(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 345 936 B1**

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **30.08.95**

(51) Int. Cl.⁶: **C23C 10/04**, H01F 1/04, C21D 8/12, C21D 9/46

(21) Application number: **89304300.0**

(22) Date of filing: **28.04.89**

(54) Method of refining magnetic domains of electrical steels.

(30) Priority: **10.06.88 US 205711**
10.06.88 US 206051

(43) Date of publication of application:
13.12.89 Bulletin 89/50

(45) Publication of the grant of the patent:
30.08.95 Bulletin 95/35

(84) Designated Contracting States:
DE FR GB IT SE

(56) References cited:
EP-A- 0 193 324
GB-A- 2 167 324
JP-A-61 133 321
US-A- 3 932 235
US-A- 3 990 923

(73) Proprietor: **ALLEGHENY LUDLUM CORPORATION**
1000 Six PPG Place
Pittsburgh
Pennsylvania 15222 (US)

(72) Inventor: **Ames, Stuart Leslie**
119 Oak Manor Drive
Sarver
Pennsylvania 16055 (US)
Inventor: **Breznak, Jeffrey Michael**
715 Pittsburgh Street
Springdale
Pennsylvania 15144 (US)

(74) Representative: **Sheader, Brian N. et al**
Eric Potter & Clarkson
St. Mary's Court
St. Mary's Gate
Nottingham NG1 1LE (GB)

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.3)

Description

This invention relates to a method for improving core loss by refining the magnetic domain wall spacing of electrical steels, particularly electrical steel sheet or strip.

Grain-oriented silicon steel is conventionally used in electrical applications, such as power transformers, distribution transformers, generators, and the like. The ability of the steel to permit cyclic reversals of the applied magnetic field with only limited energy loss is a most important property. Reductions of this loss, which is termed "core loss", is desirable.

In the manufacture of grain-oriented silicon steel, it is known that the Goss secondary recrystallization texture, (110)[001] in terms of Miller's indices, results in improved magnetic properties, particularly permeability and core loss over nonoriented silicon steels. The Goss texture refers to the body-centered cubic lattice comprising the grain or crystal being oriented in the cube-on-edge position. The texture or grain orientation of this type has a cube edge parallel to the rolling direction and in the plane of rolling, with the (110) plane being in the sheet plane. As is well known, steels having this orientation are characterized by a relatively high permeability in the rolling direction and a relatively low permeability in a direction at right angles thereto.

In the manufacture of grain-oriented silicon steel, typical steps include providing a melt having of the order of 2-4.5% silicon, casting the melt, hot rolling, cold rolling the steel to final gauge e.g., of 7 to 14 mils (0.178 to 0.356 mm), typically of 7 or 9 mils (0.178 or 0.229 mm), with an intermediate annealing when two or more cold rollings are used, decarburizing the steel, applying a refractory oxide base coating, such as a magnesium oxide coating, to the steel, and final texture annealing the steel at elevated temperatures in order to produce the desired secondary recrystallization and purification treatment to remove impurities such as nitrogen and sulfur. The development of the cube-on-edge orientation is dependent upon the mechanism of secondary recrystallization wherein during recrystallization, secondary cube-on-edge oriented grains are preferentially grown at the expense of primary grains having a different and undesirable orientation.

As used herein, "sheet" and "strip" are used interchangeably and mean the same unless otherwise specified.

It is also known that through the efforts of many prior art workers, cube-on-edge grain-oriented silicon steels generally fall into two basic categories: first, regular or conventional grain-oriented silicon steel, and second, high permeability grain-oriented silicon steel. Regular grain-oriented silicon steel is generally characterized by permeabilities of less than 1850 at 10 Oersted (796 A/m) with a core loss of greater than 0.400 watts per pound (WPP) (0.88 watts/kg)at 1.5 Tesla at 60 Hertz for nominally 9-mil (0.229mm) material. High permeability grain-oriented silicon steels are characterized by higher permeabilities which may be the result of compositional changes alone or together with process changes. For example, high permeability silicon steels may contain nitrides, sulfides, and/or borides which contribute to the precipitates and inclusions of the inhibition system which contributes to the properties of the final steel product. Furthermore such high permeability silicon steels generally undergo cold reduction operations to final gauge wherein a final heavy cold reduction of the order of greater than 80% is made in order to facilitate the grain orientation. While such higher permeability materials are desirable, such materials tend to produce larger magnetic domains than conventional material. Generally, larger domains are deleterious to core loss.

It is known that one of the ways that domain size and thereby core loss values of electrical steels may be reduced is if the steel is subjected to any of various practices designed to induce localized strains in the surface of the steel. Such practices may be generally referred to as "domain refining by scribing" and are performed after the final high temperature annealing operation. If the steel is scribed after the final texture annealing, then there is induced a localized stress state in the texture-annealed sheet so that the domain wall spacing is reduced. These disturbances typically are relatively narrow, straight lines, or scribes, generally spaced at regular intervals. The scribe lines are substantially transverse to the rolling direction and typically are applied to only one side of the steel.

In fabricating these electrical steels into transformers, the steel inevitably suffers some deterioration in core loss quality due to cutting, bending, and construction of cores during fabrication, all of which impart undesirable stresses in the material. During fabrication incident to the production of stacked core transformers and, more particularly, in the power transformers of the United States, the deterioration in core loss quality due to fabrication is not so severe that a stress relief anneal (SRA) is essential to restore usable properties. For such end uses there is a need for a flat, domain-refined silicon steel which need not be subjected to stress relief annealing. In other words, the scribed steel used for this purpose does not have to possess domain refinement which is heat resistant.

However, during the fabrication incident to the production of most distribution transformers in the United States, the steel strip is cut and subjected to various bending and shaping operations which produce much more worked stresses in the steel than in the case of power transformers. In such instances, it is necessary and conventional for manufacturers to stress relief anneal (SRA) the product to relieve such stresses. During stress relief annealing, it has been found that the beneficial effect on core loss resulting from some scribing techniques, such as mechanical and thermal scribing, are lost. For such end uses, it is required and desired that the product exhibit heat resistant domain refinement (HRDR) in order to retain the improvements in core loss values resulting from scribing.

It has been suggested in prior patent art that contaminants or intruders may be effective in refining the magnetic domain wall spacing or grain-oriented silicon steel. U.S. Patent 3,990,923 - Takashina et al, dated November 9, 1976, discloses that chemical treatment may be used on primary recrystallized silicon steel to control or inhibit the growth of secondary recrystallization grains. British Patent Application 2,167,324A discloses a method of subdividing magnetic domains or grain-oriented silicon steels to survive an (SRA). The method includes imparting a strain to the sheet, forming an intruder on the grain-oriented sheet, the intruder being of a different component or structure than the electrical sheet and doing so either prior to or after straining and thereafter annealing such as in a hydrogen reducing atmosphere to result in imparting the intruders into the steel body. Numerous metals and nonmetals are identified as suitable intruder materials.

Japanese Patent Document 61-133321A discloses a method for making orientated electric steel sheet with ultra low core loss which comprises removing all or parts or a surface coating on the steel sheet to expose the underlying steel, applying a chemical coating to the sheet, forming distortions at intervals and then heat treating to cause the chemical coating to react with the exposed steel, to provide heat resistant domain refinement. Stress relief annealing may then be carried out if it is desired to obtain stress free steel.

Japanese Patent Document 61-139-679A discloses a process of coating final texture annealed oriented magnetic steel sheet in the form of linear or spot shapes, at intervals with at least one compound selected from the group of phosphoric acid, phosphates, boric acid, borates, sulfates, nitrates, and silicates, and thereafter baking at 300-1200 °C, and forming a penetrated body different from that of the steel to refine the magnetic domains.

Japanese Patent Document 61-284529A discloses a method of removing the surface coatings from final texture annealed magnetic steel sheets at intervals, coating one or more of zinc, zinc alloys, and zincated alloy at specific coating weights, coating with one or more of metals having a lower vapor pressure than zinc, forming impregnated bodies different from the steel in composition or in structure at intervals by heat treatment or insulating film coating treatment to refine the magnetic domains.

