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(71) Applicant: **JFE Steel Corporation**
Tokyo, 100-0011 (JP)

(72) Inventors:
- **Omura, Takeshi**
  Tokyo, 100-0011 (JP)
- **Sashi, Kazumichi**
  Tokyo, 100-0011 (JP)
- **Hayakawa, Yasuyuki**
  Tokyo, 100-0011 (JP)
- **Kawano, Masaki**
  Tokyo, 100-0011 (JP)
- **Yoshikawa, Shinichi**
  Tokyo, 100-0011 (JP)

(74) Representative: **Grünecker, Kinkeldey,**
Stockmair & Schwanhäusser
Anwaltssozietät
Leopoldstrasse 4
80802 München (DE)

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(54) METHOD FOR MANUFACTURING A GRAIN-ORIENTED ELECTRICAL STEEL SHEET

(57) By using a treatment solution containing an Al compound in the form of a solution or a colloidal solution and a stable compound at a high temperature as an annealing separator, a superior annealing separation effect can be obtained without causing any dust problem and line contamination. In addition, when the above annealing separator is used in final annealing or the like in a manufacturing process of a grain-oriented electrical steel sheet, a grain-oriented electrical steel sheet can be obtained which has no forsterite coating or which has superior forsterite coating properties.

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Description

Technical Field

[0001] The present invention relates to an annealing separator which prevents sticking between grain-oriented electrical steel sheets in annealing and to an annealing method using the above annealing separator.

[0002] In addition, the present invention also relates to a method for manufacturing a grain-oriented electrical steel sheet using the above annealing separator. Incidentally, as types of grain-oriented electrical steel sheets, there are a steel sheet having a forsterite coating (i.e. forsterite-based coating) and a steel sheet having no forsterite coating, and the present invention relates to manufacturing methods of the respective steel sheets.

Background Art

[0003] An electrical steel sheet is a material which has been widely used as an iron core material for transformers and rotary machines. In particular, a grain-oriented electrical steel sheet is a steel sheet which achieves a significantly superior low iron loss by highly preferentially growing crystal grains in {110}<001>orientation, which is called the Goss orientation. Among properties required for an electrical steel sheet, in particular, iron loss properties are regarded as important properties since they directly relate to an energy loss of a product.

[0004] In addition, in an electrical steel sheet, punchability and bending workability are also important properties. That is, when iron cores of transformers and rotary machines are formed, an electrical steel sheet is formed into a predetermined shape through various processes such as punching, shearing, and bending. In addition, when a steel strip passes through a processing line in which the above various processes are performed, a steel sheet may be warped or the like in some cases. Hence, the properties described above are important.

[0005] In general, a grain-oriented electrical steel sheet is manufactured by a process disclosed in paragraph [0005] of Japanese Unexamined Patent Application Publication No. 2003-41323 and the like. That is, a steel sheet obtained by rolling is processed by recrystallization annealing, and a single batch annealing called final annealing is then carried out. By this batch annealing, the secondary recrystallization is promoted, and as a result, crystal grains in the Goss orientation are highly preferentially grown.

[0006] By the way, a steel sheet which is wound in the form of a coil is heated in batch annealing, and in general, final annealing for manufacturing a grain-oriented electrical steel sheet is necessarily performed at a high temperature; hence, sticking occurs between parts of the steel sheet which is wound in the form of a coil. In order to prevent this sticking, a technique has been widely used in which an annealing separator primarily composed of MgO is applied so as to form a forsterite coating in annealing. It is believed that the forsterite coating is formed by reaction between MgO contained in an annealing separator and SiO_2 contained in oxides formed on a steel sheet surface (however, Fe is also contained in the coating).

[0007] This forsterite coating has superior annealing separation properties and has various advantageous features for the properties of a grain-oriented electrical steel sheet. For example, on the forsterite coating, a hard coating (tensile coating) can be formed with superior adhesion, and by applying a tension to a steel sheet, the iron loss can be decreased.

[0008] On the other hand, since the forsterite coating is a hard glass coating, a grain-oriented electrical steel sheet having a forsterite coating is inferior in both punchability and bending workability. That is, there have been problems in that a punching mold is worn out in a shorter time and in that burrs are formed on a sheared surface of a steel sheet. In addition, since peeling is liable to occur in bending process, superior peeling resistance on bending is required which prevents peeling even when a bending process or the like is performed after stress-relief annealing.

[0009] In order to solve the problems described above, for example, the following have been proposed:

(1) as a method for obtaining a grain-oriented electrical steel sheet having superior workability (in which the workability is regarded as importance), a method for manufacturing a grain-oriented electrical steel sheet without forming a forsterite coating itself which is disadvantageous to the workability; and

(2) in consideration of the importance of low iron losses or the like, a method for forming a forsterite coating having superior peeling resistance on bending which prevents peeling even when a bending process or the like is performed after stress-relief annealing.

[0010] As the method (1), a method for changing a component of an annealing separator has been attempted, that is, a method has been attempted in which an annealing separator containing no MgO which reacts with SiO_2 present on a steel sheet surface is applied after recrystallization annealing, followed by final annealing.

[0011] As annealing separators primarily composed of a material other than MgO, there have been known an annealing separator primarily composed of alumina (powder) disclosed in Japanese Unexamined Patent Application Publication Nos. 6-136448, 7-118750, and 5-156362, and an annealing separator primarily composed of alumina and/or silica disclosed in Japanese Unexamined Patent Application Publication Nos. 11-61261 and 8-134542. These annealing separators may be electrostatically sprayed onto a steel sheet or may be formed into a water slurry or a suspension using an alcohol or the like, followed by application to a steel sheet. However, since having poor adhesion properties to a steel sheet, the above annealing separators are liable to be peeled away while traveling in a production line after application of the annealing separator. As a result, for example, there have been problems in that 1) control of the application amount is difficult, 2) yield of the annealing separator is low, and 3) dust is generated and contamination of a production line may occur thereby.

[0012] As an annealing separator having superior adhesion properties to a steel sheet, an annealing separator primarily composed of colloidal alumina aggregates in the form of feathers has been disclosed in Japanese Unexamined Patent Application Publication No. 10-121142. However, there has been a problem in that this annealing separator is not easily uniformly applied to a steel sheet. In addition, since this annealing separator must be removed by pickling or alkaline washing before an insulating coating is further formed, it is not convenient from a production-process point of view.

[0013] Accordingly, heretofore, as the most practical method, a costly and time-consuming method has been carried out in which after being once formed, a forsterite coating is then removed by pickling, chemical polishing, electrolytic polishing, or the like.

[0014] In addition, an attempt has been made in which a grain-oriented electrical steel sheet having superior workability is manufactured without using an annealing separator. For example, in the Japanese Unexamined Patent Application Publication No. 2000-129356, a technique has been proposed in which crystal grains in the Goss orientation are secondary recrystallized in a composition system containing no inhibitor-forming elements, and it has been also disclosed that by this method, a final annealing temperature is decreased and that an annealing separator is not required. However, even though the temperature is low for final annealing, sticking between steel sheets cannot be totally prevented at such temperature, and in view of stable production, there have been problems.

[0015] On the other hand, as the method (2), a technique has been disclosed in the above Japanese Unexamined Patent Application Publication No. 2003-41323 in which after recrystallization annealing, magnetic properties and coating properties can be simultaneously obtained by performing batch annealing twice with continuous annealing performed therebetween. That is, according to a conventional technique, the progress of secondary recrystallization and the formation of a forsterite coating are both realized in final annealing. However, since optimum annealing conditions for the respective purposes do not coincide with each other, when it is attempted to improve the magnetic properties, the coating properties are degraded, and on the other hand, when it is attempted to improve the coating properties, the magnetic properties are degraded. On the contrary to the above technique, the technique disclosed in Japanese Unexamined Patent Application Publication No. 2003-41323 is to obtain the function of final annealing by performing batch annealing twice so as to promote the secondary recrystallization by first batch annealing and so as to form a forsterite coating by second batch annealing.

[0016] In the above gazette, it is disclosed that when adhesion between steel sheets may occur in the first batch annealing, an annealing separator may be applied. However, when an annealing separator primarily composed of MgO is used in the first batch annealing after the recrystallization annealing, the formation of a forsterite coating in the second batch annealing is adversely influenced, and as a result, it becomes very difficult to obtain superior coating properties. In addition, according to the method disclosed in the above Japanese Unexamined Patent Application Publication No. 2003-41323, although decarburization is preferably performed after the first batch annealing, a coating such as a forsterite coating disadvantageously interferes with the decarburization.

[0017] On the other hand, when it is attempted to perform the first batch annealing without using an annealing separator primarily composed of MgO, various problems similar to those of the above (1) may arise.

Disclosure of Invention

[Problems to be Solved by the Invention]

[0018] The present invention was made to solve the above problems and proposes an annealing separator which contains no MgO, which has superior application properties to a steel sheet and superior adhesion thereto after the application, and which can manufacture a grain-oriented electrical steel sheet without generating a dust problem and line contamination caused thereby, and in addition, the present invention also proposes an annealing method using the above annealing separator.

[0019] In addition, the present invention relates to a method for manufacturing a grain-oriented electrical steel sheet, which is suitably used as an iron core material of transformers and rotary machines, by using the above annealing separator. In particular, the present invention proposes a method for manufacturing a grain-oriented electrical steel sheet having a forsterite coating with superior coating properties and a grain-oriented electrical steel sheet having superior workability without any forsterite coating.

[Means for Solving the Problems]

(4) Method for Manufacturing Grain-Oriented Electric Steel Sheet Having No Forsterite Coating

[0020] The present invention provides a method as defined in claim 1. Preferred embodiments are set out in the dependent claims.

[0021] Further, the method for manufacturing a grain-oriented electrical steel sheet may comprise a step of performing hot rolling of a slab formed from molten steel having a composition in which the content of C is 0.08 mass percent or less, the content of Si is 2.0 to 8.0 mass percent, the content of Mn is 0.005 to 1.0 mass percent, the content of Al is decreased to 150 ppm or less, and the contents of N, S, and Se are each decreased to 50 ppm or less, a step of then performing cold rolling once, or twice or more with intermediate annealing performed therebetween, to obtain a steel sheet having a final sheet thickness, a step of then performing recrystallization annealing, and a step of then performing final annealing in accordance with the annealing method described in the above (1), in which the amount of the annealing separator applied to the steel sheet before annealing in the final annealing is set to 0.005 to 5 g/m^2 per one surface.

[0022] In this preferable embodiment of the present invention, it is preferable that the annealing separator be composed of an Al compound and a Si compound as a primary component, the ratio of the Al compound to the Si compound calculated based on $Al_2O_3/(Al_2O_3+SiO_2)$ be 40 to 95 mass percent, and the annealing separator have a viscosity of 25 mPa·s or less and be in the form of a solution or a colloidal solution.

[0023] Water is preferably used as a base solvent. In addition, the Al compound is preferably at least one of an Al compound having a hydroxyl group and an organic acid group and a dehydrated product (including partly dehydrated product) of an Al compound having a hydroxyl group and an organic acid group. More preferably, the Al compound is at least one of a basic Al acetate, a basic Al formate, a basic Al chloride, a basic Al nitrate, a basic Al oxalate, a basic Al sulfamate, a basic Al lactate, and a basic Al citrate or a mixture containing two or more of the above compounds.

[0024] The present invention preferably provides
annealing of the grain-oriented electrical steel sheet, comprising the steps of applying an annealing separator to a steel sheet and annealing the steel sheet coated with the annealing separator,
wherein the annealing separator comprises an Al compound in the form of a solution or a colloidal solution and further comprises at least one compound selected from the group consisting of a Si compound, a Sr compound, a Ca compound, a Zr compound, a Ti compound, and a Ba compound, the content of the Al compound is 40 to 95 mass percent in terms of a solid component ratio represented by the following equation (2), and the viscosity of the annealing separator is 25 mPa·s or less.

Solid component ratio of Al compound=(solid component of Al compound)/{(solid component of Al compound)+ (solid component of said at least one compound(sum))} ····· equation (2)

[0025] In the above equation, the solid components of the compounds are calculated based on the following respective forms:

the Al compound ····· Al_2O_3, the Si compound ····· SiO_2,
the Sr compound ····· SrO, the Ca compound ····· CaO,
the Zr compound ····· ZrO_2, the Ti compound ····· TiO_2, and
the Ba compound ····· BaO.

