oxide layer of the sheet, and promote the reaction designated by the chemical equilibrium ③ rightward, so that the reaction occurs continuously. The reaction between HCl and oxide layer is as follows:





[0022] The oxide layer corrupted by HCl degrades to a loose and porous substance, the binding force of which with the sheet is reduced substantially. By slightly being pickled and brushed after high-temperature annealing, such oxide layer can be easily removed. Thus, the grain-oriented silicon steel with mirror-like surface and smooth surface can be finally obtained after hot stretching and flattening process.

[0023] The glass film undercoating formed during the conventional high-temperature annealing for grain-oriented silicon steel presents a relative high hardness, which will degrade the punching performance of the silicon steel sheet, molds will be damaged in some extents during the manufacturing. Meanwhile, a pinned structure of the oxide in the body of sheet hinders the magnetic domain wall movement, which will negatively affect the magnetic performance. The grain-oriented silicon steel without undercoating can substantially improve the processability of the silicon steel, and the processability thereof can be further improved due to the absence of the pinned structure, so that a product with extra low iron core loss can be obtained.

[0024] Prior to the present invention, patents for obtaining grain-oriented surface silicon steel mainly relate to MgO and chloride or Al_2O_3 . The former will result in instability of the magnetic performance, and the latter cannot remove the embedded oxide formed during decarburizing annealing process. Some one utilizes the Al_2O_3 separator added with chloride, however, the chloride itself needs the assistance of certain moisture for reacting with the embedded oxide to remove the same.

[0025] The invention inventively introduces the alkaline earth metal oxide, based on the water solubility of the alkaline earth metal oxide, the moisture introduced during the high-temperature annealing can be controlled easily. Such a method is easy, and can stably obtain excellent grain-oriented silicon steel products. The apparatus concerned is conventional apparatus for producing grain-oriented steel, which has excellent practicability and spreadability, which features good expectation of popularizing.

Brief Description of Drawings

[0026]

Fig.1 is a sectional optical photograph of a steel sheet of comparative example 1 (separator: MgO 65Wt% plus SiO_2 35 Wt%).

Fig.2 is a sectional optical photograph of a steel sheet of comparative example 2 (separator: MgO 90Wt% plus CaCl_2 Wt%).

Fig.3 is a sectional optical photograph of a steel sheet of comparative example 3 (separator: Al_2O_3 100 Wt%).

Fig.4 is a sectional optical photograph of a steel sheet of an embodiment of the invention (the separator: Al_2O_3 86 Wt% plus CaO 4Wt% plus MgCl_2 10 Wt%).

Detailed Description of the Invention

[0027] Hereinafter, the present invention will be described in connection with embodiments.

[0028] A 500Kg-vacuum furnace is used for steel-smelting, the chemical composition of a steel blank is (in Wt%): 0.045% by weight of C, 3.25% by weight of Si, 0.006% by weight of S, 0.027% by weight of Als, 0.006% by weight of N, 0.15% by weight of Cu, 0.012 % by weight of Mn and a balance consisting of Fe and inevitable impurities. After being heated under 1150°C , the blank is hot rolled to form a hot rolled sheet with a thickness of 2.6mm. The hot rolled sheet is normalized and annealed for 1 minutes, and then is pickled and cold rolled to form the sheet with a final thickness of 0.285mm. The cold rolled sheet undergoes decarburizing annealing treatment under 835°C for 120s, so there are two levels of the oxygen content on the surface: 0.8 and 1.6g/m^2 ; after the process of nitriding, the nitrogen content of the steel sheet is 250ppm. The decarburized and annealed sheet is coated by the annealing separator (the material proportion is shown in Table 2), after being wound, the sheet undergoes high-temperature annealing at 1200°C , which temperature is held for 20 hours, in the protective atmosphere of dry nitrogen and hydrogen, then the sheet is coated with an insulation coating, stretched and flattened, and annealed after unwound.

Table 2 (% by weight)

description	Al_2O_3	alkaline earth metal oxide	alkali metal chloride/alkaline earth chloride
Embodiment 1	98	CaO 1	MgCl_2 1
Embodiment 2	86	CaO 4	MgCl_2 10
Embodiment 3	77	CaO 8	MgCl_2 15

(continued)

description	Al ₂ O ₃	alkaline earth metal oxide	alkali metal chloride/alkaline earth chloride
Embodiment 4	86	BeO 4	LiCl 10
Embodiment 5	86	MgO 4	NaCl 10
Embodiment 6	86	SrO 4	KCl 10
Embodiment 7	86	BaO 4	RbCl 10
Embodiment 8	86	MgO 4	BeCl ₂ 10
Embodiment 9	86	SrO 4	CaCl ₂ 10
Embodiment 10	86	BaO 4	SrCl ₂ 10
Embodiment 11	86	CaO 4	BaCl ₂ 10
Embodiment 12	86	CaO 4	ZnCl ₂ 10
comparative example 1	65 parts of MgO 35 parts of SiO ₂		
comparative example 2	90 parts of MgO + 10 parts of CaCl ₂		
comparative example 3	Al ₂ O ₃ 100 parts		

[0029] The average values of the electromagnetic performance of the resulted products and the surface qualities thereof are shown in table 3.