Japanese Patent Document 62-51202 discloses a process for improving the core loss of silicon steel by removing the forsterite film formed after final finish annealing, and adhering different metal, such as copper, nickel, antimony by heating.

What is needed is a method for refining the magnetic domain wall spacing of grain-oriented silicon steel, having a base coating e.g., of forsterite, thereon, which is heat resistant. The method should be compatible with conventional processing of regular and high permeability silicon steels and should use the thermally insulative coating, e.g., the forsterite base coating, on the sheet to facilitate the domain refinement. Still further, the method should be useful with numerous techniques including conventional methods for removing the base coating in selected patterns.

The invention provides a method as defined in claim 1. Preferred embodiments are given in the dependent claims 2 to 14.

Broadly, in accordance with the present invention, there is provided a method for refining the magnetic domain wall spacing of grain-oriented silicon steel sheet or strip having an insulation base coating, the method including removing portions of the base coating to expose a line pattern of the underlying silicon steel, and applying a metallic contaminant to the silicon steel. The metallic contaminant may be copper, tin, nickel, zinc or antimony, or combinations or compounds thereof. The exposed steel is free of thermal and plastic stresses and is not dependent on such stresses to be effectively domain refined. Thereafter the steel and contaminant thereon are annealed at a temperature of 760 °C (1400 °F) or more in a protective atmosphere to diffuse sufficient and controlled amounts of contaminant into the exposed steel to produce lines of permanent pores to effect heat resistant domain refinement and reduced core loss in stress-free steel.

According to an embodiment of the invention a barrier coating of phosphorus or silicate, or combinations or compounds thereof, is applied to the steel sheet for sealing the base coating prior to applying said metallic contaminant.

The invention will be further described with reference to the accompanying drawings, in which:

Figure 1 is a photomicrograph of a copper-filled groove in the silicon steel base coating in accordance with the present invention.

Figure 2 is a 150X photograph of an X-ray map of copper of Figure 1.

Figure 3 is a 3000X photomicrograph of a silicon steel after diffusion anneal showing porosity in accordance with the present invention.

Figure 4 is a 30X photomicrograph illustrating nodules of antimony on a steel surface.

Figures 5 and 6 are photomicrographs in cross section on Ni-Sn strip.

Figures 7 to 10 are 3000X photographs of X-ray maps of nickel, tin, phosphorus, and iron in the Ni-Sn strip in the steel.

Broadly, the method of the present invention relates to a method for refinement of the domain structure of grain-oriented silicon steel sheet having relatively large grain sizes by controlled surface chemical contamination. The method takes final textured annealed silicon steel as the starting sheet material, having the electrically and thermally insulating base coating in place, and then by any of numerous techniques, locally removes the coating to expose the bare metal. No plastic strain or stress of any sort needs to be imposed on the metal and thereafter the exposed bare metal is contaminated by other materials on the areas of the exposed metal pattern. The steel is then annealed to diffuse or alloy the contaminant into the iron-silicon steel sheet product. The resulting domain refinement is heat resistant as it survives stress relief annealing.

The starting material for the chemical striping process of the present invention is final textured annealed grain-oriented silicon steel having an insulative coating in place. Such an insulative coating can be the conventional base coating, also called forsterite or mill glass coating. Preferably, the as-scrubbed final texture annealed grain-oriented silicon steels may be used. Such steels may be of the regular or conventional grain-oriented silicon steels or of high permeability grain-oriented silicon steels. The particular compositions of such steels are not critical to the present invention and they may be conventional compositions. As used herein the steel melts initially contained the nominal composition as follows:

	C	N	Mn	S	Si	Cu	B	Fe
Steel 1	.030	<50ppm	.038	.017	3.15	.30	10ppm	Bal.
Steel 2	.030	50ppm	.07	.022	3.15	.22	--	Bal.
Steel 3	.038	45ppm	.078	.026	3.25	.25	5-6ppm	Bal.

Steel 1 is a high permeability grain-oriented silicon steel and Steel 2 is a conventional grain-oriented silicon steel and Steel 3 is a modified conventional grain-oriented silicon steel. As used herein, all compositions are by weight percent, unless otherwise specified.

Steels 1, 2 and 3 were produced by casting, hot rolling, normalizing, cold rolling to final gauge with an intermediate annealing when two or more cold rolling stages were used, decarburizing, coating with MgO, and final texture annealing to achieve the desired secondary recrystallization of cube-on-edge orientation. After decarburizing the steel, a refractory oxide base coating containing primarily magnesium oxide was applied before final texture annealing at elevated temperature; such annealing caused a reaction at the steel surface to create a forsterite base coating. Although the steel melts of Steels 1, 2, and 3 initially contained the nominal compositions recited above, after final texture annealing, the C, N and S were reduced to trace levels of less than about 0.001% by weight.

In accordance with the present invention, it is important that portions of the coating be removed to expose a line or stripe pattern in the underlying silicon steel. How the coating is removed is not critical to the present invention except that, contrary to the prior art, the underlying steel need not be subjected to any mechanical, thermal, or other stresses and strains as a result of the coating removal operation. In other words, the exposed steel must be free of any thermal and plastic stresses prior to any subsequent steps of applying the metallic contaminant. An advantage of the present invention is that any of various techniques may be used to remove the selected portions of the base coating. For example, conventional mechanical scribing or laser means may be used to develop a controlled pattern of markings on the strip surface. The line or stripe pattern selected for the removed base coating may be conventional patterns used in prior art scribing techniques. Preferably, the pattern may comprise removing the coating in generally parallel lines substantially transverse to the rolling direction of the steel having a line width and spacing as may be conventional. Other patterns may also be useful, depending on whether the grain-oriented silicon steel is of the cube-on-edge, cube-on-face, or other orientation.

In accordance with the present invention, the exposed silicon steel would be plated or coated by selected metals and metal alloys. Preferably the metals are selected such that they have a diffusion rate slower than iron in silicon steels. The metals and metal alloys suitable for the present invention are referred to as contaminant or diffuser materials. As used herein, "contaminant" refers to those certain suitable metal and metal alloys selectively applied to the exposed areas of steel sheet in accordance with this invention. It has been found that various metallic contaminants may be used selected from copper, tin, nickel, zinc or antimony, or combinations or compounds thereof. The metallic contaminants may be applied as a coating to the silicon steel using various conventional means such as electroless deposition or electrolytic plating. Because of the insulative nature of the base coating, the metallic contaminant can only be applied in the selected line pattern or stripes which conform to the pattern of base coating removal. What is important at this point is that the base glass insulation on the silicon steel facilitates selective deposition of the metallic contaminant in the predetermined or preselected pattern.

The silicon steel having the selected portions of base coating removed and having the metallic contaminant applied is thereafter annealed at a time and temperature in a protective atmosphere to diffuse sufficient and controlled amounts of contaminant into the exposed steel to produce permanent pores to effect heat resistant domain refinement and reduced core loss. The annealing has the effect of a diffusion anneal to cause minor alloying of the metallic contaminant with the iron-silicon steel sheet to effect heat resistant domain refinement. The annealing temperature ranges from about 1400 ° F (760 ° C) or more and may range up to 2100 ° F (1150 ° C). Preferably, the temperatures range up to 1800 ° F (982 ° C) and more preferably, from about 1400 to 1700 ° F (760 to 927 ° C).

It is desirable that the anneal temperature be at least equal to or greater than the temperature that would normally be used for a stress relief anneal in order that the property effects developed would be stable with respect to any subsequent lower temperature treatment such as a stress relief anneal (SRA). In other words, the improvements in core loss would be the result of heat resistant domain refinement. The time for the anneal may range up to 20 hours and preferably may range from 30 minutes to 5 hours at a temperature sufficient to produce the magnetic domain refining. As a practical consideration, the diffusion anneal should be higher than a conventional stress relief anneal of about 1425 ° F (774 ° C) which may be used by transformer manufacturers following fabrication. Temperatures of the order of up to 1650 ° F (899 ° C) are sufficient to effect the heat resistant domain refinement without requiring an additional separator coating to prevent adjacent coil laps from thermally welding together during the annealing. Lower temperature anneals may also be successful.