[0026] The annealing separator may contain at least one compound selected from the group consisting of the Si compound, the Sr compound, the Ca compound, the Zr compound, the Ti compound, and the Ba compound in the form of a solution or a colloidal solution.

Best Mode for Carrying Out the Invention

[0027] Through intensive research carried out by the inventors of the present invention on an annealing separator having superior application properties and adhesion properties after application, it was discovered that when an annealing separator is composed of an Al compound and a stable compound at a high temperature as a primary component, and when the Al compound is present in the form of a solution or a colloidal solution, the problems described above can be solved. In addition, the inventors of the present invention also found a preferable viscosity of the annealing separator, a preferable solid component ratio of the Al compound, and a preferable amount of the annealing separator applied to a steel sheet. Hereinafter, experiments performed for making the present invention will be described.

<Experiment 1>

[0028] A steel slab was manufactured by continuous casting from a component composition in which 0.020 mass percent of C, 3.30 mass percent of Si, 0.070 mass percent of Mn, and 400 mass ppm of Sb were contained, and the contents of Al, N, S, and Se were decreased to 38 mass ppm, 33 mass ppm, 18 ppm, and less than 10 ppm (less than the analytical limit), respectively. Subsequently, the steel slab was processed by cold rolling once, or twice or more with intermediate annealing performed therebetween, so as to obtain a steel sheet having a final sheet thickness. Next, the steel sheet thus cold-rolled was processed by recrystallization annealing and final annealing.

[0029] In this experiment, before the final annealing, an aqueous colloidal solution (solid component concentration: 3.0 mass percent) of silica sol (colloidal silica) was used as an annealing separator and was applied to surfaces (two surfaces) of the steel sheet in an amount of 0.1 to 3.0 g/m^2 per one surface by a roll coater.

[0030] After the application, baking treatment was performed at ultimate temperature of the steel sheet of 250°C, followed by spontaneous cooling. From the difference in weight of the steel sheet before the application and after the baking treatment, the amount of the annealing separator thus adhered was estimated, and this weight was regarded as an application amount of the annealing separator.

[0031] In the final annealing, after a temperature of 850°C was maintained for 30 hours in a nitrogen atmosphere, a temperature of 1,000°C was then maintained for 5 hours in an Ar atmosphere.

[0032] For the steel sheet thus obtained, three measurement items, that is, the application properties of the annealing separator, adhesion properties thereof after drying, and annealing separation effect in the final annealing were tested.

[0033] The details of the above performance evaluation methods are as follows. Evaluation methods in Experiments 2 and 3, and examples which will be described later are the same as described below.

· Application Properties

[0034] The steel sheet coated with the annealing separator was evaluated by visual inspection.

○: Application is uniformly performed on the entire steel sheet.
Δ: Application is performed on the entire steel sheet but is not uniformly performed.
×: Application is performed on part of the steel sheet and is not performed on the rest thereof.

· Adhesion Properties after Drying

[0035] After the annealing separator was baked, while being processed by brushing for 10 seconds, the steel sheet was washed with running water at a flow rate of approximately 1.0 m/s. Subsequently, after water was removed by a ringer roll, drying was performed at 200°C for 10 seconds. Next, the weight of the steel sheet was again measured, and the application amount of the annealing separator was again calculated. The difference in weight of the annealing separator before and after the water washing was obtained and was regarded as a peeled amount. Based on the peeled amount thus obtained, the evaluation was performed as follows.

○: The peeled amount is 10% or less of the application amount of the annealing separator.
Δ: The peeled amount is more than 10% to less than 80% of the application amount of the annealing separator.
×: The peeled amount is 80% or more of the application amount of the annealing separator.

· Annealing Separation Effect

[0036] While a pressing load of 0.74 MPa was being applied after the application of the separator, the final annealing was performed. Subsequently, stuck steel sheets were separated by a tensile tester to measure a strength required for separation (peeling strength), and the evaluation was then performed as follows.

○: No sticking between steel sheets occurs (peeling strength of 10 N or less).
Δ: Sticking between steel sheets partly occurs (peeling strength in the range of more than 10 N to less than 60 N).
×: Steel sheets are totally stuck to each other (peeling strength of 60 N or more).

[0037] Test results are shown in Table 1. Although the annealing separator used in Experiment 1 had good application properties and annealing separation effect, the adhesion properties to the steel sheet was insufficient under all the conditions.

Table 1

Application amount (g/m^2)	Viscosity (mPa·s)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)
0.1	3.1	○	Δ	0.05	○	3
0.5	3.1	○	Δ	0.20	○	0
1	3.1	○	Δ	0.65	○	0
2	3.1	○	×	1.70	○	0
3	3.1	○	×	2.90	○	2

[0038] According to the above results of Experiment 1, it was understood that although having the annealing separation effect in the final annealing, silica sol has a problem of adhesion properties to a steel sheet as an annealing separator. Accordingly, in order to use silica sol as an annealing separator and in order to improve the adhesion properties to a steel sheet, the effectiveness of addition of an alumina sol as a film-forming component was investigated by the inventors of the present invention.

<Experiment 2>

[0039] In the same manufacturing process as that in Experiment 1, to steel sheet surfaces (two surfaces) before the final annealing, an annealing separator (solid component concentration: 2.0 mass percent) formed of an aqueous colloidal solution primarily composed of an alumina sol (colloidal alumina) and a silica sol was applied in an application amount of 0.5 g/m^2 per one surface by a roll coater. Subsequently, baking was performed at ultimate temperature of the steel sheet of 250°C, followed by spontaneous cooling. Next, as was the case of Experiment 1, after a temperature of 850°C was maintained for 30 hours in a nitrogen atmosphere, a temperature of 1,000°C was maintained for 5 hours in an Ar atmosphere as the final annealing.

[0040] For the steel sheet thus obtained, three measurement items, that is, the application properties of the annealing separator, adhesion properties thereof after drying, and annealing separation effect in the final annealing were tested by methods similar to those in Experiment 1.

[0041] The ratio of the alumina sol to the silica sol was changed in the range of 20 to 100 mass percent based on $Al_2O_3/(Al_2O_3+SiO_2)$, and the viscosity of the annealing separator was changed in the range of 3.5 to 100 mPa·s. In this experiment, the viscosity of the annealing separator was changed by using an alumina sol having a different viscosity. The viscosity of the alumina sol can be controlled, for example, by the shape of sol particles and the solid component ratio thereof. For example, when the appearance of the sol particles is in the form of feathers, a high viscosity is obtained, and when the appearance is similar to a sphere (or a particle shape) or an oval (or a bar shape), a low viscosity is obtained.

[0042] In Table 2, the experimental results are shown which were obtained when the ratio of the alumina sol to the silica sol was changed. When the ratio of the alumina sol was low, the adhesion properties of the annealing separator were insufficient. On the other hand, when the ratio of the alumina sol was excessive, since a film-forming function was excessively enhanced, uniform application to a steel sheet became difficult, and as a result, appearance defects of products occurred. By the way, the annealing separation effect was superior under all the conditions.

[0043] In addition, in Table 3, the experimental results are shown which were obtained when the viscosity of the annealing separator was changed. When the viscosity was increased, the application properties to a steel sheet were seriously degraded, and as a result, part applied with the annealing separator and part not applied therewith were generated. At the part not applied with the annealing separator, sticking between steel sheets occurred; hence, it was understood that in order to ensure superior application properties and to obtain the annealing separation effect, it is necessary to control the viscosity.

Table 2

Alumina sol·silica sol ratio Al_2O_3/ $(Al_2O_3+SiO_2)$: mass%	Viscosity (mPa·s)	Application properties	Adhesion properties of annealing separator	Removed amount (g/m^2)	Annealing separation effect	Peeling strength (N)
10	3.5	○	Δ	0.2	○	0
20	3.5	○	Δ	0.1	○	0
40	3.5	○	○	0.05	○	0
50	3.5	○	○	0	○	0
75	3.5	○	○	0	○	0
90	3.5	○	○	0	○	0
100	3.5	Δ	○	0	○	0

Table 3

Alumina sol·silica sol ratio Al_2O_3/ $(Al_2O_3+SiO_2)$: mass%	Viscosity (mPa·s)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)
60	3.5	○	○	0	○	0
60	10	○	○	0	○	0
60	25	○	○	0	○	10
60	50	×	○	0	Δ	28
60	100	×	○	0	Δ	45

<Experiment 3>

[0044] Next, in the same manufacturing process as that in Experiment 1, to steel sheet surfaces (two surfaces) before the final annealing, an annealing separator (solid component concentration: 2.5 mass percent) formed of an aqueous colloidal solution primarily composed of an alumina sol and a silica sol was applied in a amount in the range of 0.001 to 6 g/m^2 per one surface. The viscosity of the annealing separator was set to 2.5 mPa·s and the ratio of the alumina sol to the silica sol was set to 75 mass percent based on $Al_2O_3/(Al_2O_3+SiO_2)$.

[0045] Subsequently, baking was performed at ultimate temperature of the steel sheet of 250°C, followed by spontaneous cooling. Next, as was the case of Experiment 1, after a temperature of 850°C was maintained for 30 hours in a nitrogen atmosphere, a temperature of 1,000°C was maintained for 5 hours in an Ar atmosphere for the final annealing.

[0046] For the steel sheet thus obtained, three measurement items, that is, the application properties of the annealing separator, adhesion properties thereof after drying, and annealing separation effect in the final annealing were tested by methods similar to those in Experiment 1.

[0047] In Table 4, the experimental results are shown which were obtained when the application amount was changed. When the application amount was excessively small, the annealing separation effect was insufficient, and sticking between steel sheets occurred. On the other hand, when the application amount was increased, the adhesion properties of the annealing separator to a steel sheet were degraded. Accordingly, in order to ensure superior adhesion properties to a steel sheet and to obtain the annealing separation effect, the application amount of the annealing separator is preferably controlled.

Table 4

Alumina sol·silica sol ratio $Al_2O_3/(Al_2O_3+SiO_2)$: mass%	Viscosity (mPa·s)	Application amount (g/m^2)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)
75	2.5	0.001	○	○	0	×	100
75	2.5	0.005	○	○	0	○	10
75	2.5	0.05	○	○	0	○	0
75	2.5	0.5	○	○	0	○	0
75	2.5	1	○	○	0	○	0
75	2.5	2	○	○	0	○	0
75	2.5	3	○	○	0	○	0
75	2.5	6	○	Δ	1.2	○	0

[0048] According to the experimental results described above, it was first discovered that superior application properties and superior adhesion properties after application can be obtained when a compound, such as silica, having superior stability in annealing at a high temperature and an Al compound in the form of a solution or a colloidal solution used as a film-forming component are used as a primary component of the annealing separator, and in addition, when the solid component ratio of the Al compound and the viscosity are controlled. As a result, the present invention was finally made.

[0049] Next, an annealing separator, a method for annealing a grain-oriented electrical steel sheet, and a method for manufacturing a grain-oriented electrical steel sheet, according to the present invention will be described in detail.

[0050] First, the reasons for restriction of the annealing separator will be described. The restriction is generally determined at the point of time when the annealing separator is applied to a steel sheet.

[0051] As a primary component of the annealing separator, an Al compound in the form of a solution or a colloidal solution and a stable compound at a high temperature are used, that is, as the stable compound, at least one know compound other than MgO is used which has superior high temperature stability and which does not react or is unlikely to react in batch annealing. In addition, the stable compound at a high temperature may be in the form of a solution or a colloidal solution as is the Al compound. That is the annealing separator may be in the form of a solution or a colloidal solution.

[0052] In this case, the form of a solution means the state in which the compound is dissolved in a medium such as water or an organic solvent. In addition, the form of a colloidal solution means the state in which particles of the above compound having a size of approximately 100 nm or less are stably dispersed in the above medium with the assistance of structure parts of functional groups or the like, which parts have affinity for the medium. In both cases, liquid used as the medium is collectively called a solvent. Since the colloidal solution does not look like suspension and is transparent, it is similar to a solution; however, when colloidal particles are present, the presence thereof can be confirmed by measurement of light scattering.

[0053] In addition, the primary component indicates a composition component other than an auxiliary agent and an additive which will be described later. Hence, the primary component occupies approximately 65 mass percent or more of the entire annealing separator component (that is, a material forming a solute or colloid) after drying and preferably occupies 75 mass percent or more.