Table 3

Separator	Surface oxygen content	Electromagnetic performance		Surface appearance
		B ₈ , T	P _{17/50} , W/kg	
Embodiment 1	0.8 g/m ²	1.897	0.753	Smooth surface, no undercoating
	1.6 g/m ²	1.905	0.745	Smooth surface, no undercoating
Embodiment 2	0.8 g/m ²	1.891	0.783	Smooth surface, no undercoating
	1.6 g/m ²	1.897	0.774	Smooth surface, no undercoating
Embodiment 3	0.8 g/m ²	1.899	0.735	Smooth surface, no undercoating
	1.6 g/m ²	1.903	0.734	Smooth surface, no undercoating
Embodiment 4	0.8 g/m ²	1.888	0.779	Smooth surface, no undercoating
	1.6 g/m ²	1.897	0.748	Smooth surface, no undercoating
Embodiment 5	0.8 g/m ²	1.889	0.776	Smooth surface, no undercoating
	1.6 g/m ²	1.895	0.773	Smooth surface, no undercoating
Embodiment 6	0.8 g/m ²	1.900	0.769	Smooth surface, no undercoating
	1.6 g/m ²	1.900	0.743	Smooth surface, no undercoating

(continued)

Separator	Surface oxygen content	Electromagnetic performance		Surface appearance
		B ₈ , T	P _{17/50} , W/kg	
Embodiment 7	0.8 g/m ²	1.890	0.782	Smooth surface, no undercoating
	1.6 g/m ²	1.903	0.775	Smooth surface, no undercoating
Embodiment 8	0.8 g/m ²	1.895	0.768	Smooth surface, no undercoating
	1.6 g/m ²	1.893	0.760	Smooth surface, no undercoating
Embodiment 9	0.8 g/m ²	1.899	0.772	Smooth surface, no undercoating
	1.6 g/m ²	1.903	0.769	Smooth surface, no undercoating
Embodiment 10	0.8 g/m ²	1.887	0.766	Smooth surface, no undercoating
	1.6 g/m ²	1.890	0.760	Smooth surface, no undercoating
Embodiment 11	0.8 g/m ²	1.897	0.771	Smooth surface, no undercoating
	1.6 g/m ²	1.910	0.743	Smooth surface, no undercoating
Embodiment 12	0.8 g/m ²	1.887	0.775	Smooth surface, no undercoating
	1.6 g/m ²	1.899	0.762	Smooth surface, no undercoating
comparative example 1	0.8 g/m ²	1.927	0.705	The surface includes partial undercoating
	1.6 g/m ²	1.921	0.720	The surface includes complete undercoating
comparative example 2	0.8 g/m ²	1.825	0.997	The surface includes partial undercoating
	1.6 g/m ²	1.857	0.897	The surface includes partial undercoating
comparative example 3	0.8 g/m ²	1.865	0.903	The surface includes partial undercoating
	1.6 g/m ²	1.847	0.937	The surface includes partial undercoating

[0030] It can be seen from Figs.1-4 and Table 3 that there is few oxide residual existing on the surface of the silicon steel sheet coated with the separator of the invention, and the magnetic performance of the steel sheet are good. Thus, it can be seen that the grain-oriented steel sheet with mirror-like surface having good magnetic performance can be manufactured by the effective finish process on the surface of the grain-oriented silicon steel in the present invention.

[0031] On one hand, the high-temperature annealing separator of the present invention effectively purifies the steel and prevents coils of the steel from binding, and on the other hand, the present invention provides a corrosive atmosphere during the annealing with high temperature to remove the oxide layer at near-surface, so that grain-oriented silicon steel with mirror-like surface having good magnetic performance can be produced.

Claims

1. An annealing separator for manufacturing a grain-oriented silicon steel with good magnetic performance, which consists of a composition as follows:

77~98% by weight of Al_2O_3 powder;
1~8% by weight of alkaline earth metal oxide powder;
1~15% by weight of alkali metal chloride and/or alkaline earth metal chloride.

2. The annealing separator for manufacturing a grain-oriented silicon steel with good magnetic performance according to Claim 1, wherein the alkaline earth metal oxide comprises BeO, MgO, CaO, SrO or BaO.

3. The annealing separator for manufacturing a grain-oriented silicon steel with good magnetic performance according to Claim 1, wherein the alkali metal chloride comprises LiCl, NaCl, KCl or RbCl.

4. The annealing separator for manufacturing a grain-oriented silicon steel with good magnetic performance according to Claim 1, wherein the alkaline earth metal chloride comprises BeCl_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 or ZnCl_2 .

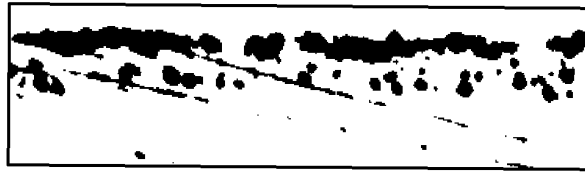


FIG. 1



FIG. 2



FIG. 3

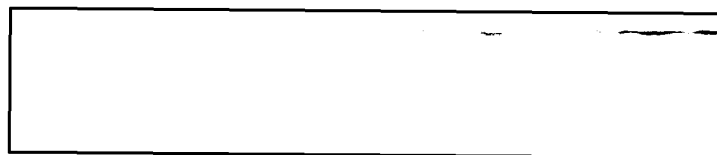


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/072771

A. CLASSIFICATION OF SUBJECT MATTER

C21D 1/68 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

WPI, EPODOC, CN-PAT, CNKI: al2o3, cl, beo, mgo, cao, sro, bao, separat+, part+, depart+, coat+, medium, agent, anneal+, alumina, chloride, alkaline earth, oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CN1125773A (NIPPON STEEL CORP) 03 Jul.1996 (03.07.1996) whole document	1-4

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
20 Jul.2011(20.07.2011)Date of mailing of the international search report
04 Aug. 2011 (04.08.2011)Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China
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Facsimile No. 86-10-62019451Authorized officer
WU Chenchen
Telephone No. (86-10)62084743

INTERNATIONAL SEARCH REPORT
Information on patent family members

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