As is known, substantially complete homogeneity is a highly desirable condition for soft magnetic materials. It has been found that proper time and temperature develops and stabilizes the permanent pores and further diffuses the contaminants into the steel to provide a substantially homogeneous steel sheet throughout the steel thickness. Generally, annealing at the higher temperatures facilitates homogeneity. For all annealing in accordance with the present invention, the strip may be annealed either in coil form or as a strand anneal of the continuously moving strip following the application of the metallic contaminant.

In order to better understand the present invention, the following examples are presented. Unless otherwise stated, the metallic contaminants used in the examples hereof were selected from the plating solutions described in Table I and were electrolytically plated.

TABLE I

Plating Metal	Solutions and Conditions
Tin	Stannous Sulfate 80 gm/l Sulfuric Acid 52 ml/l Ambient Temperature Stainless or Tin Anodes *.125 A/in^2 (1.94 A/dm^2); 1 min.
Nickel	Nickel Sulfate 328 gm/l Nickel Chloride 60 gm/l Boric Acid 211 gm/l Temperature 130°F Nickel Anodes *.25 A/in^2 (3.88 A/dm^2); 15-30 secs.
Copper	Copper Cyanide 24 gm/l Sodium Cyanide 39 gm/l Sodium Hydroxide 39 gm/l Ambient Temperature Copper Anodes *.25 A/in^2 (3.88 A/dm^2); 30-60 secs.
Zinc	Zinc Sulfate 375 gm/l Ammonium Chloride 16 gm/l Temperature 100°F Stainless Anodes *.25 A/in^2 (3.88 A/dm^2); 30 secs.
Ni-Sn	Stannous Chloride 53 gm/l Nickel Chloride 328 gm/l Ammonium Bifluoride 62 gm/l Ammonium Hydroxide (to give pH 2.5) Temperature 150°F Stainless or Nickel Anodes *0.2 A/in^2 (3.1 A/dm^2); 1½ mins.
Antimony	Antimony Oxide 60 gm/l Hydrofluoric Acid (48%) 120 ml/l Beta-napthol 1 eyedrop/l Ambient Temperature Stainless Anodes *.07 A/in^2 (1.09 A/dm^2); 2 mins.

---

*Current density pertains to total strip area.

Example I

Two Epstein packs of nominally 8-mil (0.2mm) high permeability grain-oriented silicon steel sheet having the composition of steel 1 were mechanically scribed in the as-scrubbed condition. The scribing effectively removed portions of the base coating in a pattern of substantially parallel lines substantially transverse to the rolling direction of the steel strip. Each Epstein pack had twelve (12) strips, and each strip was 3 cm wide and had the scribe lines spaced at about 5 mm intervals. Immediately following the mechanical scribing, a stress relief anneal at 1500 °F (816 °C) for two hours was performed. The samples were then electrolytically plated with copper using the copper solution described in Table I and subsequently annealed at 1650 °F (899 °C) for 5 hours in a protective atmosphere to diffuse the metallic contaminant into the silicon steel sheet body. Percentages in parentheses indicate change compared to initial properties. The magnetic properties were determined in a conventional manner for Epstein packs.

TABLE II

Epstein Pack	Initial As-Scrubbed			Mechanically Scribed			2 hr. at 1500°F(816°C) Stress-Relief Anneal			Chemically-Striped (Copper) + 1650° F(899°C) /5hr. Anneal		
	Permeability	Core Loss		Permeability	Core Loss		Permeability	Core Loss		Permeability	Core Loss	
	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)
B	1935	.417 (0·189)	.561 (0·255)	1932	.359 (0·163)	.489 (0·222)	1935	.416 (0·189)	.559 (0·254)	1933	(0·176) .388 (-7%)	(0·238) .525 (-6%)
C	1938	.416 (0·189)	.556 (0·252)	1935	.356 (0·162)	.481 (0·218)	1937	.410 (0·186)	.551 (0·250)	1936	(0·178) .391 (-6%)	(0·240) .529 (-5%)

As shown by the data in Table II, the mechanical scribing resulted in some core loss improvement as would be expected, resulting from some plastic deformation damage to the underlying silicon steel. Such improvement was not thermally stable and after the 1500 °F (816 °C) stress relief anneal the plastic deformation was removed and the properties returned substantially to their initial unscribed values of the base-coated final texture annealed silicon steel. The steel exhibited only the pattern of exposed underlying metal. The chemical striping treatment in accordance with the present invention with copper followed by the diffusion anneal at 1650 °F (899 °C) shows a significant core loss improvement averaging about 6% and clearly demonstrates the chemical striping of the present invention can be effective independent of any plastic or thermal stress or deformation of the steel. Furthermore, following a subsequent stress relief anneal at 1450 °F (788 °C) for 2 hours, the samples demonstrate a permanent core loss improvement indicating a heat-resistant domain refinement in each sample. Such samples confirm that thermal or plastic deformation of the exposed silicon steel plays no role in heat resistant domain refinement.

Figure 1 is a Scanning Electron Microscope photomicrograph of a groove, i.e. the silicon steel exposed through the base coating, filled with copper after plating the sample with copper. Figure 2 is a 150X photograph of an x-ray map showing copper in the line pattern of the silicon steel sample.

Example II

Single-strip Epstein samples 8 mils (0.2mm) thick by 3 cm wide of the steel composition of Example I were subjected to a chemical pickling in HCℓ-1% HF acid to remove all of the insulative base coating from the texture annealed strips. A plastic stencil with slits was attached to the steel surface, such that the pattern of slits formed substantially parallel lines substantially transverse to the rolling direction of the steel strip as in Example I. Each sample with the stencil thereon was electroplated with copper as described in Example I, and then annealed at 1650 °F (899 °C) for 2 hours (with the stencil removed) to diffuse the metallic contaminant into the silicon steel body. Percentages in parentheses indicate changes compared to original properties. The magnetic properties were determined in a conventional manner for single strip tests.

TABLE III

Sample No.	Original Properties			Chemically-Striped with copper $^+$ 2 hr./1650 °F (899 °C) anneal		
	Permeability	Core Loss		Permeability	Core Loss	
	@10H (796 A/m)	@1.5T (w/kg)	@1.7T (w/kg)	@10H (796 A/m)	@1.5T (w/kg)	@1.7T (w/kg)
160/163/9	1912	.437 (0.198)	.544 (0.247)	1913	.385 (0.175) (-12%)	.525 (0.238) (-3%)
160/163/10	1935	.449 (0.204)	.579 (0.263)	1946	.422 (0.192) (-6%)	.567 (0.257) (-2%)
160/163/11	1921	.495 (0.225)	.634 (0.288)	1939	.442 (0.201) (-11%)	.587 (0.266) (-8%)

Results shown in Table III show considerably improved properties of core loss after the diffusion anneal although the samples at no stage were subjected to a plastic deformation or stress. The improved properties demonstrate unequivocally that plastic deformation plays no role in domain refining by chemical striping in accordance with the present invention.

A metallographic examination of various samples in the diffusion-annealed zone showed no extensive attack of the substrate steel by the plated deposit which is consistent with the small amount of contaminant deposited and the relatively low diffusion temperatures used. Structures at high magnification tended to be varied and complicated as is not unusual in diffusion-couple metallurgy. The data suggest that the domain refinement of the present invention is not dependent on development and/or preservation of subtle composition gradients within the chemically striped or treated region. Rather, it appears that the effect is the Kirkendall porosity phenomenon which is well known in diffusion-couple metallurgy. Although there is no intent to be bound by theory, the Kirkendall related mechanism appears to suggest that contaminants of a different chemical nature can be successfully used as chemical stripe contaminants and that the precise chemical character is not as important as the diffusion rate with respect to the iron base material. Furthermore, in keeping with Kirkendall diffusion theory, it appears that lower diffusion temperatures would tend to exaggerate the Kirkendall porosity and that preferably the subsequent annealing should occur within the lower range of 1400 to 1700 °F (760 to 927 °C).