[0054] The liquid used as a solvent is not particularly limited, and either water or an organic solvent may be used. As the organic solvent, although methanol, isopropanol, ethylene glycol or the like may be generally used, the organic solvent is not limited thereto. Water is preferably used as a solvent in view of cost, wide selectability of the compound, and the like. In this case, in order to adjust liquid properties or the like, approximately 50 mass percent or less of an organic solvent may be mixed with water. Hereinafter, an annealing separator which contains water as a primary solvent is called an aqueous annealing separator.

[0055] Since the Al compound and the stable compound at a high temperature hardly react with base iron unlike MgO which is used for a conventional annealing separator, a coating which seriously degrades punching properties such as a forsterite coating is not formed. As a result, in the case in which a grain-oriented electrical steel sheet having superior punchability is supplied, the annealing separator described above is very effective.

[0056] The reason at least two types of compounds are used as a primary component of the annealing separator are to obtain a significant annealing separation effect by the stable compound at a high temperature and also to obtain a superior film-forming effect by the Al compound in the form of a solution or a colloidal solution. When these two compounds are used in combination, an annealing separator for steel sheets can first be obtained having superior application properties and adhesion properties to a steel sheet after application, and in particular, the properties required for an annealing separator for grain-oriented electrical steel sheets can be satisfied.

[0057] In order to ensure the film-forming function, the Al compound is limited to a compound which forms colloid in a solvent such as water. That is, when the Al compound is not in a colloidal state, the film-forming effect cannot be obtained, and as a result, the adhesion properties cannot be obtained. For example, when alumina in the form of a slurry or suspension is applied, the film is not formed. The particle diameter of the colloid of the Al compound is preferably set to approximately 50 nm or less. As for the lower limit, there is not preferable particle diameter limit, and even in the vicinity of the analytical limit, a sufficient effect can be obtained.

[0058] In the case of an aqueous annealing separator, the Al compound is preferably an aluminum compound having a hydroxyl group and an organic acid group and/or a dehydrated product (may include a partly dehydrated product, and hereinafter, the dehydrated product is the same as described above) of the above Al compound. More preferably, the Al compound is Al, an aluminum compound having a hydroxyl group and an organic acid group and/or a dehydrated product thereof. In particular, for example, there may be mentioned at least one of a basic Al acetate, a basic Al formate, a basic Al chloride, a basic Al nitrate, a basic Al oxalate, a basic Al sulfamate, a basic Al lactate, and a basic Al citrate or a mixture containing at least two of the above compounds.

[0059] Among those mentioned above, the basic aluminum acetate has a molecular formula represented by $Al_x(OH)_y(CH_3COO)_z$, (x, y, and z are 1 or more), and in particular, $Al_2(OH)_5(CH_3COO)$ is preferable. This compound can be present in the form of from molecules dissolved in a solvent to colloidal particles of approximately several nanometers and can be preferably used as a coating raw material. According to a thermal analysis, a large peak because of dehydration reaction is observed at 200 to 230°C, and a network structure between molecules is formed through dehydration condensation by heating, thereby forming a film. The basic aluminum acetate or the like may be partly or entirely dehydrated.

[0060] In the case in which an organic solvent is used as a solvent, as a preferable Al compound, a material similar to that used for the aqueous annealing separator may also be used.

[0061] As the stable compound at a high temperature other than MgO, a known compound may be used and is not particularly limited; however, for example, a Si compound, a Sr compound, a Ca compound, a Zr compound, a Ti compound, and a Ba compound may be mentioned. As a particular compound, an oxide such as SiO_2, SrO, TiO_2, BaO, or CaO may be mentioned.

[0062] In order to contain the stable compound at a high temperature in the form of a solution or a colloidal solution, in the case of an aqueous annealing separator, for example, a compound is preferably used which is chemically modified to have a hydrophilic group such as a hydroxyl group. However, in the case of the stable compound at a high temperature, as another method, there may be used a compound in the state in which the surface thereof is covered with a known hydrophilic material in a solvent.

[0063] When an organic solvent is used, based on a concept similar to that described above, the stable compound at a high temperature may be designed by using a lipophilic group or the like.

[0064] By the way, the high temperature in the case of the stable compound at a high temperature indicates an annealing temperature; however, for a grain-oriented electrical steel sheet, a compound which is stable at 1,200°C is satisfactory, and a compound which is stable at 1,300°C is more preferable. A compound which neither reacts by itself nor reacts with a steel sheet or an oxide (such as SiO_2, FeO, Fe_3O_4, or Fe_2SiO_4) on the surface thereof at the temperatures mentioned above may be used as the stable compound at a high temperature.

[0065] When each of the above compounds is present together with the Al compound, an effect of improving the application properties of an annealing separator can be obtained, and among the above compounds, a Si compound is preferable in view of the application properties, annealing separation properties, and the like. As the Si compound, silica in the form of colloid, that is, so-called colloidal silica is particularly preferable because of a relatively low cost in addition to high stability with an alumina sol. The colloidal silica is inorganic colloid primarily composed of SiO_2 and is often amorphous.

[0066] Although an Al compound (hereinafter referred to as "non-colloidal Al compound") which is not in the form of a solution nor a colloidal solution, such as alumina particles, is stable at a high temperature, the effect of improving the application properties of the Al compound in the form of a solution or a colloidal silica is not significant. Hence, although addition of the non-colloidal Al compound as part of a primary component is not prohibited, a compound which is stable at a high temperature other than the non-colloidal Al compound is preferably contained. In addition, the non-colloidal Al compound is not taken into calculation of the solid component ratio which will be described later.

[0067] The Al compound preferably has a solid component ratio of 40 to 95 mass percent which is represented by the following equation (1).

Solid component ratio of Al compound=(solid component of Al compound)/{(solid component of Al compound)+ (solid component of stable compound at a high temperature(sum))} ····· equation (1)

[0068] However, the solid component of the Al compound is calculated based on the form of Al_2O_3 and that of the stable compound at a high temperature is calculated based on the form of a primary compound obtained after baking. For example, when a silica sol is used, silica, that is, SiO_2 is a primary compound, and when a titania sol is used, titania, that is, TiO_2 is a primary compound. In addition, when a baking step is not particularly provided, calculation is performed based on a primary compound which is obtained when baking treatment is performed.

[0069] When the solid components are practically only formed of the compounds described above, the equation (1) can be represented by the following equation (3).

Solid component ratio of Al compound=(solid component of Al compound)/(total solid component) ····· equation (3)

[0070] In the above equation, the solid component indicates the quantity contained in an annealing separator component after drying.

[0071] When the solid component ratio of the Al compound is 40 mass percent or less, the Al compound which is a film-forming component is not sufficient, and hence the adhesion properties of the annealing separator become insufficient. In addition, when the solid component ratio is more than 95 mass percent, the amount of a highly reactive Al compound is excessively increased, and as a result, the coating liquid is not stabilized. Hence, a uniform coating cannot be formed, and as a result, a product with defective appearance is obtained. The solid component ratio of the Al compound is preferably 50 mass percent or more, more preferably 60 mass percent or more, and even more preferably 70 mass percent or more.

[0072] As the stable compound at a high temperature, when at least one compound selected from the group consisting of a Si compound, a Sr compound, a Ca compound, a Zr compound, a Ti compound, and a Ba compound is used, the solid component ratio of the Al compound can be represented by the following equation (2).

Solid component ratio of Al compound=(solid component of Al compound)/{(solid component of Al compound)+ (solid component of said at least one compound (sum)} ····· equation (2)

[0073] However, the solid components of the above compounds are preferably calculated based on the following respective forms:

the Al compound ····· Al_2O_3, the Si compound ····· SiO_2,
the Sr compound ····· SrO, the Ca compound ····· CaO,
the Zr compound ····· ZrO_2, the Ti compound ····· TiO_2, and
the Ba compound ····· BaO.

[0074] When a Si compound is used as the stable compound at a high temperature, that is, when the solid component is primarily composed of an Al compound and a Si compound, the ratio of the Al compound to the Si compound calculated based on $Al_2O_3/(Al_2O_3+SiO_2)$ is preferably set to 40 to 95 mass percent.

[0075] The viscosity of the annealing separator is set to 25 (mPa·s) or less. When the viscosity is more than 25 (mPa·s), the application properties are seriously degraded, so that uniform application of the annealing separator to a steel sheet is interfered with. In addition, as a result, part which is not coated with the annealing separator is generated, and hence adhesion between steel sheets occurs in final annealing. The viscosity of the present invention is a viscosity of the annealing separator at a liquid temperature of 25°C measured by an Oswald viscometer.

[0076] When a colloidal slurry is used instead of the colloidal solution, uniform coating cannot also be obtained. Some reasons for this are believed that the viscosity is not appropriate and that the change in viscosity is large due to aggregation of colloidal particles in the slurry.

[0077] Furthermore, when S (elemental substance) or a compound containing S (hereinafter, the above two are collectively called "S-containing compound") is added to the annealing separator as an auxiliary agent, superior magnetic properties can be stably imparted to a grain-oriented electrical steel sheet. Although the reason for this has not been clearly understood, it is construed that a S-containing compound is decomposed in batch annealing, and that the S then enters the steel and is segregated in grain boundaries. That is, it is believed that by the S thus segregated, grain growth is suppressed and that as a result, secondary recrystallization is stabilized.

[0078] When the amount of the segregated S is excessive, secondary recrystallization defects may adversely occur in some cases. In order to preferentially avoid this type of defect, the amount of a S-containing compound for addition is preferably set to approximately 25 mass percent or less in terms of the solid component ratio to the annealing separator component after baking. In addition, even when a baking step is not particularly provided, evaluation is performed based on the solid component ratio of a S-containing compound which is to be formed when baking treatment is performed.

[0079] The S-containing compound is not particularly limited; however, an inorganic S compound such as a sulfate (including a sulfite) or a metal sulfide is preferably used. In particular, for example, strontium sulfate, magnesium sulfate, and magnesium sulfide may be mentioned.

[0080] As an application mean of an annealing separator, various methods generally used for industrial purposes, such as roll coater, flow coater, spray, and knife coater, may be used.

[0081] In addition, the annealing separator of the present invention is preferably baked by heating after application. As a baking method, for example, a general method, such as a hot-wind type, an infrared type, or an induction heating type method, may be used. Conditions of baking treatment may be determined in consideration of various situations; however, in general, a preferable temperature is in the range of approximately 150 to 400°C, and a preferable time is in the range of approximately 1 to 300 seconds.

[0082] In order to further improve the properties such as the application properties of an annealing separator and the adhesion properties thereof to a steel sheet, additives such as a surfactant and/or a corrosion inhibitor may also be blended. The content of an additive is preferably set to 10 mass percent or less to the annealing separator component after baking in order to maintain a sufficient annealing separation effect as the annealing separator.

[0083] As the surfactant, commercial available nonionic, anionic, cationic surfactants may all be used.

[0084] As is the surfactant, a corrosion inhibitor type is not particularly limited, and commercially available products may be used.

[0085] Although being particularly preferably applied to a grain-oriented electrical steel sheet, the annealing separator of the present invention is not prohibited to be applied to other steel sheets.

[0086] In addition, the annealing separator of the present invention is effective when a steel strip wound in the form of a coil is heated in a furnace; however, it may also be applied to the case in which steel sheets which are piled up are processed by heat treatment.

[0087] Next, preferable conditions for manufacturing a grain-oriented electrical steel sheet in accordance with the present invention will be described.

[0088] To the composition of a product sheet and that of a starting material (molten steel or steel slab), known components preferably used for a grain-oriented electrical steel sheet may all be applied. Hereinafter, as for preferable molten steel components of a representative composition, the reasons for restriction of the respective components will be described.

C: 0.08 mass percent or less

[0089] When the content of C is more than 0.08 mass percent, it becomes difficult to decrease the content to 50 mass ppm or less (at which no magnetic aging occurs) in a manufacturing process, and hence the content is preferably set to 0.08 mass percent of less. In particular, although the lower limit is not necessarily determined, from an industrial point of view, the lower-limit is approximately 5 mass ppm.