Example III

Single strips of a high permeability grain-oriented silicon steel of the steel described in Examples I and II were mechanically scribed or in some cases electrically discharge scribed in the as-scrubbed condition. The scribing effectively removed portions of the base coating in a pattern of substantially parallel lines substantially transverse to the rolling direction of the steel strip. The lines were about 3 mm wide on single strip 8-mil (0.2 mm) Epstein samples and spaced at about 5 mm intervals The samples were then electrolytically plated with various metallic contaminants from the plating solutions listed in Table I. the plating resulted in the grooves in the base coating being at least half filled with the metallic contaminant, as judged under a microscope. After plating, the samples were diffusion annealed as indicated in a substantially hydrogen atmosphere.

TABLE IV

Sample No.	Original Properties			Chemically-Striped			Metal	Anneal	
	Permeability	Core Loss		Permeability	Core Loss			Time (hrs)	Temperature (°F)(°C)
	@10H (796 A/m)	@1.5T (wpp)(w/kg)	@1.7T (wpp)(w/kg)	@10H	@1.5T (wpp)(w/kg)	@1.7T (wpp)(w/kg)			
B13	1875	.447(0·203)	.658(0·299)	1875	.433(0·197)	.644(0·292)	Sn	4	1475(802)
B15	1911	.448(0·203)	.649(0·295)	1910	.406(0·184)	.590(0·268)	Sn	4	1475(802)
B16	1899	.448(0·203)	.641(0·291)	1896	.410(0·186)	.610(0·277)	Sn	4	1475(802)
P1-10	1865	.473(0·215)	.721(0·327)	1885	.455(0·207)	.644(0·292)	Ni	1	1600(871)
P1-11	1858	.496(0·209)	.766(0·348)	1849	.476(0·216)	.733(0·333)	Ni	1	1600(871)
P1-12	1893	.494(0·224)	.712(0·323)	1829	.480(0·218)	.650(0·295)	Ni	3	1600(871)
D-3	1909	.434(0·197)	.610(0·277)	1902	.398(0·181)	.593(0·269)	Sb	6	1650(899)
D-4	1910	.471(0·214)	.694(0·315)	1911	.459(0·208)	.670(0·304)	Sb	6	1650(899)
D-5	1918	.455(0·207)	.668(0·303)	1911	.442(0·201)	.653(0·296)	Sb	6	1650(899)
D-6	1914	.424(0·192)	.674(0·306)	1911	.439(0·199)	.631(0·286)	Sb	6	1650(899)
K-2	1912	.441(0·200)	.655(0·297)	1911	.417(0·189)	.627(0·285)	Zn	3.5	1650(899)
K-3	1908	.416(0·189)	.568(0·258)	1907	.389(0·177)	.564(0·256)	Zn	3.5	1650(899)
K-12	1933	.418(0·190)	.586(0·266)	1924	.390(0·177)	.551(0·250)	Zn	3.5	1650(899)
K-16	1923	.432(0·196)	.607(0·276)	1923	.393(0·178)	.584(0·265)	Zn	3.5	1650(899)
J-18	1916	.394(0·179)	.534(0·242)	1914	.380(0·173)	.519(0·236)	Ni-Sn	3.5	1650(899)
K-5	1893	.400(0·182)	.593(0·269)	1892	.376(0·171)	.546(0·248)	Ni-Sn	3.5	1650(899)
K-14	1920	.414(0·188)	.579(0·263)	1921	.375(0·171)	.520(0·236)	Ni-Sn	3.5	1650(899)
L-7	1914	.423(0·192)	.613(0·278)	1914	.396(0·180)	.546(0·248)	Ni-Sn	3.5	1650(899)

As the data show in Table IV, for the tin, nickel, and antimony contaminants provided by the plating solutions and conditions set forth in Table I, the steels exhibited improvement in core loss properties at both 1.5 and 1.7 Tesla with little or no loss in permeability. Since the samples were heated at temperature above typical 1425 °F (774 °C) stress relief annealing, the core loss improvements were permanent with respect to heating at that temperature. In other words, the improvements were "heat proof".

Example IV

Additional samples were tested to measure the thermal stability of the magnetic properties of samples treated in accordance with the present invention. If the magnetic property improvement is a result of Kirkendall porosity, then these improvements should exhibit exceptional stability. All of the samples are 8 or 12 strip Epstein packs. Each strip of nominally 8-mil (0.2mm) steel of composition of Example I, was prepared by lightly mechanically scratching through the thin base glass to expose bare steel and was electroplated with the metals shown in Table V with lines about 0.25 mm wide and spaced at about 5 mm intervals. The strips were then stacked and then annealed at 1650°F (899°C) for 5 hours for diffusion. A considerable improvement in core loss properties was evident. The Epstein packs were then subjected to a further anneal at 2100°F (1150°C) for 2 hours or 10 hours as indicated. Percentages in parentheses indicate change compared to initial properties.

TABLE V

Sample No.	Initial Properties			Chemically-Striped with 1650°F (899°C) /5hr. Anneal			After Further Anneal at 2100°F (1149 °C)		
	Permeability	Core Loss		Permeability	Core Loss		Permeability	Core Loss	
	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)	@10H (796 A/m)	@1.5T (wpp) (W/kg)	@1.7T (wpp) (W/kg)
Zinc Stripe									
160-6/3	1931	.420 (0·191)	.590 (0·268)	1930	.378 (0·172) (-10%)	.519(0·236) (-12%)	**1912	.369(0·168) (-12%)	.508(0·231) (-14%)
Nickel-Tin Stripe									
160-6/4	1916	.414 (0·188)	.588 (0·267)	1929	.369 (0·168) (-11%)	.506(0·230) (-14%)	**1911	.370(0·168) (-11%)	.511(0·232) (-13%)
Copper Stripe									
160-6/1	1920	.422 (0·192)	.577 (0·262)	1926	.369 (0·168) (-13%)	.494(0·224) (-14%)	**1916	.381(0·173) (-10%)	.513(0·233) (-11%)
W	1926	.435 (0·197)	.584 (0·265)	1918	.393(0·178) (-10%)	.530(0·241) (-9%)	*1977	.406(0·184) (-7%)	.547(0·248) (-6%)
X	1926	.428 (0·194)	.572 (0·260)	1885	.395(0·179) (-9%)	.551(0·250) (-4%)	*1923	.414(0·188) (-3%)	.551(0·250) (-4%)
Y	1908	.460 (0·209)	.629 (0·	1896	.413 (0·188) (-10%)	.569(0·258) (-10%)	*1909	.425(0·193) (-8%)	.583(0·265) (-7%)
Z	1921	.474 (0·215)	.626	1874	.410(0·186) (-14%)	.591(0·268) (-6%	*1915	.417(0·189) (-12%)	.562(0·255) (-10%)

**Sample annealed 10 hrs. at 2100°F (1149 °C)
*Sample annealed 2 hrs. at 2100°F (1149 °C)

The data and results of Table V show that the core loss improvement persisted up to 2100 °F (1150 °C) which demonstrates the unique and exceptional stability of the domain refining of the present invention. Furthermore, the Scanning Electron Microscope (SEM) chemical analysis by X-ray showed that the previously chemical striped areas were now of the same composition as the matrix steel. In other words, the high temperature had homogenized the strip and the contaminant was no longer localized but part of the overall residual impurity in the bulk of the sample. The homogeneity and low stress state of the soft magnetic material is a desired result.

In view of the discoveries of the present invention, it is believed that the metal contaminants chosen will perform as expected if the diffusion rates are slower than the self-diffusion rate of iron in the ferrous base alloy. Furthermore, the slower the rate of the diffusion through iron, the more suitable the metal may be as a contaminant to produce the permanent porosity. For example, copper is of the order of 4 times slower than iron in diffusion through iron. Nickel is of the order of 500 times slower. Such metallic elements having slower diffusion rates in iron should result in the Kirkendall porosity phenomenon and the benefits of the present invention.

Although the metallic contaminants can provide heat resistant domain refinement resulting from domain refinement of unstressed grain-oriented silicon-irons having a good base coating thereon, reproduceability was poor in those cases where the base coating was inadequate. It appears that the naturally-occurring forsterite base coating which results from the final texture annealing sometimes permits spurious plating of the metal contaminant through pores and cracks in the forsterite. Such was evident when nodules of antimony, for example, were found appearing and growing directly out of pores in the forsterite base coating in areas located away from the exposed underlying silicon steel and between the substantially parallel lines as shown in Figure 4.

It has been found that, in accordance with an embodiment of the invention, the use of an additional sealant coating or barrier coating applied to the forsterite before applying the metallic contaminant to the exposed silicon steel stripes results in a striking improvement in consistency and reproduceability to effect heat resistant domain refinement The main purpose of introducing the barrier coating in the process is to seal the pores and cracks in the forsterite coating. Table VI identifies several coatings which are believed to be useful in acting as a barrier coating in accordance with the present invention. The similarity between all of these coatings is that they are all water soluble and cure at relatively low temperatures. Furthermore, these barriers coatings contain phosphorus or silicates, or combinations or compounds thereof as the primary constituent of the coating. Preferably the coating primary constituent is a metal phosphate or metal silicate, and more preferably, the coating should be one that when cured sets up essentially as a magnesium phosphate layer.

TABLE VI

Designation	Barrier Coating and Conditions	Concentration
SC	Phosphoric Acid (85%) Magnesium Oxide Nalcoag (1050)$^{\text{Regd. T.M.}}$ Chromic Trioxide Water	202 gm/l 22 gm/l 318 ml/l 46 gm/l Balance
Cured: 1000 ° F (538 ° C) - 1 min.(air)		
CS	Sodium Silicate (40-42 Be) Water	500 ml/l Balance
Cured: 800 ° F (427 ° C) - 1 min.(air)		
PS	Phosphoric Acid (85%) Magnesium Oxide Kasil #1$^{\text{Regd. T.M.}}$ Ammonium Hydroxide (58%) Chromic Trioxide Dupanol$^{\text{Regd. T.M.}}$ (2%) Water	120 gm/l 18 gm/l 22 gm/l 21 ml/l .34 gm/l 1.0 ml/l Balance
Cured: 800 ° F (427 ° C) - 1 min.(air)		
P	Phosphoric Acid (85%) Magnesium Oxide Ammonium Hydroxide (58%) Chromic Trioxide Dupanol$^{\text{Regd. T.M.}}$ (2%) Water	118 gm/l 18 gm/l 20 ml/l .34 gm/l 1.0 ml/l Balance
Cured: 800 ° F (427 ° C) -1min.(air)		

In order to better understand the present embodiment the following further examples are presented.

Example V

Tests were performed to demonstrate the effect of the barrier coating on enhancing the heat resistant domain refinement process. All of the samples were obtained from various heats of nominally 8-mil (0.2mm) gauge silicon steel having the typical composition of Steel 1. Single strips of Steel 1 were mechanically scribed into the as-scribed condition. The scribing effectively removed portions of the base coating in a pattern of substantially parallel lines substantially transverse to the rolling direction of the steel strip. The lines were about 0.25 mm wide and spaced at about 5 mm intervals. Each sample was then coated with barrier coating "P" from Table VI after the step of removing the base coating. All of the samples were thereafter electroplated with either zinc or copper from the plating solution listed in Table I. The magnetic properties are Epstein single strip results from strips of 30 x 3 cm. After electroplating, all of the samples were subjected to a diffusion annealing step at time and temperature set forth in Table VII. Percentages indicate change in core loss properties compared to original properties. The magnetic properties were determined in a conventional manner for single strip tests.

TABLE VII

	Original Properties				After 5hr/1650°F (899°C) Diffusion Anneal					After 10hr/1650°F (899°C) Diffusion Anneal				
	Permeability	Core Loss			Permeability	Core Loss				Permeability	Core Loss			
	@10H (796 A/m)	@1.5T (wpp) (w/kg)	@1.7T (wpp) (w/kg)	Contaminant	@10H (796A/m)	@1.5T (wpp) (w/kg)	cf. Change	@1.7T (wpp) (w/kg)	cf. Change	@10H (796 A/m)	@1.5T (wpp) (w/kg)	cf. Change	@1.7T (wpp) (w/kg)	cf. Change
G1	1935	.430 (0.195)	.585 (0.267)	Zinc	1940	.386 (0.175)	-10%	.523 (0.237)	-11%	1940	.386 (0.175)	-10%	.530 (0.241)	- 9%
G5	1922	.420 (0.191)	.636 (0.289)		1908	.406 (0.184)	- 3%	.592 (0.269)	- 7%	1946	.413 (0.188)	- 2%	.607 (0.276)	- 5%
L9	1907	.412 (0.187)	.604 (0.274)		1910	.358 (0.163)	-13%	.512 (0.232)	-15%	--	--	--	--	--
G3	1922	.499 (0.227)	.677 (0.307)	Copper	1923	.430 (0.195)	-14%	.579 (0.263)	-14%	1924	.463 (0.210)	- 7%	.623 (0.283)	- 8%
G7	1932	.525 (0.238)	.700 (0.318)		1934	.442 (0.201)	-16%	.598 (0.271)	-14%	1938	.405 (0.184)	-23%	.545 (0.247)	-22%
F9	1952	.446 (0.202)	.628 (0.285)		1951	.417 (0.189)	- 7%	.602 (0.273)	- 4%	1954	.396 (0.180)	-11%	.573 (0.260)	- 9%
K13	1904	.478 (0.217)	.666 (0.302)		1909	.421 (0.191)	-12%	.598 (0.271)	-10%	--	--	--	--	--
J2	1938	.473 (0.215)	.625 (0.284)		1932	.391 (0.178)	-17%	.536 (0.243)	-14%	--	--	--	--	--
Average Improvement (all strips)							-12%		-11%			-11%		-10%

When compared with the control samples which were magnetically tested as received before any treatment, Table VII presents data which shows that most of the samples had an attractive improvement in core loss averaging of the order of 10 to 12%. For comparison purposes, samples from the same batches of material were capable of providing 15-20% improvement in core losses by conventional mechanical scribing techniques. A further advantage of the present invention is that such improvement in core loss may be the result of heat resistant domain refinement.

Example VI

By way of further examples, additional tests were performed to demonstrate the domain refining process on different silicon steels having compositions of Steels 1, 2 and 3 for Epstein test packs. Each sample is prepared in a manner similar to that in the previous Example V, with required modifications to produce the different grain-oriented silicon steels at nominally 7-mil (0.18mm) or 8-mil (0.2mm) gauge, thereafter processed in accordance with the previous example under the experimental conditions described in Table VIII with parallel bands of treated regions about 5 mm apart. The magnetic properties were determined in a conventional manner for Epstein packs.

TABLE VIII

Steel	Gauge (mils) (mm)	Contaminant	Initial Properties			3½ hr. 1650°F (899 °C) Diffusion Anneal			7 hr. 1650°F (899 °C) Diffusion Anneal		
			Permeability	Core Loss		Permeability	Core Loss		Permeability	Core Loss	
			@10H (796 A/m)	@1.5T (wpp)(W/kg)	@1.7T (wpp)(W/kg)	@10H (796 A/m)	@1.5T (wpp)(W/kg)	@1.7T (wpp)(W/kg)	@10H (796 A/m)	@1.5T (wpp)(W/kg)	@1.7T (wpp)(W/kg)
1	8 (0.2)	Copper	1920	.422(0.192)	.577(0.262)	1926	.386(0.175)	.520(0.236)	1926	.389(0.177)	.494(0.224)
1	8 (0.2)	Ni-Sn	1916	.414(0.188)	.588(0.267)	1929	.378(0.172)	.516(0.234)	1929	.369(0.168)	.506(0.230)
1	8 (0.2)	Zinc	1919	.420(0.191)	.590(0.268)	1931	.390(0.177)	.539(0.245)	1930	.378(0.172)	.519 (0.236)
2	7 (0.18)	Copper	1855	.441(0.200)	.678(0.308)	1853	.417(0.189)	.642(0.291)	--	--	--
3	7 (0.18)	Copper	1868	.418(0.190)	.632(0.287)	1866	.388(0.176)	.604(0.274)	--	--	--

The data of Table VIII show that the domain refining process of the present invention can reduce the core loss in 8-mil (0.2mm) gauge material of Steel 1 by up to 11% when compared to initial properties. The best improvement was obtained with the contaminant copper. The core loss is 7-mil (0.18mm) material of Steel 2 was reduced by about 5% at 1.5T and by 5% at 1.7T. The core loss in 7-mil (0.18mm) material of Steel 3 was reduced by about 7% at 1.5T and by about 4% at 1.7T.