Si: 2.0 to 8.0 mass percent

[0090] Si is an effective element which increases the electrical resistance of steel and which improves the iron loss, and in order to obtain the above effect, the content is preferably set to 2.0 mass percent or more. On the other hand, when the content is more than 8.0 mass percent, the workability and magnetic flux density are degraded, and hence the upper limit is preferably set to 8.0 mass percent. Hence, a preferable content of Si is in the range of 2.0 to 8.0 mass percent.

Mn: 0.005 to 1.0 mass percent

[0091] Mn is an effective element which improves the hot workability, and the content is preferably set to 0.005 mass percent or more. On the other hand, when the content of Mn is excessive, the magnetic flux density is decreased. Accordingly, in view of the above point, a preferable content of Mn is 1.0 mass percent or less. Hence, the content of Mn is preferably set in the range of 0.005 to 1.0 mass percent.

[0092] In manufacturing a grain-oriented electrical steel sheet, in order to develop the Goss orientation in secondary recrystallization, an element (inhibitor-forming element) forming an inhibitor is generally added. However, it has also been understood in recent years that when impurity elements in steel are decreased, the Goss orientation can be developed without using an inhibitor.

[0093] In order to obtain the Goss oriented crystal grains by secondary recrystallization without using an inhibitor, the content of Al is preferably decreased to 150 mass ppm or less, and the contents of N, S, and Se are also preferably decreased to 50 mass ppm or less. The elements mentioned above are preferably decreased as small as possible in view of magnetic properties, and for example, the content of Al is more preferably decreased to 100 mass ppm or less. However, when the components described above are decreased, the cost may be increased in some cases; hence, when the components in the range described above are allowed to remain, any problems may not occur at all. The lower-limit content of each element determined from a cost reduction point of view is currently approximately 10 mass ppm.

[0094] When an inhibitor is used, the above elements are inversely added in accordance with the inhibitor which is to be used. For example, it is generally performed that when AlN is used as an inhibitor, 0.015 to 0.04 mass percent of Al and 0.005 to 0.015 mass percent of N are added; when BN is used, 0.001 to 0.006 mass percent of B and 0.005 to 0.015 mass percent of N are added; when MnSe and/or MnS is used, 0.005 to 0.06 mass percent of at least one of Se and S is added.

[0095] In addition, Sb and/or Sn in a total amount of approximately 0.005 to 0.1 mass percent is preferably added to a grain-oriented electrical steel sheet since the magnetic properties are further improved.

[0096] Besides the above elements, when Ge, Mo, Te, and Bi each in an amount of 0.1 mass percent or less, P, Cu, and Cr each in an amount of 0.2 mass percent or less, and Ni in an amount of 0.5 mass percent or less are contained, any particular problems may not arise. In addition, the balance is preferably composed of iron and inevitable impurities.

[0097] From molten steel having the above components, a slab having a common dimension may be manufactured by a common ingot casting method or continuous casting method or a thin cast slab (so-called thin slab) having a thickness of 100 mm or less may be manufactured by a direct casting method. A slab is reheated and then hot-rolled by a common method; however, without performing heating after casting, hot rolling may be directly performed. In the case of a thin cast slab, hot rolling may be performed, or without performing hot rolling, subsequent steps may be performed.

[0098] The hot-rolled steel sheet is then annealed (normalizing) whenever necessary. In particular, when a band texture is formed in hot rolling, in order to realize a primary recrystallization texture of uniform-sized grains so as to promote development of secondary recrystallization, hot-rolled steel sheet annealing is preferably performed.

[0099] In order to dissolve the band texture, the temperature for hot-rolled steel sheet annealing is preferably increased to 800°C or more. On the other hand, in order to realize a primary crystallization texture of uniform-sized grains, it is not preferable when the grain diameter becomes excessively large and coarse by hot-rolled steel sheet annealing, and hence the hot-rolled steel sheet annealing temperature is preferably set to 1,100°C or less. Hence, in order to highly develop the Goss oriented texture in a product sheet, the hot-rolled steel sheet annealing temperature is preferably set in the range of 800 to 1,100°C. In addition, a preferable annealing time of the hot-rolled steel sheet annealing is 1 to 300 seconds.

[0100] Next, after forming a cold-rolled steel sheet by performing cold rolling once or more, recrystallization annealing is performed. When cold rolling is performed twice or more, intermediate annealing is performed between cold rolling steps. The intermediate annealing is preferably performed at 900 to 1,200°C for approximately 1 to 300 seconds.

[0101] In order to further develop the Goss oriented texture, the temperature of cold rolling may be increased to 100 to 250°C. This is sometimes called warm rolling; however, in the present invention, this rolling is regarded as one type of cold rolling. For the same purpose as described above, during cold rolling, aging treatment at a temperature in the range of 100 to 250°C may be performed once or more.

[0102] The recrystallization annealing is mainly performed in order to form a primary recrystallization texture and is preferably performed by continuous annealing. In the recrystallization annealing, when decarburization is required, a humid atmosphere is used; however, when decarburization is not required, a dry atmosphere may be used. As preferable recrystallization annealing conditions, the temperature is 750 to 1,100°C and the time is approximately 1 to 300 seconds.

[0103] When the content of C in a steel sheet in the secondary recrystallization annealing (final annealing, or a first batch annealing step when the final annealing is performed by two batch annealing steps) is controlled in the range of

100 to 250 mass ppm, particularly in a grain-oriented electrical steel sheet containing no inhibitor, it is preferable in order to improve the magnetic flux density. The control of the amount of C may be performed by the recrystallization annealing or may be subsequently performed in a different step.

[0104] A technique in which the amount of Si is increased by siliconizing method may be applied to a steel sheet after, for example, the recrystallization annealing.

[0105] The annealing separator of the present invention is applied before or after the recrystallization annealing.

[0106] Since a conventional annealing separator has inferior adhesion properties to a steel sheet, application thereof before recrystallization annealing cannot be performed since line contamination occurs by peeling of the annealing separator during the recrystallization annealing. This situation is similar to the case of an annealing separator primarily composed of MgO which requires long-time heating for forming a coating. However, since the annealing separator of the present invention has superior adhesion properties to a steel sheet and will not cause line contamination by peeling, the application may be performed either before or after the recrystallization annealing.

[0107] In this process, the application amount of the annealing separator of the present invention is preferably set to 0.005 g/m^2 or more in order to obtain sufficient effect of preventing adhesion between steel sheets. On the other hand, in order to ensure the adhesion properties of the annealing separator, the application amount thereof is preferably set to 5 g/m^2 or less. Hence, the application amount of the annealing separator is preferably set in the range of 0.005 to 5 g/m^2. A more preferable lower limit is 0.05 g/m^2 and a more preferable upper limit is 2 g/cm^2.

[0108] Although the preferable application amount in manufacturing a grain-oriented electrical steel sheet is as described above, in accordance with various heat treatment conditions and required quality, an amount of the annealing separator, which is outside the range described above, may also be used.

[0109] The annealing separator may be applied only to one surface of a steel sheet; however, in order to reliably obtain the effect, application is preferably performed on the two surfaces. The change in composition or the like of the annealing separator between the front and the rear surfaces of a steel sheet is not prohibited; however, from a manufacturing point of view, the same annealing separator is preferably applied to the two surfaces.

[0110] When a grain-oriented electrical steel sheet is manufactured which has no forsterite coating and which has superior magnetic properties and workability, after the recrystallization annealing and the application of the annealing separator of the present invention, final annealing is performed by batch annealing. The purpose of the final annealing is to promote the secondary recrystallization and to decrease impurities (purification). As the annealing conditions, known conditions which can achieve those purposes may be used. Although a preferable final annealing temperature is approximately 750 to 1,300°C, the temperature may be set to approximately 750 to 1,000°C in the first half and may be set to approximately 900 to 1,300°C in the second half. In this case, the secondary recrystallization is primarily promoted in the first half, and the purification is primarily promoted in the second half. As a preferable final annealing time, a holding time in the above temperature range is approximately 1 to 300 hours.

[0111] In a conventional technique in which an annealing separator primarily composed of MgO is used, since a thick coating is formed, a time required for the purification becomes longer than that in the case in which an annealing separator is not used. However, according to the annealing separator of the present invention, although the Al compound forms a coating, an effect in which the purification is not interfered with can be observed.

[0112] In the case in which the final annealing is performed while the content of C is maintained at approximately 100 to 250 mass ppm in order to improve the magnetic properties, the content of C is preferably decreased, after the secondary recrystallization is performed, to 50 ppm or less at which no magnetic aging occurs. As a method for decreasing the content of C, there may be mentioned a method in which decarburization is performed during the final annealing and a method in which a decarburization step is additionally performed after the final annealing. In order to perform decarburization during the final annealing, high temperature annealing at 1,000°C or more in an atmosphere containing hydrogen may be performed during the final annealing, and in particular, during the second half thereof.

[0113] As the decarburization step additionally performed after the final annealing, for example, (1) annealing (decarburization annealing) in an oxidizing atmosphere, (2) surface polishing for mechanically removing graphite in a surface layer, and (3) chemically removing graphite in a surface layer such as electrolytic washing, chemical polishing or plasma irradiation are effectively performed. The reasons the decarburization can be performed by the methods (2) and (3) are that by the end of the final annealing, C in the form of graphite precipitates in the surface layer of a steel sheet, and decarburization inside the steel is already completed.

[0114] As for a phenomenon in which graphite precipitates in a surface layer of a steel sheet as described above, for example, the mechanism is construed as follows. C forms a metastable cementite in steel; however, in an activated state in which surface energy is high, graphite is formed. Hence, before precipitating as cementite in base iron during cooling, C precipitates in the form of graphite in a surface layer. By the way, in consideration of the phase diagram of pure iron, the solubility of graphite is slightly lower than that of cementite. Hence, it is believed that since solid solution C in a surface layer is decreased to a concentration which is equilibrium with graphite, the concentration gradient between the solid solution C in the surface layer and that in the base iron is generated, and hence decarburization from the base iron proceeds.

[0115] However, when a dense or firm coating layer is formed on the surface in the final annealing (for example, when a conventional annealing separator primarily composed of MgO is used), surface activation is interfered with, and as s result, the precipitation of graphite in a surface layer of a steel sheet is also interfered with. The coating formed from the annealing separator of the present invention has superior adhesion properties; however, the precipitation of graphite in a surface layer of a steel sheet is not adversely influenced although the reason for this has not been understood, and hence the above decarburization method can be preferably used.

[0116] After the final annealing, in order to decrease the iron loss, the shape is effectively corrected by applying a tensile strength through flattening annealing. When this flattening annealing is performed in a humid atmosphere, the decarburization may be simultaneously performed (one type of method (1) described above).

[0117] In addition, the technique for increasing the amount of Si by a siliconizing method may be further employed after the final annealing. This technique is effectively used in order to further decrease the iron loss.

[0118] In the case in which steel sheets are laminated for forming an iron core, when insulating coating is performed on the surfaces of the steel sheets after the flattening annealing, the iron loss of the laminate is effectively improved. In particular, in order to ensure superior punchability, an organic coating containing a resin is preferably used as the insulating coating. On the other hand, in order to preferentially obtain the weldability, an inorganic coating is preferably used as the insulating coating.

[0119] In addition, a step only for removing the annealing separator is not particularly required.

[0120] When a grain-oriented electrical steel sheet having superior forsterite coating properties and magnetic properties is manufactured, after the recrystallization annealing and the application of the annealing separator of the present invention, first batch annealing is performed in order to realize the secondary recrystallization. In this case, as the annealing conditions, known annealing conditions which can promote the secondary recrystallization may be used. As preferable conditions, the temperature is approximately 750 to 1,100°C and the time is approximately 1 to 300 hours.

[0121] Subsequently, although the forsterite coating is formed in second batch annealing, as a preparation stage therefor, subscale formation is first performed by continuous annealing. When the first batch annealing is performed while a predetermined amount of C is contained in order to improve the magnetic properties, in this continuous annealing forming the subscale, decarburization is preferably simultaneously performed. For annealing conditions (time, temperature, atmosphere, and the like) of the above continuous annealing, known annealing conditions may be used so as to easily and stably form the forsterite coating in a subsequent batch annealing. A preferable annealing temperature is approximately 750 to 1,000°C, a preferable annealing time is approximately 1 to 300 seconds, and a preferable atmosphere is an oxidizing atmosphere containing a hydrogen gas and a nitrogen gas.