Example VII

Further tests were performed to compare the results of domain refining with and without a barrier coating on silicon steel having the composition of Steel 1 for single strip Epsteins. Each sample was prepared in a manner similar to that in Example V. The strips were mechanically scratched to remove the thin base coating in a pattern of substantially parallel lines transverse to the rolling direction. For those samples so marked, the barrier coating "P" was applied after removing the lines of base coating. All the samples were thereafter electroplated with nickel or nickel-tin as indicated in Table IX from the appropriate plating solution of Table I and subjected to a diffusion anneal at time and temperature of 1 to 5 hours at 1600 to 1650 °F (871 to 899 °C) in hydrogen. The magnetic properties are Epstein single strip results of nominally 8-mil (0.2 mm) strip of 30 x 3 cm. Percentages in parentheses indicate change compared to original properties.

TABLE IX

Not Barrier Coated

Nickel Chemical Stripe

Sample #	Original Properties			Chemical Stripe + Diffusion Anneal		
	Permeability	Core Loss				
	μ10H (796 A/m)	@1.5T (wpp) (W/Kg)	@1.7T (wpp) (W/Kg)	μ10H (796A/m)	@1.5T (wpp) (W/Kg)	@1.7T (wpp) (W/Kg)
P1-10	1865	.473 (0.215)	.721 (0.327)	1885	.455 (0.207) (-4%)	.644 (0.292) (-11%)
P1-11	1858	.496 (0.225)	.766 (0.348)	1849	.476 (0.216) (-4)	.733 (0.333) (-4)
P1-12	1893	.494 (0.224)	.712 (0.323)	1879	.480 (0.218) (-3)	.650 (.0295) (-9)
Average	1872	.488 (0.222)	.733 (0.333)	1871	.470 (0.213) (-4%)	.676 (0.307) (-8%)
Nickel-Tin Chemical Stripe						
J-18	1916	.394 (0.179)	.534 (0.161)	1914	.380 (0.173) (-4%)	.519 (0.236) (-3%)
K-5	1893	.400 (0.182)	.595 (0.270)	1892	.376 (0.171) (-6)	.546 (0.248) (-8)
K-14	1920	.414 (0.188)	.579 (0.263)	1921	.375 (0.170) (-9)	.520 (0.236) (-10)
L-7	1914	.423 (0.192)	.613 (0.278)	1914	.396 (0.180) (-6)	.546 (0.248) (-11)
Average	1911	.408 (0.185)	.580 (0.263)	1910	.383 (0.174) (-6%)	.533 (0.242) (-8%)

Barrier Coated

Nickel Chemical Stripe						
N-41/5	1917	.470 (0.213)	.646 (0.293)	1867	.398 (0.181) (-15%)	.555 (0.252) (-14%)
N-41/10	1918	.433 (0.197)	.594 (0.270)	1843	.379 (0.172) (-12)	.525 (0.238) (-12)
N-41/4	1899	.469 (0.213)	.657 (0.298)	1844	.427 (0.194) (-9)	.620 (0.281) (-6)
Average	1911	.457 (0.207)	.632 (0.287)	1851	.401 (0.182) (-12%)	.567 (0.257) (-10%)
Nickel-Tin Chemical Stripe						
G2	1940	.419 (0.190)	.567 (0.257)	1932	.363 (0.165) (-13%)	.502 (0.228) (-11%)
G6	1936	.489 (0.222)	.665 (0.302)	1936	.428 (0.194) (-12)	.574 (0.261) (-14)
L4	1894	.443 (0.201)	.659 (0.299)	1896	.392 (0.178) (-12)	.561 (0.255) (-15)
L9	1907	.412 (0.187)	.604 (0.274)	1910	.358 (0.163) (-13)	.512 (0.232) (-15)
Average	1919	.441 (0.200)	.624 (0.283)	1919	.385 (0.175) (-13%)	.537 (0.244) (-14%)

The data of Table IX clearly shows the benefits of the present invention. For comparable samples, the barrier coated samples improved the consistency and reproductibility of the results. All the barrier coated samples had better core loss values than comparable samples which were not so coated. Furthermore, none of the barrier coated samples exhibited any nodules of metallic contaminant on the surface of the sample in areas located away from the exposed pattern line. This finding indicated that the barrier coating had blocked any pores or cracks in the base-glass coating which could have exposed bare metal which would have been plated with the contaminant.

In the course of such experiments, it was unexpectedly found that the barrier coating not only seals the pores and cracks in the base coating of the grain-oriented silicon steel, but it also acts synergistically with the major contaminant in the striped area of the steel during and after the diffusion anneal. Particularly, it is noted that with zinc or nickel-tin as the major contaminant, phosphorus was evident in the permanent defect produced in the steel.

Metallographic examination of various samples in the diffusion annealed zone showed no extensive attack of the substrate steel by the plated deposit which is consistent with the small amount of contaminant deposited and the relatively low diffusion temperatures employed. Structures at high magnification tended to be varied and complicated as is not usual in diffusion-couple metallurgy. Confirmation of interdiffusion between the steel and the contaminant as well as the steel, the contaminant, and phosphorus is shown in Figures 5 to 10. In Figure 5, a cross section at 375X through the Ni-Sn stripe after a two-hour diffusion anneal at 1650°F (899°C) shows nodules on the surface of the steel. Figure 6 shows the same nodule at 3000X. Figures 7, 8, 9 and 10 clearly display by scanning Electron Microscope X-ray mapping the intrusion of nickel, tin phosphorus, and iron into the diffusion zone.

As was an object of the present invention, a method has been developed for providing heat resistant domain refinement for grain-oriented silicon steels to improve the core loss values. A further advantage of the method of the present invention is the ability to remove portions of the base coating to expose a pattern of the underlying silicon steel such as in lines substantially transverse to the rolling direction by any conventional or unconventional means provided that the steel exposed through the base coating is free from thermal and plastic stresses. The barrier coating enhances the core loss improvements and the reproduceability of such improvements. An advantage of the present invention is that a semifinished sheet product having a barrier coating and metallic contaminant can be produced for subsequent annealing by the customer before or after fabricating into transformer cores.

Claims

1. A method for refining the magnetic domain wall spacing of grain-oriented silicon steel sheet or strip having an insulation base coating thereon, characterized in the method comprising:

removing portions of the base coating to expose a line pattern of the underlying silicon steel;

applying a metallic contaminant to the exposed silicon steel, the metallic contaminant having a diffusion rate lower than iron in the silicon steel, the exposed steel being free of thermal and plastic stresses;

thereafter annealing the steel and contaminant thereon at a temperature of 760 ° C (1400 ° F) or more in a protective atmosphere to diffuse sufficient and controlled amounts of contaminant into the exposed steel to produce lines of permanent pores and so effect heat resistant domain refinement and reduced core loss of stress-free steel.

2. A method according to claim 1, wherein the step of annealing the steel and contaminant thereon includes temperatures up to 982 ° C (1800 ° F) to produce lines of permanent pores stable up to 1149 ° C (2100 ° F).

3. A method according to claim 1 or 2, wherein the step of annealing the steel and contaminant thereon includes temperature of from 760 ° C to 927 ° C (1400 to 1700 ° F) to develop and stabilize the permanent pores.

4. A method according to claim 1, wherein the step of annealing the steel and contaminant thereon includes temperatures up to 1149 ° C (2100 ° F) to further diffuse the contaminants into the steel to provide a substantially homogenous steel sheet throughout the steel thickness.

5. A method according to any one of the preceding claims, wherein the metallic contaminant is copper, tin, nickel, zinc or antimony, or combinations or compounds thereof.

6. A method according to any one of the preceding claims, further comprising, prior to applying said metallic contaminant, applying to the base coated steel a barrier coating having a primary constituent of phosphorus or silicate, or combinations or compounds thereof, for sealing the base coatings.