[0122] Before the above continuous annealing, a step of removing the annealing separator of the present invention is not necessary. That is, even when the forsterite coating is applied to a steel sheet with the annealing separator of the present invention provided therebetween, the adhesion properties of the forsterite coating are superior, and in addition, the purification is not interfered with by the presence of the annealing separator of the present invention.

[0123] Next, an annealing separator primarily composed of MgO is applied to the surface of the steel sheet, followed by the second batch annealing. Since this second batch annealing is performed for forming the forsterite coating and for the purification to reduce impurities, known annealing conditions which can achieve these two purposes may be used. A preferable annealing temperature is approximately 900 to 1,300°C, and a preferable annealing time is approximately 1 to 300 hours. As the annealing separator primarily composed of MgO, a known compound may be used. For example, a compound is preferably used in which approximately 80 to 99 mass percent of MgO as a solid component and, whenever necessary, at least one of TiO_2, $SrSO_4$, $MgSO_4$ and the like as the balance are contained.

[0124] After the second batch annealing, the technique may be further used in which the amount of Si is increased by a siliconizing method.

[0125] Subsequently, a tensile coating is finally applied whenever necessary, followed by baking. In addition, the shape may be corrected by flattening annealing, and furthermore, flattening annealing which simultaneously bakes the tensile coating may also be performed.

[0126] The grain-oriented electrical steel sheet of the present invention indicates an electrical steel sheet in which the secondary recrystallization is realized. Hence, in addition to the Goss oriented grains, the case in which Cube oriented grains ({100}<001>orientation or {100}<011>orientation) are recrystallized is also included in Claims of the present invention. A texture in which crystal grains are preferentially oriented in the Cube orientation can be formed by a known method, and for example, it may be performed by the control of a rolling texture; however, a process after the recrystallization annealing is approximately similar to that for realizing the secondary recrystallized grains which are preferentially oriented in the Goss orientation.

[Examples]

(Example 1)

[0127] By the following method, a grain-oriented electrical steel sheet having superior forsterite coating properties and magnetic properties was manufactured.

[0128] A steel slab which contained 0.020 mass percent of C, 3.35 mass percent of Si, 0.050 mass percent of Mn, and 380 mass ppm of Sb, and which also contained 320 mass ppm of Al and 80 mass ppm of N as an inhibitor-forming element, the balance being iron and inevitable impurities, was manufactured by continuous casting. After being heated to 1,200°C, the steel slab was hot-rolled to form a hot-rolled steel sheet having a thickness of 2.0 mm, followed by hot-rolled steel sheet annealing at 1,050°C for 60 seconds. Next, a cold-rolled steel sheet having a thickness of 0.30 mm was formed by cold rolling, followed by recrystallization annealing at 900°C for 10 seconds in a dry atmosphere having a dew point of -45°C.

[0129] After the recrystallization annealing, first batch annealing was performed. An annealing separator shown in Table 5 was applied before or after the recrystallization annealing. The application of the annealing separator was performed by a roll coater, and baking treatment was then performed at ultimate temperature (sheet temperature) of the steel sheet of 250°C, followed by spontaneous cooling. The baking was performed by direct flame of a propane gas. The first batch annealing was performed at 850°C for 40 hours in a nitrogen atmosphere, so that the secondary recrystallization was completed.

[0130] Subsequently, the application properties of the annealing separator, the adhesion properties thereof after drying, and the annealing separation effect after the first batch annealing were respectively examined, and samples having superior properties were further processed in subsequent steps, so that product sheets were obtained.

[0131] In the subsequent steps, first, continuous annealing was performed for forming superior subscale, and an annealing separator primarily composed of MgO was then applied. Since the first batch annealing was performed while 100 to 150 mass ppm of C remained, in the continuous annealing performed for this subscale formation, decarburization was also simultaneously performed. The continuous annealing was performed at 835°C for 120 seconds in an oxidizing atmosphere having a dew point of 55°C.

[0132] As an annealing separator used for the second batch annealing, a compound containing 95 mass percent of MgO and 5 mass percent of TiO_2 as a solid component was used. Subsequently, the second batch annealing was performed at 1,200°C for 5 hours in a dry hydrogen atmosphere.

[0133] Finally, application of a tensile coating, baking thereof, and stress-relief annealing were performed. The tensile coating was composed of a compound containing phosphoric acid, chromic acid, and colloidal silica and was baked at a temperature of 800°C. The stress-relief annealing was performed at 800°C for 3 hour in a nitrogen atmosphere.

[0134] Table 5 shows the components of the annealing separator and the application conditions thereof. Annealing separators containing powdered SiO_2 and/or Al_2O_3 as a primary component other than No. 26 were applied in the form of an aqueous slurry, and No. 26 was suspended in an alcohol so as to have a solid component of 5 mass percent and was then applied by spraying. Although the dilution ratios were varied depending on the application amount, annealing separators primarily composed of a compound other than a powder were diluted with water to form a colloidal solution, followed by application. As an auxiliary agent, 3 percent by weight of strontium sulfate, magnesium sulfate, or magnesium sulfide was added as shown in the table. A solid component other than that shown in Table 5 was not added; however, whenever necessary, 0.5 mass percent or less of a surfactant (non-ionic type) or the like was added.

[0135] As for the annealing separators used in the first batch annealing, the order of the step of applying the annealing separator (classification was made whether the application was performed before or after the recrystallization annealing), the application properties of the annealing separators, the adhesion properties thereof after drying, and the annealing separation effect after the first batch annealing are shown in Table 6.

[0136] In Nos. 14 and 19, since the viscosity of the annealing separator was out of the range of the present invention, the application properties were seriously inferior, and at parts of a steel sheet to which the annealing separator could not be applied, sticking therebetween occurred. In Nos. 12 and 15, the ratio of the Al compound to the Si compound was outside of a preferable range of the present invention. In No. 12, since the content of the Al compound served as a film-forming component was small, the adhesion of the annealing separator to a steel sheet was inferior. On the other hand, in No. 15, the content of a highly reactive Al compound is large, the coating liquid was not stabilized, and hence a uniform coating could not be formed. As a result, appearance defects occurred.

[0137] In Nos. 1 to 4, since the primary component was other than that of the present invention, the adhesion properties to a steel sheet were insufficient. Since the application amount of the annealing separator was not sufficient in No. 5, adhesion between steel sheets occurred in the final annealing. Since the application amount of the annealing separator was excessive in No. 17, the adhesion to a steel sheet was insufficient, and hence peeling occurred.

[0138] In Nos. 3, 4, 6, 7, 12, and 26, two cases were performed, that is, the application of the annealing separator was performed before the recrystallization annealing in one case and was performed after the recrystallization annealing in the other case. The annealing separators of the present invention showed superior application properties, adhesion properties after drying, and annealing separation effect after the first batch annealing regardless of the order of the step of applying the annealing separator. In Nos. 3, 4, and 26, which were comparative examples, different annealing separation effects were observed depending on the order of the step of applying the annealing separator. The reason for this is believed that when the application was performed before the recrystallization annealing, since the annealing separator having inferior adhesion to a steel sheet was peeled away, the amount of the annealing separator provided on the steel sheet was decreased in the first batch annealing, and hence adhesion between steel sheets occurred. On the other hand, when the application was performed after the recrystallization annealing, the peeled amount of the annealing separator was small, and an amount required for preventing the adhesion between steel sheets remained. Hence, it is believed that no adhesion between steel sheets occurred.

[0139] Table 7 shows the magnetic properties, forsterite coating properties, and contents (in base iron, that is, each content was obtained by analysis performed after a coating on a steel sheet surface was removed) of Al, C, N, S, and Se after the second batch annealing, which were obtained when the samples coated with the annealing separators of the present invention were processed by the subsequent steps to form product sheets. The forsterite coating properties were evaluated by a minimum bending radius at which coating peeling was not generated when a sample processed by stress-relief annealing was wound around a cylinder. The magnetic properties were measured in accordance with JIS C2550 using an Epstein test piece having a size of 30x300 mm. B_8 indicates a magnetic flux density (T) at a magnetic force of 800 A/m, and $W_{17/50}$ indicates an iron loss value (W/kg) at a frequency of 50 Hz and at a maximum magnetic flux density of 1.7 T.

[0140] When the annealing separators of the present invention were used, the magnetic properties and the forsterite coating properties were compatibly obtained, and in addition, purification to reduce impurities was performed without causing any problems. In addition, when a compound containing S was added as an auxiliary agent (Nos. 8, 10, and 11), further improvement in magnetic properties was observed.

Table 5

No.	Primary component of separator			Application amount (g/m^2)	Viscosity (mPa·s)	Alumina(sol) silica(sol) ratio $Al_2O_3/(Al_2O_3+SiO_2)$:mass%	Remarks
	Al compound	Si compound	Others				
1	Powdered Al_2O_3	-	-	1.2	-	100	Comparative example
2	-	Powdered SiO_2	-	1.2	-	0	Comparative example
3	Powdered Al_2O_3	Powdered SiO_2	-	1.2	-	60	Comparative example
4	-	Colloidal silica	-	1.2	2.5	0	Comparative example
5	Basic Al acetate	Colloidal silica	-	0.001	1.8	75	Comparative example
6	Basic Al acetate	Colloidal silica	-	0.05	1.8	75	Example
7	Basic Al acetate	Colloidal silica	-	0.1	1.8	75	Example
8	Basic Al acetate	Colloidal silica	Sr sulfate	0.1	1.8	75	Example
9	Basic Al acetate	Colloidal silica	-	0.5	1.8	75	Example
10	Basic Al acetate	Colloidal silica	Mg sulfate	0.5	1.9	75	Example
11	Basic Al acetate	Colloidal silica	Mg sulfide	0.5	1.7	75	Example

(continued)

No.	Primary component of separator			Application amount (g/m^2)	Viscosity (mPa·s)	Alumina(sol) silica(sol) ratio $Al_2O_3/(Al_2O_3+SiO_2)$:mass%	Remarks
	Al compound	Si compound	Others				
12	Basic Al acetate	Colloidal silica	-	1.2	3.2	25	Example
13	Basic Al acetate	Colloidal silica	-	1.2	1.8	75	Example
14	Basic Al acetate	Colloidal silica	-	1.2	50	75	Comparative example
15	Basic Al acetate	-	-	1.2	2.5	100	Comparative example
16	Basic Al acetate	Colloidal silica	-	3	1.8	75	Example
17	Basic Al acetate	Colloidal silica	-	6	1.8	75	Comparative example
18	Basic Al chloride	Colloidal silica	-	1.2	1.9	75	Example
19	Basic Al chloride	Colloidal silica	-	1.2	100	75	Comparative example
20	Basic Al nitrate	Colloidal silica	-	1.2	3.5	75	Example
21	Basic Al formate	Colloidal silica	-	1.2	2.1	75	Example
22	Basic Al lactate	Colloidal silica	-	1.2	2.5	75	Example
23	Basic Al citrate	Colloidal silica	-	1.2	2.4	75	Example
24	Basic Al oxalate	Colloidal silica	-	1.2	3.1	75	Example
25	Basic Al sulfamate	Colloidal silica	-	1.2	2.8	75	Example
26	Powdered Al_2O_3	Powdered SiO_2	-	1.2	1.6*	75	Comparative example
*: After components are suspended in an alcohol having a viscosity of 1.6, spray coating is performed.							