7. A method according to claim 6, wherein the step of applying the barrier coating is performed followed by the step of removing portions of both the barrier and base coatings and thereafter followed by applying the metallic contaminant.

8. A method according to claim 6, wherein the step of removing portions of the base coating is performed before applying the barrier coating to the base coating and after applying said barrier coating the metallic contaminant is applied to the exposed steel.

9. A method according to claim 6, 7 or 8, wherein the barrier coating is a metal-phosphate-based coating containing at least 25 percent, by weight, of phosphorus in the dried coating.

10. A method according to claim 9, wherein the barrier coating is a magnesia-based coating.

11. A method according to anyone of claims 6 to 10, wherein the step of annealing the steel uses a reducing atmosphere of hydrogen or nitrogen of mixtures thereof.

12. A method according to any one of the preceding claims, wherein the pattern comprises generally parallel lines of exposed steel extending substantially transverse to the rolling direction of the steel.

13. A method according to any one of the preceding claims, wherein the base coating is forsterite.

14. A method according to any one of the preceding claims, wherein prior to the annealing step and after applying the metallic contaminant, the silicon steel is fabricated into an article of manufacture.

Patentansprüche

1. Verfahren zum Vergüten des magnetischen Domänenwandabstands von kornorientiertem Siliziumstahlblech oder -band mit einer darauf befindlichen Isolierungsgrundierung, dadurch gekennzeichnet, daß das Verfahren

   die Entfernung von Teilen der Grundierung zur Freilegung eines Linienmusters des darunter liegenden Siliziumstahls;

   die Applikation einer metallischen Verunreinigung auf den freiliegenden Siliziumstahl, wobei die metallische Verunreinigung eine niedrigere Diffusionsrate aufweist als das Eisen in dem Siliziumstahl und der freiliegende Stahl von thermischen und plastischen Spannungen frei ist, und

   das anschließende Anlassen des Stahls und der darauf befindlichen Verunreinigung bei einer Temperatur von 760 ° C (1400 ° F) oder mehr in einer Schutzatmosphäre zur Diffusion ausreichender und gesteuerter Mengen des Verunreinigungsmittels in den freiliegenden Stahl mit dem Ziel einer Produktion von Linien bleibender Poren unter Gewährleistung einer wärmebeständigen Domänenvergütung und eines verminderten Kernverlusts des spannungsfreien Stahls

   umfaßt.

2. Verfahren nach Anspruch 1, wobei die Stufe des Anlassens des Stahls und der darauf befindlichen Verunreinigung Temperaturen bis zu 982 ° C (1800 ° F) zur Produktion von Linien von bis zu 1149 ° C (2100 ° F) stabilen bleibenden Poren einschließt.

3. Verfahren nach Anspruch 1 oder 2, wobei die Stufe des Anlassens des Stahls und der darauf befindlichen Verunreinigung zum Entwickeln und Stabilisieren der bleibenden Poren eine Temperatur von 760 ° C bis 927 ° C (1400 bis 1700 ° F) einschließt.

4. Verfahren nach Anspruch 1, wobei die Stufe des Anlassens des Stahls und der darauf befindlichen Verunreinigung zum weiteren Diffundieren der Verunreinigungen in den Stahl mit dem Ziel einer Bereitstellung eines über die Stahldicke hinweg praktisch homogenen Stahlblechs Temperaturen bis zu 1149 ° C (2100 ° F) einschließt.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die metallische Verunreinigung auf Kupfer, Zinn, Nickel, Zink oder Antimon oder Kombinationen oder Verbindungen derselben besteht.

6. Verfahren nach einem der vorhergehenden Ansprüche, zusätzlich umfassend (vor Applikation der metallischen Verunreinigung) die Applikation einer Sperrschicht mit einem Hauptbestandteil in Form von Phosphor oder Silikat oder Kombinationen oder Verbindungen derselben zum Versiegeln der Grundierungen auf den grundierten Stahl.

7. Verfahren nach Anspruch 6, wobei nach Applikation der Sperrschicht Teile sowohl der Sperrschicht als auch der Grundierungen entfernt und anschließend die metallische Verunreinigungen appliziert werden.

8. Verfahren nach Anspruch 6, wobei Teile der Grundierung entfernt werden, bevor die Sperrschicht auf die Grundierung appliziert wird, und die metallische Verunreinigung auf den freiliegenden Stahl appliziert wird, nachdem die Sperrschicht appliziert wurde.

9. Verfahren nach Anspruch 6, 7 oder 8, wobei es sich bei der Sperrschicht um eine Schicht auf Metallphosphatbasis mit mindestens 25 Gew.-% Phosphor in der getrockneten Schicht handelt.

10. Verfahren nach Anspruch 9, wobei die Sperrschicht aus einer Schicht auf Magnesiumoxidbasis besteht.

11. Verfahren nach einem der Ansprüche 6 bis 10, wobei in der Stufe des Anlassens des Stahls eine reduzierende Atmosphäre aus Wasserstoff oder Stickstoff oder Gemischen derselben benutzt wird.

12. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Muster im allgemeinen parallele Linien von freiliegendem Stahl, die im wesentlichen quer zur Walzrichtung des Stahls verlaufen, umfaßt.

13. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Grundierung aus Forsterit besteht.

14. Verfahren nach einem der vorhergehenden Ansprüche, wobei vor der Anlaßstufe und nach Applikation der metallischen Verunreinigung der Siliziumstahl zu einem Gegenstand verarbeitet wird.

Revendications

1. Procédé de raffinage de l'espacement entre les parois des domaines magnétiques d'une feuille ou bande d'acier au silicium à grains orientés ayant, sur le dessus, un revêtement de base isolant, caractérisé en ce que ce procédé comprend :

l'enlèvement de parties du revêtement de base pour exposer une configuration de lignes de l'acier au silicium sous-jacent ;

l'application d'une impureté métallique sur l'acier au silicium exposé, l'impureté métallique ayant une vitesse de diffusion inférieure au fer dans l'acier au silicium, l'acier exposé étant exempt de contraintes thermiques et plastiques ;

ensuite, le recuit de l'acier et de l'impureté à une température de 760 °C (1400 °F) ou plus dans une atmosphère protectrice pour diffuser des quantités suffisantes et contrôlées d'impureté dans l'acier exposé, pour produire des lignes de pores permanents et effectuer ainsi un raffinage des domaines résistant à la chaleur et une perte réduite dans le coeur de l'acier exempt de contraintes.

2. Procédé selon la revendication 1, dans lequel l'étape de recuit de l'acier et de l'impureté inclut des températures jusqu'à 982 °C (1800 °F) pour produire des lignes de pores permanentes stables jusqu'à 1149 °C (2100 °F).

3. Procédé selon la revendication 1 ou 2, dans lequel l'étape de recuit de l'acier et de l'impureté inclut des températures de 760 °C à 927 °C (1400 °F à 1700 °F) pour développer et stabiliser les pores permanentes.

4. Procédé selon la revendication 1, dans lequel l'étape de recuit de l'acier et de l'impureté inclut des températures jusqu'à 1149 °C (2100 °F) pour mieux diffuser les impuretés dans l'acier et fournir une feuille d'acier substantiellement homogène à travers l'épaisseur de l'acier.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'impureté métallique est le cuivre, l'étain, le nickel, le zinc ou l'antimoine, ou les combinaisons ou composés de ceux-ci.

6. Procédé selon l'une quelconque des revendications précédentes, comprenant en outre, avant l'application de ladite impureté métallique, l'application, sur l'acier revêtu d'un revêtement de base, d'un revêtement barrière ayant un constituant primaire de phosphore ou silicate, ou les combinaisons ou composés de ceux-ci, pour sceller les revêtements de base.

7. Procédé selon la revendication 6, dans lequel l'étape d'application du revêtement barrière est effectuée, suivie de l'étape d'enlèvement de parties tant des revêtements barrière que de base, suivie ensuite de l'application de l'impureté métallique.

8. Procédé selon la revendication 6, dans lequel l'étape d'enlèvement de parties du revêtement de base est effectuée avant d'appliquer le revêtement barrière sur le revêtement de base et, après l'application dudit revêtement barrière, l'impureté métallique est appliquée sur l'acier exposé.