Table 6

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	Remarks
1	After	○	×	1.10	○	0	Comparative example

(continued)

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	Remarks
2	After	○	×	1.05	○	0	Comparative example
3	Before	○	×	1.05	×	65	Comparative example
	After	○	×	1.10	○	0	Comparative example
4	Before	○	×	1.10	Δ	50	Comparative example
	After	○	×	1.00	○	0	Comparative example
5	After	○	○	0	×	90	Comparative example
6	Before	○	○	0	○	5	Example
	After	○	○	0	○	5	Example
7	Before	○	○	0	○	2	Example
	After	○	○	0	○	3	Example
8	After	○	○	0	○	2	Example
9	After	○	○	0	○	0	Example
10	After	○	○	0	○	0	Example
11	After	○	○	0	○	0	Example
12	Before	○	Δ	0.80	○	0	Example
	After	○	Δ	0.75	○	0	Example
13	After	○	○	0	○	0	Example
14	After	×	○	0	Δ	20	Comparative example
15	After	Δ	○	0	○	0	Comparative example
16	After	○	○	0.15	○	0	Example
17	After	○	Δ	1.5	○	0	Comparative example
18	After	○	○	0	○	0	Example
19	After	×	○	0	Δ	40	Comparative example
20	After	○	○	0	○	0	Example
21	After	○	○	0	○	0	Example
22	After	○	○	0	○	0	Example
23	After	○	○	0	○	0	Example

(continued)

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	Remarks
24	After	○	○	0	○	0	Example
25	After	○	○	0	○	0	Example
26	Before	○	×	1.0	×	70	Comparative example
	After	○	×	1.0	○	0	Comparative example

Table 7

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after second batch annealing) (mass ppm)					Remarks
					Al	N	C	S	Se	
6	Before	1.90	1.03	25	5	<5	10	<4	<10	Example
7	Before	1.91	1.03	30	5	<5	5	<4	<10	Example
8	After	1.92	0.98	30	8	<5	10	5	<10	Example
9	After	1.91	1.03	25	9	<5	8	<4	<10	Example
10	After	1.92	0.99	30	5	<5	8	6	<10	Example
11	After	1.92	0.97	30	7	<5	6	5	<10	Example
13	After	1.90	1.05	35	5	<5	10	<4	<10	Example
16	After	1.89	1.06	30	8	<5	8	<4	<10	Example
18	After	1.90	1.04	25	9	<5	13	<4	<10	Example
20	After	1.91	1.04	30	5	<5	15	5	<10	Example
21	After	1.90	1.05	30	6	<5	11	<4	<10	Example
22	After	1.89	1.05	25	6	<5	6	<4	<10	Example
23	After	1.90	1.03	30	8	<5	7	5	<10	Example
24	After	1.91	1.02	30	8	<5	9	5	<10	Example
25	After	1.91	1.02	25	7	<5	9	<4	<10	Example

(Example 2)

[0141] By the following method, a grain-oriented electrical steel sheet having superior forsterite coating properties and magnetic properties was manufactured.

[0142] A steel slab containing no inhibitor-forming elements was manufactured by continuous casting, in which 0.019 mass percent of C, 3.28 mass percent of Si, 0.073 mass percent of Mn, and 330 mass ppm of Sb were contained, and in which the contents of Al, N, S, and Se were decreased to 38 mm ppm, 30 mass ppm, 18 mass ppm, and less than

10 mass ppm (lower than the analytical limit), respectively. In this slab, the balance was iron and inevitable impurities. After being heated to 1,200°C, the steel slab was hot-rolled to form a hot-rolled steel sheet having a thickness of 2.0 mm, followed by hot-rolled steel sheet annealing at 1,050°C for 60 seconds.

[0143] Next, a cold-rolled steel sheet having a thickness of 0.30 mm was formed by cold rolling, followed by recrystallization annealing at 900°C for 10 seconds in a dry atmosphere having a dew point of -45°C.

[0144] After the recrystallization annealing, the first batch annealing was performed. The annealing separator was applied before or after the recrystallization annealing according to Table 8. The application of the annealing separator was performed by a roll coater, and baking treatment was then performed at ultimate sheet temperature of 250°C, followed by spontaneous cooling. The baking was performed by direct flame of a propane gas. The first batch annealing was performed at 865°C for 50 hours in a nitrogen atmosphere, so that the secondary recrystallization was completed.

[0145] Subsequently, the application properties of the annealing separator, the adhesion properties thereof after drying, and the annealing separation effect after the first batch annealing were respectively examined, and samples having superior properties were further processed in subsequent steps, so that product sheets were obtained.

[0146] In the subsequent steps, first, continuous annealing was performed for forming superior subscale, and an annealing separator primarily composed of MgO was then applied. Since the first batch annealing was performed while 100 to 150 mass ppm of C remained, in the continuous annealing performed for this subscale formation, decarburization was also simultaneously performed. The continuous annealing was performed at 850°C for 80 seconds in an oxidizing atmosphere having a dew point of 60°C. In addition, the annealing separator used in this example was an annealing separator containing 92.5 mass percent of MgO and 7.5 mass percent of TiO_2 as a solid component.

[0147] Subsequently, the second batch annealing was performed. According to the steel composition of this example, high-temperature annealing at approximately 1,200°C required for purification of an inhibitor component was not necessary, and annealing may be performed under conditions in which the forsterite coating can be formed. Hence, the second batch annealing was performed at a temperature of 1,100°C, which was lower than that used in the past, for 5 hours, and the atmosphere was dry hydrogen.

[0148] Finally, application of a tensile coating, baking thereof, and stress-relief annealing were performed. The tensile coating was composed of a compound containing phosphoric acid, chromic acid, and colloidal silica and was baked at a temperature of 800°C. The stress-relief annealing was performed at 800°C for 3 hour in a nitrogen atmosphere. As the components and application conditions of the annealing separator, the conditions of the corresponding Nos. shown in Table. 5 were performed as was the case of Example 1.

[0149] Table 8 shows the order of the step of applying the annealing separator (before or after the recrystallization annealing), application properties of the annealing separator, adhesion properties thereof after drying, and annealing separation effect after the first batch annealing. As was the case of Example 1, regardless of the order of the step of applying the annealing separator, the steel manufactured by the method of the present invention showed superior application properties of the annealing separator, adhesion properties thereof after drying, and annealing separation effect after the first batch annealing. Hence, it is understood that the annealing separator of the present invention can be effectively applied to a composition type which contains no inhibitor.

[0150] Table 9 shows the magnetic properties, forsterite coating properties, and contents of Al, C, N, S, and Se after the second batch annealing, which were obtained when the samples coated with the annealing separators of the present invention were processed by the subsequent steps to form product sheets. The measurement methods of the respective properties were the same as those in Example 1.

[0151] When the annealing separators in the range of the present invention were used, the magnetic properties and the forsterite coating properties were compatibly obtained, and in addition, the content of impurity was an acceptable level which would not cause any problems.

Table 8

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	Remarks
1	Before	○	×	1.15	Δ	45	Comparative example
	After	○	×	1.00	○	0	Comparative example

(continued)

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	Remarks
2	Before	○	×	1.00	Δ	35	Comparative example
	After	○	×	1.00	○	0	Comparative example
3	After	○	×	1.05	○	0	Comparative example
4	After	○	×	1.15	○	0	Comparative example
5	After	○	○	0	×	60	Comparative example
6	After	○	○	0	○	3	Example
7	After	○	○	0	○	3	Example
8	Before	○	○	0	○	3	Example
	After	○	○	0	○	2	Example
9	Before	○	○	0	○	0	Example
	After	○	○	0	○	0	Example
10	After	○	○	0	○	0	Example
11	After	○	○	0	○	0	Example
12	After	○	Δ	0.8	○	0	Example
13	After	○	○	0	○	0	Example
14	Before	×	○	0	Δ	40	Comparative example
	After	×	○	0	Δ	25	Comparative example
15	After	Δ	○	0	○	0	Comparative example
16	After	○	○	0.2	○	0	Example
17	After	○	Δ	2	○	0	Comparative example
18	After	○	○	0	○	0	Example
19	After	×	○	0	Δ	35	Comparative example
20	After	○	○	0	○	0	Example
21	After	○	○	0	○	0	Example
22	After	○	○	0	○	0	Example
23	After	○	○	0	○	0	Example
24	After	○	○	0	○	0	Example

(continued)

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	Remarks
25	After	○	○	0	○	0	Example

Table 9

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after second batch annealing) (mass ppm)					Remarks
					Al	N	C	S	Se	
6	After	1.91	1.01	25	10	<5	10	10	<10	Example
7	After	1.90	1.02	25	9	<5	12	11	<10	Example
8	Before	1.92	0.99	30	8	<5	5	8	<10	Example
9	Before	1.91	1.03	25	9	<5	6	10	<10	Example
10	After	1.92	0.99	30	9	<5	5	12	<10	Example
11	After	1.92	0.98	25	11	<5	8	11	<10	Example
13	After	1.90	1.04	30	11	<5	9	10	<10	Example
16	After	1.89	1.05	30	14	<5	13	12	<10	Example
18	After	1.90	1.04	30	9	<5	8	12	<10	Example
20	After	1.90	1.05	25	13	<5	11	12	<10	Example
21	After	1.91	1.03	25	15	<5	9	11	<10	Example
22	After	1.91	1.03	30	16	<5	5	13	<10	Example
23	After	1.91	1.03	30	12	<5	6	12	<10	Example
24	After	1.90	1.05	25	11	<5	6	9	<10	Example
25	After	1.91	1.04	30	14	<5	7	11	<10	Example

(Example 3)

[0152] By the following method, a grain-oriented electrical steel sheet without any forsterite coating, having superior magnetic properties and workability was manufactured.

[0153] A steel slab which contained 0.020 mass percent of C, 3.31 mass percent of Si, 0.060 mass percent of Mn, and 450 mass ppm of Sb, and which also contained 300 mass ppm of Al and 70 mass ppm of N as an inhibitor-forming element, the balance being iron and inevitable impurities, was manufactured by continuous casting. After being heated to 1,200°C, the steel slab was hot-rolled to form a hot-rolled steel sheet having a thickness of 1.8 mm, followed by hot-rolled steel sheet annealing at 950°C for 60 seconds. Next, a cold-rolled steel sheet having a thickness of 0.27 mm was formed by cold rolling, followed by recrystallization annealing at 880°C for 10 seconds in a dry atmosphere having a dew point of -45°C. Subsequently, the final annealing was performed.

[0154] The annealing separator was applied before or after the recrystallization annealing in accordance with Table 10. The application of the annealing separator was performed by a roll coater, and baking was then performed at ultimate sheet temperature of 250°C, followed by spontaneous cooling. The baking was performed by direct flame of a propane gas. In the final annealing, after the secondary recrystallization was performed at 860°C for 45 hours in a N_2 atmosphere, purification was performed at 1,200°C for 5 hours in a H_2 atmosphere. As the components and application conditions of the annealing separator, the conditions of the corresponding Nos. shown in Table. 5 were performed as was the case of Example 1.

[0155] Subsequently, the application properties of the annealing separator, the adhesion properties thereof after drying, and the annealing separation effect after the final annealing were respectively examined, and samples having superior results were further processed in subsequent steps, so that product sheets were obtained.

[0156] In the subsequent steps, application of an insulating coating film, baking thereof, stress-relief annealing were performed. As the insulating coating film, a chromate insulating coating film containing an organic resin, which has been generally used, was used, and baking was performed at 300°C. The stress-relief annealing was performed at 750°C for 2 hours in a nitrogen atmosphere.

[0157] Table 10 shows the application properties of the annealing separator, adhesion properties thereof after drying, annealing separation effect after the final annealing, magnetic properties, insulating coating properties, and contents of Al, C, N, S, and Se after the final annealing. In Nos. 14 and 19, since the viscosity of the annealing separator was outside of the present invention, the application properties were seriously inferior, and sticking occurs between parts of a steel sheet at which application was not performed. In Nos. 12 and 15, the ratio of the Al compound to the silicon compound was outside of the present invention. In No. 12, since the amount of the Al compound, which was a film-forming component, was small, the adhesion properties of the annealing separator to a steel sheet were inferior. On the other hand, in No. 15, the amount of a highly reactive Al compound was large, the coating liquid was not stabilized, and hence a uniform coating could not be formed. As a result, appearance defects occurred.

[0158] In Nos. 1 to 4, since the primary component of the annealing separator was outside of the present invention, the adhesion properties to a steel sheet were insufficient. In No. 5, since the application amount of the annealing separator was insufficient, adhesion between steel sheets occurred in the final annealing. In No. 17, since the application amount of the annealing separator was excessive, the adhesion properties to a steel sheet were insufficient, and as a result, peeling occurred. In Nos. 1-1, 4-1, 5, 6-1, 14, and 19, the evaluation of the magnetic properties and peeling resistance on bending could not be performed due to adhesion between steel sheets.

[0159] In Nos. 1, 4, 6, 11, and 16, two types of evaluation were performed on the order of the step of applying the annealing separator, that is, the application of the annealing separator was performed before the recrystallization annealing for one evaluation and was performed after the recrystallization for the other evaluation. Regardless of the order of the step of applying the annealing separator, the annealing separators of the present invention showed superior application properties, adhesion properties after drying, annealing separation effect after the final annealing. In Nos. 1 and 4, which were the comparative examples, depending on the order of the step of applying the annealing separator, different annealing separation effects were obtained. The reason for this is believed that the above difference is caused by the difference in adhesion amount of the annealing separator in the final annealing as was described in Example 1.