9. Procédé selon la revendication 6, 7 ou 8, dans lequel le revêtement barrière est un revêtement à base de phosphate métallique contenant au moins 25 % en poids de phosphore dans le revêtement séché.

10. Procédé selon la revendication 9, dans lequel le revêtement barrière est un revêtement à base de magnésie.

11. Procédé selon l'une quelconque des revendications 6 à 10, dans l'étape de recuit de l'acier utilise une atmosphère réductrice d'hydrogène ou d'azote ou de mélanges de ceux-ci.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel la configuration comprend des lignes généralement parallèles d'acier exposé s'étendant substantiellement transversalement par rapport à la direction de laminage de l'acier.

13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le revêtement de base est de la forstérite.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel, avant l'étape de recuit et après l'application de l'impureté métallique, l'acier au silicium est usiné en un article manufacturé.

Fig. 1

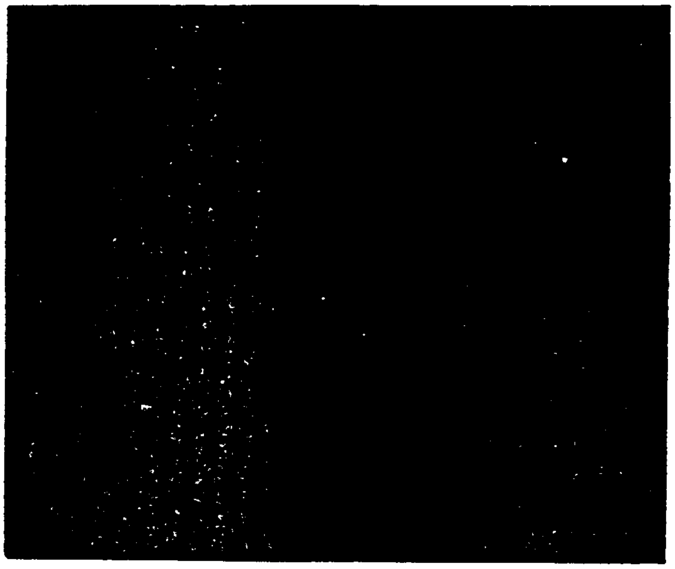

Fig. 2

Fig. 3

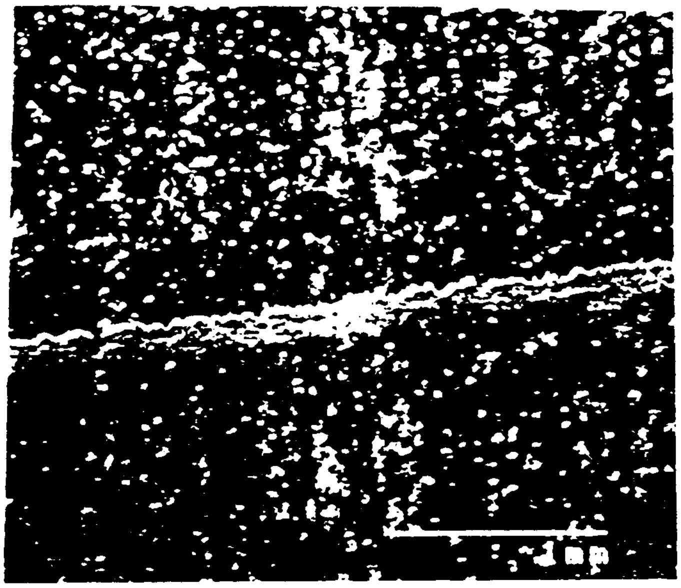

Fig. 4

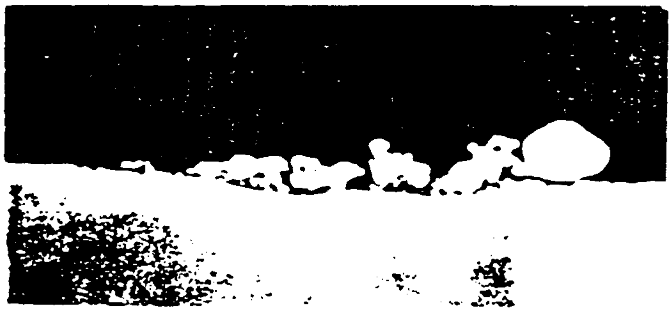

Fig. 5

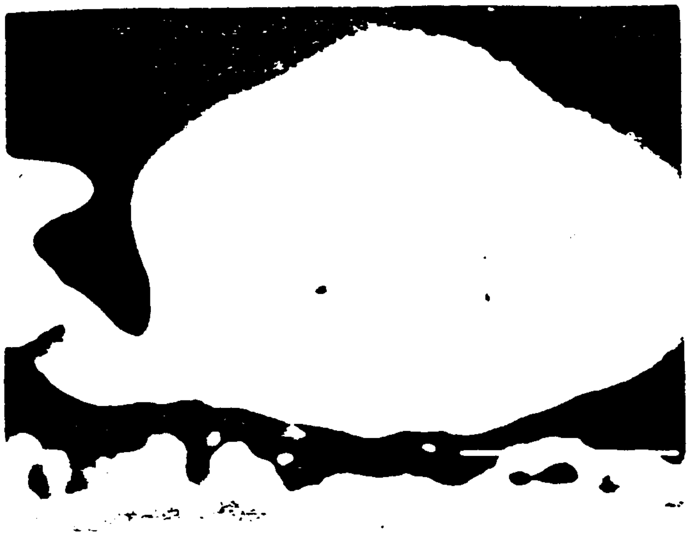

Fig. 6

Fig. 7

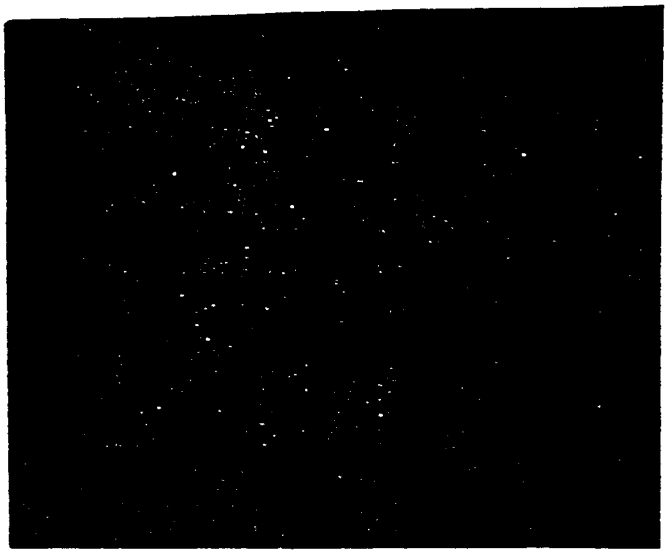

Fig. 8

Fig. 9

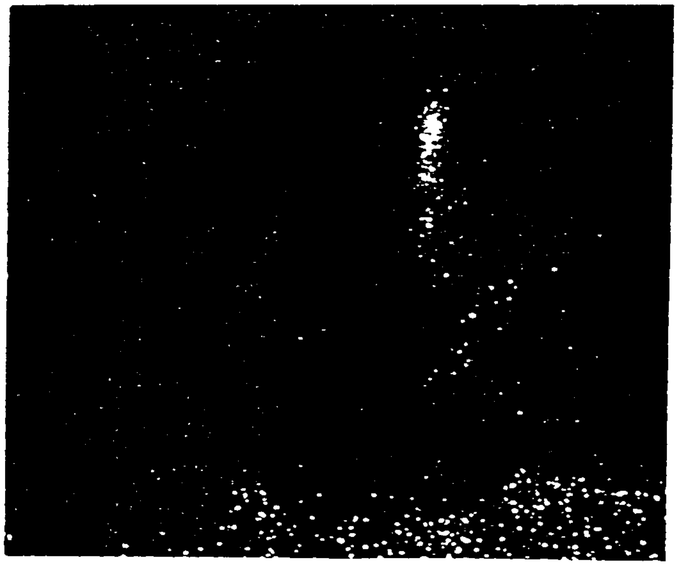

Fig. 10