[0160] It is understood that when the annealing separator according to the present invention was applied, superior application properties of the annealing separator, adhesion properties thereof after drying, annealing separation effect after the final annealing, magnetic properties, insulating coating properties, and purification of reducing impurities are obtained. In particular, as for the coating properties, properties superior to that of the forsterite coating shown in Examples 1 and 2 were obtained. Hence, it is understood that even to a grain-oriented electrical steel sheet using an inhibitor which requires purification by high-temperature annealing, the annealing separator of the present invention can be advantageously applied.

Table 10

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after final annealing) (mass ppm)					Remarks (comparative example/example)
										Al	N	C	S	Se	
1-1	Before	○	×	1.10	△	35	-	-	-	5	<5	10	5	<10	Comparative
1-2	After	○	×	1.05	○	0	1.87	1.06	45	5	<5	13	5	<10	Comparative
2	After	○	×	1.10	○	0	1.86	1.07	50	6	<5	11	5	<10	Comparative
3	After	○	×	1.15	○	0	1.84	1.04	55	5	<5	18	<4	<10	Comparative
4-1	Before	○	×	1.05	△	40	-	-	-	6	<5	10	5	<10	Comparative
4-2	After	○	×	1.05	○	0	1.85	1.03	45	6	<5	13	<4	<10	Comparative
5	After	○	○	0	×	75	-	-	-	4	<5	14	7	<10	Comparative
6-1	Before	○	○	0	○	2	1.87	1.06	15	6	<5	10	5	<10	Example
6-2	After	○	○	0	○	2	1.87	1.05	15	5	<5	16	<4	<10	Example
7	After	○	○	0	○	4	1.86	1.05	15	6	<5	18	5	<10	Example
8	After	○	○	0	○	3	1.89	1.05	20	5	<5	15	6	<10	Example
9	After	○	○	0	○	3	1.84	1.04	15	7	<5	13	5	<10	Example
10	After	○	○	0	○	0	1.89	101	20	5	<5	11	<4	<10	Example
11-1	Before	○	○	0	○	0	1.89	1.02	15	6	<5	10	5	<10	Example
11-2	After	○	○	0	○	0	1.89	1.01	15	5	<5	10	6	<10	Example
12	After	○	△	0.6	○	0	1.86	1.06	40	8	<5	18	5	<10	Example
13	After	○	○	0	○	0	1.87	1.07	15	6	<5	15	5	<10	Example
14	After	×	○	0	△	16	-	-	-	7	<5	13	<4	<10	Comparative
15	After	△	○	0	○	0	1.87	1.02	20	5	<5	14	<4	<10	Comparative
16-1	Before	○	○	0	○	0	1.85	1.04	20	6	<5	10	5	<10	Example

(continued)

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after final annealing) (mass ppm)					Remarks (comparative example/example)
										Al	N	C	S	Se	
16-2	After	○	○	0	○	0	1.86	1.01	15	4	<5	18	<4	<10	Example
17	After	○	Δ	1.00	○	0	1.85	1.05	45	6	<5	16	5	<10	Comparative
18	After	○	○	0	○	0	1.89	1.02	10	7	<5	18	5	<10	Example
19	After	×	○	0	Δ	35	-	-	-	5	<5	16	5	<10	Comparative
20	After	○	○	0	○	0	1.84	1.06	15	6	<5	16	6	<10	Example
21	After	○	○	0	○	0	1.86	1.02	20	8	<5	11	5	<10	Example
22	After	○	○	0	○	0	1.87	1.06	20	5	<5	18	<4	<10	Example
23	After	○	○	0	○	0	1.87	1.05	20	6	<5	10	5	<10	Example
24	After	○	○	0	○	0	1.88	1.04	15	4	<5	18	5	<10	Example
25	After	○	○	0	○	0	1.84	1.04	15	6	<5	12	<4	<10	Example

(Example 4)

[0161] By the following method, a grain-oriented electrical steel sheet without any forsterite coating, having superior magnetic properties and workability was manufactured.

[0162] A steel slab containing no inhibitor-forming elements was manufactured by continuous casting, in which 0.018 mass percent of C, 3.32 mass percent of Si, 0.070 mass percent of Mn, and 300 mass ppm of Sb were contained, and in which the contents of Al, N, S, and Se were decreased to 40 mm ppm, 25 mass ppm, 15 mass ppm, and less than 10 mass ppm, respectively. In this slab, the balance was iron and inevitable impurities. After being heated to 1,200°C, the steel slab was hot-rolled to form a hot-rolled steel sheet having a thickness of 1.8 mm, followed by hot-rolled steel sheet annealing at 950°C for 60 seconds. Next, after a cold-rolled steel sheet having a thickness of 0.35 mm was formed by cold rolling, followed by recrystallization annealing at 880°C for 10 seconds in a dry atmosphere having a dew point of -45°C, the final annealing was performed.

[0163] The annealing separator was applied before or after the recrystallization annealing in accordance with Table 11. The application of the annealing separator was performed by a roll coater, and baking was then performed at ultimate sheet temperature of 250°C, followed by spontaneous cooling. The baking was performed by direct flame of a propane gas. In the final annealing, after the secondary recrystallization was performed at 875°C for 45 hours in a N_2 atmosphere, a temperature of 1,000°C was maintained for 5 hours in an Ar atmosphere. After the final annealing, decarburization annealing was performed in an oxidizing atmosphere, so that the content of C in base iron was decreased.

[0164] Subsequently, as the components and application conditions of the annealing separator, as was the case of Example 1, the conditions of the corresponding Nos. shown in Table. 5 were performed. Next, the application properties of the annealing separator, the adhesion properties thereof after drying, and the annealing separation effect after the final annealing were respectively examined, and samples having superior results were further processed in subsequent steps, so that product sheets were obtained.

[0165] In the subsequent steps, application of an insulating coating film, baking thereof, stress-relief annealing were performed. As the insulating coating film, a chromate insulating coating film containing an organic resin, which has been generally used, was used, and baking was performed at 300°C. The stress-relief annealing was performed at 750°C for 2 hours in a nitrogen atmosphere.

[0166] Table 11 shows the application properties of the annealing separator, adhesion properties thereof after drying, annealing separation effect after the final annealing, magnetic properties, insulating coating film properties, and contents of Al, C, N, S, and Se after the final annealing. As was the case of Example 3, the steel to which the annealing separator of the present invention was applied showed superior results regardless of the order of the step of applying the annealing separator.

Table 11

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after final annealing) (mass ppm)					Remarks (comparative example/example)
										Al	N	C	S	Se	
1	After	○	×	1.10	○	0	1.85	1.34	50	40	26	15	15	<10	Comparative
2-1	Before	○	×	1.00	△	15	-	-	-	38	28	10	11	<10	Comparative
2-2	After	○	×	1.05	○	0	1.84	1.36	55	38	22	14	11	<10	Comparative
3-1	Before	○	×	1.05	△	20	-	-	-	38	28	10	11	<10	Comparative
3-2	After	○	×	1.15	○	0	1.88	1.29	45	41	24	18	15	<10	Comparative
4	After	○	×	1.00	○	0	1.83	1.38	50	38	26	12	14	<10	Comparative
5	After	○	○	0	×	80	-	-	-	40	30	16	13	<10	Comparative
6	After	○	○	0	○	2	1.83	1.40	15	40	24	20	13	<10	Example
7	After	○	○	0	○	4	1.82	1.34	20	41	22	17	10	<10	Example
8-1	Before	○	○	0	○	3	1.88	1.29	20	38	28	10	11	<10	Example
8-2	After	○	○	0	○	3	1.88	1.28	20	35	19	15	16	<10	Example
9	After	○	○	0	○	3	1.84	1.25	20	39	28	19	20	<10	Example
10-1	Before	○	○	0	○	0	1.88	1.30	15	38	28	10	11	<10	Example
10-2	After	○	○	0	○	0	1.88	1.24	15	36	18	15	15	<10	Example
11	After	○	○	0	○	0	1.88	1.25	20	36	18	15	16	<10	Example
12-1	Before	○	△	0.7	○	0	1.84	1.28	55	38	28	10	11	<10	Example
12-2	After	○	△	0.5	○	0	1.87	1.26	45	40	26	21	15	<10	Example
13	After	○	○	0	○	0	1.85	1.39	15	41	19	26	11	<10	Example
14	After	×	○	0	△	29	-	-	-	40	24	16	13	<10	Comparative
15	After	△	○	0	○	0	1.84	1.37	15	40	25	18	16	<10	Comparative

(continued)

No.	Order of step of applying annealing separator (before or after recrystallization annealing)	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after final annealing) (mass ppm)					Remarks (comparative example/example)
										Al	N	C	S	Se	
16	After	○	○	0	○	0	1.83	1.38	15	40	21	14	17	<10	Example
17	After	○	Δ	0.80	○	0	1.83	1.41	50	41	22	19	18	<10	Comparative
18	After	○	○	0	○	0	1.88	1.25	20	37	27	21	11	<10	Example
19	After	×	○	0	Δ	19	-	-	-	40	23	16	16	<10	Comparative
20	After	○	○	0	○	0	1.84	1.35	20	37	20	11	12	<10	Example
21	After	○	○	0	○	0	1.85	1.45	15	39	24	9	18	<10	Example
22	After	○	○	0	○	0	1.88	1.37	15	40	21	18	11	<10	Example
23	After	○	○	0	○	0	1.86	1.36	20	40	23	15	13	<10	Example
24	After	○	○	0	○	0	1.85	1.35	20	39	25	14	14	<10	Example
25	After	○	○	0	○	0	1.88	1.32	20	40	21	19	14	<10	Example

(Example 5)

[0167] By using the annealing separators shown in Table 12, grain-oriented electrical steel sheets were manufactured. The manufacturing process was as shown in Table 13, processes A and B (method by performing final annealing once) used the steel slab and manufacturing conditions of Example 3, and processes C and D (method by performing batch annealing twice) used the steel slab and manufacturing conditions of Example 1. As for the annealing separator, components other than the primary component and application conditions were the same as those in Example 1. Since scattering was not practically observed by a scattering method in No. 6, the annealing separator was practically regarded as a solution.

[0168] The results are shown in Table 13, and all the annealing separators of the present invention showed superior results. Among those, an annealing separator containing a Si compound as the stable compound at a high temperature had a high annealing separation effect, and in particular, a silicon compound is preferably used alone as the stable compound at a high temperature. That is, Example 1 (No. 13 in Table 6) and Example 3 (No. 13 in Table 10), in which the application amount and the viscosity were the same as those of Nos. 1 to 5 and 7 shown in Table 12 and in which a silicon compound (colloidal silica) in the form of a colloidal solution is only used, showed most preferable properties and were better than the results of this example shown in Table 13.

Table 12

No.	Primary component of separator			Application amount (g/m^2)	Viscosity (mPa·s)	Solid component ratio of Al compound (mass%)
	Al compound	Stable compound at high temperature	Others			
1	Basic Al acetate	Colloidal silica, fine TiO_2 powder	-	1.2	1.8	$Al_2O_3/(Al_2O_3+SiO_2+TiO_2)$:50
2	Basic Al acetate	Colloidal silica, fine TiO_2 powder	Sr sulfate	1.2	1.8	$Al_2O_3/(Al_2O_3+SiO_2+TiO_2)$:50
3	Basic Al acetate	Colloidal TiO2	-	1.2	1.8	$Al_2O_3/(Al_2O_3+TiO_2)$:60
4	Basic Al acetate	Colloidal SrO, BaO	-	1.2	1.8	$Al_2O_3/(Al_2O_3+SrO+BaO)$:70
5	Basic Al acetate	Fine CaO powder	Mg sulfate	1.2	1.8	$Al_2O_3/(Al_2O_3+CaO)$:80
6	Basic Al acetate	Colloidal silica	-	0.1	1.8	$Al_2O_3/(Al_2O_3+SiO_2)$:90
7	Basic Al acetate	Fine ZrO_2 powder	-	1.2	1.8	$Al_2O_3/(Al_2O_3+ZrO_2)$:70

Table 13

No.	Process *	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after final annealing/second batch annealing) (mass ppm)				
										Al	N	C	S	Se
1	A	○	○	0	○	2	1.86	1.05	20	5	<5	13	5	<10
2	A	○	○	0	○	2	1.89	1.02	20	6	<5	13	<4	<10
3-1	A	○	○	0	○	5	1.86	1.05	20	6	<5	14	5	<10
3-2	B	○	○	0	○	6	1.85	1.06	20	5	<5	13	5	<10
4	C	○	○	0	○	5	1.91	1.03	30	9	<5	10	<4	<10
5-1	C	○	○	0	○	5	1.92	0.99	30	5	<5	9	<4	<10
5-2	D	○	○	0	○	4	1.92	0.99	30	8	<5	9	5	<10
6-1	A	○	○	0	○	3	1.85	1.07	20	6	<5	15	5	<10
6-2	C	○	○	0	○	3	1.90	1.05	30	6	<5	9	5	<10
7-1	B	○	○	0	○	5	1.85	1.06	20	7	<5	12	<4	<10
7-2	D	○	○	0	○	4	1.91	1.04	30	7	<5	5	<4	<10

* A: Recrystallization annealing → application of annealing separator → final annealing
B: Application of annealing separator → recrystallization annealing → final annealing
C: Recrystallization annealing → application of annealing separator → first batch annealing → continuous annealing ~ second batch annealing
D: Application of annealing separator → recrystallization annealing → first batch annealing → continuous annealing ~ second batch annealing

(Example 6)

[0169] Steel slabs having the compositions shown in Table 14 were manufactured from molten steel by a continuous casting method, and grain-oriented electrical steel sheets were formed in accordance with the classification shown in Table 15 in a manner similar to that in Example 5. However, in No. 2, the content of C before the secondary recrystallization was not particularly adjusted, and hence decarburization was also omitted. In addition, in Nos. 1 and 7, the recrystallization annealing was performed in an oxidizing atmosphere having a dew point of 30°C, so that the content of C before the second recrystallization annealing was adjusted in the range of 100 to 150 mass ppm.

[0170] The annealing separators and the application conditions were as those of No. 13 shown in Table 5.

[0171] The results are shown in Table 15. Although depending on the composition of the steel sheets, the magnetic properties expected from the respective composition are all realized.

Table 14

No.	Steel slab composition							
	C (mass%)	Si (mass%)	Mn (mass%)	Al (mass ppm)	N (mass ppm)	S (mass ppm)	Se (mass ppm)	Others (mass ppm)
1	0.075	3.2	0.05	40	40	20	<10	
2	0.003	3.2	0.05	300	80	20	<10	
3	0.015	2.1	0.04	310	75	20	<10	
4	0.02	7.8	0.05	43	37	20	<10	Sn: 400
5	0.018	3.35	0.008	290	80	20	<10	
6	0.020	3.15	0.065	50	38	20	<10	
7	0.062	3.0	0.03	35	60	20	<10	B: 25
8	0.015	5.0	0.04	30	30	20	150	
9	0.015	3.05	0.05	35	40	150	<10	

Table 15

No.	Process *	Application properties	Adhesion properties of annealing separator	Peeled amount (g/m^2)	Annealing separation effect	Peeling strength (N)	B_8 (T)	$W_{17/50}$ (W/kg)	Minimum bending radius of peeling resistance on bending (mm)	Content in base iron (after final annealing/second batch annealing) (mass ppm)				
										Al	N	C	S	Se
1-1	A	○	○	0	○	0	1.85	1.08	20	7	<5	15	5	<10
2-1	A	○	○	0	○	0	1.82	1.16	20	6	<5	13	<4	<10
3-1	A	○	○	0	○	0	1.87	1.15	20	5	<5	13	<4	<10
1-2	B	○	○	0	○	0	1.85	1.07	20	5	<5	12	<4	<10
2-2	C	○	○	0	○	0	1.82	1.08	30	9	<5	7	6	<10
3-2	D	○	○	0	○	0	1.92	1.08	30	8	<5	8	5	<10
4	A	○	○	0	○	0	1.82	1.02	20	5	<5	11	5	<10
5	B	○	○	0	○	0	1.85	1.06	20	5	<5	14	6	<10
6	C	○	○	0	○	0	1.91	1.03	30	7	<5	9	6	<10
7	C	○	○	0	○	0	1.90	1.05	30	8	<5	6	<4	<10
8	D	○	○	0	○	0	1.91	1.05	30	6	<5	5	5	<10
9	C	○	○	0	○	0	1.90	1.06	30	6	<5	5	5	<10

* A: Recrystallization annealing → application of annealing separator → final annealing
B: Application of annealing separator → recrystallization annealing → final annealing
C: Recrystallization annealing → application of annealing separator → first batch annealing → continuous annealing ~ second batch annealing
D: Application of annealing separator → recrystallization annealing → first batch annealing → continuous annealing ~ second batch annealing

Industrial Applicability

[0172] The annealing separator for grain-oriented electrical steel sheets, according to the present invention has superior application properties and adhesion properties to a steel sheet, and in an annealing separator application step and subsequent steps performed thereafter, stable operation can be ensured. In addition, the annealing separator of the present invention has superior operating properties, such that while the adhesion properties are maintained, purification and decarburization can be performed without causing any problems and, in addition, a step of removing the coating is not required.

[0173] When this annealing separator is applied to a process for manufacturing a grain-oriented electrical steel sheet, a grain-oriented electrical steel sheet having superior magnetic properties and forsterite coating properties and a grain-oriented electrical steel sheet having superior magnetic properties and workability without forsterite coating can be easily manufactured.

Claims

1. A method for manufacturing a grain-oriented electrical steel sheet, comprising:

a step of forming a steel sheet having a final sheet thickness by rolling a slab formed from molten steel containing 0.08 mass percent or less of C, 2.0 to 8.0 mass percent of Si, and 0.005 to 1.0 mass percent of Mn;
a step of performing recrystallization annealing of the steel sheet; and
a final annealing step of performing batch annealing of the steel sheet, in which the annealing separator applied before annealing in the first batch annealing step on the electrical steel sheet to coat the same is called a first annealing separator and comprises an Al compound in the form of a solution or a colloidal solution and a stable compound which is stable at high temperature,
wherein the recrystallization annealing is performed before the application of the annealing separator in the final annealing or after the application of the annealing separator and before the batch annealing, and
the amount of the annealing separator applied to the steel sheet is set to 0.005 to 5 g/m^2 per one surface.

2. The method for manufacturing a grain-oriented electrical steel sheet according to claim 1, **characterized by**:

a subsequent step of performing continuous annealing of the steel sheet; and
a second batch annealing step of performing batch annealing following application of a second annealing separator containing MgO to the steel sheet.

3. The method for manufacturing a grain-oriented electrical steel sheet, according to claim 1 or 2,
wherein the slab is a slab formed from molten steel having a composition in which the content of Al is decreased to 150 ppm or less and the contents of N, S, and Se are each decreased to 50 ppm or less.

4. The method for manufacturing a grain-oriented electrical steel sheet, according to any of the preceding claims, wherein the step of forming a steel sheet having a final sheet thickness by rolling a slab, comprises:

forming a hot-rolled steel sheet by hot-rolling of the slab;
performing hot-rolled steel sheet annealing of the hot-rolled steel sheet whenever necessary; and
performing cold rolling once, or twice or more with intermediate annealing performed therebetween, to obtain a steel sheet having a final sheet thickness.

5. A method for manufacturing a grain-oriented electrical steel sheet, comprising:

a step of performing cold rolling once, or twice or more with intermediate annealing performed therebetween, to obtain a steel sheet having a final sheet thickness;
a step of then performing recrystallization annealing; and
a step of then performing final annealing by the method according to any of the preceding claims.

6. A method for manufacturing a grain-oriented electrical steel sheet as defined in any of the preceding claims, comprising the steps of: applying an annealing separator to a steel sheet; and annealing the steel sheet coated with the annealing separator,
wherein the annealing separator comprises:

an Al compound, which is at least one of a basic Al acetate, a basic Al formate, a basic Al chloride, a basic Al nitrate, a basic Al oxalate, a basic Al sulfamate, a basic Al lactate, and a basic Al citrate or a mixture containing at least two of the above compounds, wherein the Al compound has at least one of a hydroxyl group and an organic acid group and a dehydrated product of an Al compound having a hydroxyl group and an organic acid group, which Al compound is in the form of a solution or a colloidal solution; and at least one stable compound selected from SiO_2, SrO, TiO_2, BaO, CaO and ZrO_2 in the form of a solution or a colloidal solution, and the viscosity of the annealing separator is 25 mPa•s or less at a liquid temperature of 25°C measured by Oswald viscometer.

7. The method for manufacturing a grain-oriented electrical steel sheet, according to Claim 6,
wherein the content of the Al compound is 40 to 95 mass percent in terms of a solid component ratio represented by the following equation:

solid component ratio of Al compound = (solid component of the Al compound) / {(solid component of the Al compound) + (solid component of the stable compound at a high temperature (sum))}, where

(1) the solid component of the Al compound is calculated based on the form of Al_2O_3, and the solid component of the stable compound at a high temperature is calculated based on the form of a primary compound which is formed when the annealing separator is baked after the application thereof, or
(2) where the solid components of the compounds are calculated based on the following respective forms:

the Al compound .....Al_2O_3, the Si compound .....SiO_2,
the Sr compound .....SrO, the Ca compound .....CaO,
the Zr compound .....ZrO_2, the Ti compound .....TiO_2, and
the Ba compound .....BaO.

8. A method for manufacturing a grain-oriented electrical steel sheet, according to claim 7,
wherein the at least one stabte compound is SiO_2 in the form of a solution or a colloidal solution, wherein the ratio of the Al compound to the SiO_2 in the form of a solution or a colloidal solution calculated based on $Al_2O_3/(Al_2O_3+SiO_2)$ is 40 to 95 mass percent.

9. The method for manufacturing a grain-oriented electrical steel sheet, according to any of the Claims 6 to 8,
wherein the annealing separator further comprises S or a compound containing S at a solid component ratio of 25 mass percent or less which is obtained when the annealing separator is baked after application thereof.

10. The method for manufacturing a grain-oriented electrical steel sheet, according to Claim 9,
wherein the S or the compound containing S is at least one selected from the group consisting of Sr sulfate, Mg sulfate, and Mg sulfide.

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EUROPEAN SEARCH REPORT

Application Number
EP 12 00 6829

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	EP 1 279 747 A (KAWASAKI STEEL CO [JP]) 29 January 2003 (2003-01-29) * the whole document * -----	1-10	INV. C21D9/46 C22C38/00 C22C38/04 C22C38/60 H01F1/16
Y,D	JP 11 061261 A (KAWASAKI STEEL CO) 5 March 1999 (1999-03-05) * abstract; tables 1-4,6-8 * -----	1-10	
Y	US 5 961 744 A (YAMAZAKI SHUICHI [JP] ET AL) 5 October 1999 (1999-10-05) * column 7, line 17 - column 9, line 67 * * claims 1,2 * -----	1-10	
A	US 3 794 520 A (PAVLIK N) 26 February 1974 (1974-02-26) * the whole document * -----	1-10	
A	JP 8 188828 A (NIPPON STEEL CORP) 23 July 1996 (1996-07-23) * abstract; tables 1,2 * -----	1-10	

TECHNICAL FIELDS SEARCHED (IPC)
C21D
C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	10 January 2013	Gavriliu, Alexandru

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 00 6829

10-01-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1279747 A	29-01-2003	CN 1400319 A	05-03-2003
		EP 1279747 A2	29-01-2003
		KR 20030010502 A	05-02-2003
		US 2003116236 A1	26-06-2003
JP 11061261 A	05-03-1999	NONE	
US 5961744 A	05-10-1999	DE 69326792 D1	25-11-1999
		DE 69326792 T2	27-04-2000
		EP 0565029 A1	13-10-1993
		US 5961744 A	05-10-1999
US 3794520 A	26-02-1974	NONE	
JP 8188828 A	23-07-1996	NONE	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2003041323 A **[0005] [0015] [0016]**
- JP 6136448 A **[0011]**
- JP 7118750 A **[0011]**
- JP 5156362 A **[0011]**
- JP 11061261 A **[0011]**
- JP 8134542 A **[0011]**
- JP 10121142 A **[0012]**
- JP 2000129356 A **[0014]**