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Jackson

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[54] **HIGH PERMEABILITY CUBE-ON-EDGE ORIENTED SILICON STEEL AND METHOD OF MAKING IT**

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[58] **Field of Search** .... 148/111-112, 148/113, 121, 122, 31.55; 75/123 B

[56] **References Cited**

UNITED STATES PATENTS

3,347,718	10/1967	Carpenter et al.	148/111
3,575,739	4/1971	Fiedler	148/111
3,636,579	1/1972	Sakakura et al.	148/111
3,700,506	10/1972	Tanaka et al.	148/111
3,725,143	4/1973	Alworth et al.	75/123 B
3,764,406	10/1973	Littmann	148/111

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[57] **ABSTRACT**

Cube-on-edge oriented silicon steel and method of making it wherein the silicon steel is characterized by high permeability values. To the standard melt chemistry for cube-on-edge oriented silicon steel from about 0.002 to about 0.012 percent boron and from about 0.003 to about 0.010 percent nitrogen are added. The melt material is cast into ingots or slabs, reheated, hot rolled to hot band, annealed, pickled, cold reduced to final gauge, subjected to a decarburizing step and given a final high temperature anneal to produce the desired final orientation. The temperature of the anneal following hot rolling bears an inverse relationship to the final gauge of the silicon steel. Prior to the final anneal the silicon steel is provided with an annealing separator. A grain growth inhibitor may be provided in the environment of the stock during the primary grain growth stage of the final anneal so as to inhibit primary grain growth and to favor the growth of cube-on-edge oriented nuclei during the secondary grain growth stage.

10 Claims, No Drawings

HIGH PERMEABILITY CUBE-ON-EDGE ORIENTED SILICON STEEL AND METHOD OF MAKING IT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a cube-on-edge oriented silicon steel and method of making it, and more particularly to such a silicon steel characterized by high permeability values.

2. Description of the Prior Art

The present invention relates to the production of silicon steel sheet stock for magnetic uses and in which the body centered cubes making up the grains or crystals are oriented in the cube-on-edge position, designated (100) [001] in accordance with Miller's indices. As is well known, stocks 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. Cube-on-edge oriented silicon steel has a number of applications, primary among which is its use for the cores of magnetic apparatus such as transformers and the like.

Silicon steels having the cube-on-edge grain orientation were first produced by Goss, as taught in U.S. Pat. No. 1,965,559. From the outset, however, silicon steels of this orientation with consistently good magnetic properties were difficult to produce on a commercial basis. Aa a consequence, prior art workers have devoted much time and effort to the development of such silicon steels.

Over the years prior art workers have made rapid advances in the commercial production of cube-on-edge oriented silicon steels. For example, in U.S. Pat. No. 2,287,467 Carpenter and Jackson taught a process of wet hydrogen decarburization enabling the removal of carbon and the harmful magnetic aging caused thereby. It had long been recognized that the formation of the cube-on-edge orientation involved the grain boundary energy phenomenon. It was further recognized that an inhibitor such as sulfur in the form of sulfides, if adequately dispersed in the grain boundaries during the primary grain growth stage of the final anneal, would prevent the primary grain structure from undergoing such grain growth as would interfere with subsequent secondary grain growth. As a result, a fine grained matrix is maintained until secondary grains of the cube-on-edge orientation begin to consume the grains of other orientations. Thereafter, as the temperature rises further during the final anneal, secondary grain growth will proceed by grain boundary energy and convert the fine grain matrix into a well developed cube-on-edge structure. It was at first believed that the amount of inhibitor at the grain boundaries during the primary grain growth stage of the final anneal depended upon the amount of inhibitor in the original melt and the amount of inhibitor lost during the processing steps ahead of the final anneal. As a consequence, many of these processing steps were considered critical in order to avoid inhibitor loss.

In U.S. Pat. No. 2,599,340 Littmann and Heck taught that superior permeabilities could be obtained in silicon-steels which were hot rolled to intermediate gauge from a high slab temperature of from 2,300°F. It was determined that the high hot rolling temperature effected in part at least the solution and subsequent precipitation of inhibitor such as manganese sulfide in silicon iron. In U.S. Pat. No. 2,906,645 Carpenter et al taught the use of a magnesia annealing separator which, as a part of the process, produced an insulative mill glass on the finished silicon steel. Such a surface film or glass is highly desirable in many applications, providing electrical resistivity and protection against oxidation or carburization.

In United States Letters Pat. No. 3,333,991; 3,333,992 and 3,333,993 Kohler taught that an inhibitor could be provided in the environment of the silicon steel immediately prior to or during the primary grain growth stage of the final anneal and could be caused to diffuse into the grain boundaries. As a result, it was no longer necessary to rely solely on the amount of inhibitor present in the initial melt, and many of the processing steps ahead of the final anneal came to be considered less critical. In accordance with the last mentioned patents, sulfur and compounds thereof and selenium and compounds thereof may serve as the inhibitor. The inhibitor may be provided in the environment of the silicon steel during the primary grain growth stage of the final anneal in a number of ways. For example, sulfur or a sulfur compound which dissociates or decomposes at the temperatures of primary grain growth may be added to the annealing separator. On the other hand, the annealing atmosphere may be charged with hydrogen sulfide or any other appropriate gaseous sulfur compound. In yet another variant procedure, hydrogen sulfide or any other appropriate gaseous sulfur compound may be added to the atmosphere in the decarburizing step ahead of the final anneal. The sulfur compound reacts with the iron surface to form a controlled iron sulfide film on the material, providing a source of sulfur during the primary grain growth stage of the final anneal.

The prior art workers finally reached a stage wherein a cube-on-edge oriented silicon steel could consistently be produced on a commercial basis having good magnetic characteristics, including a permeability at H=10 oersteds averaging about 1820. Attention has since been centered upon the improvement of these magnetic characteristics. In Unites States Letters Pat. No. 3,287,183 a method of making cube-on-edge oriented silicon steel is taught wherein the product has a permeability at H=10 oersteds of at least 1,800 and up to about 1,910. In accordance with this patent, the melt composition is critical and must include from 0.025 to 0.085 percent carbon, from 2.5 to 4.0 percent silicon, from 0.005 to 0.050 sulfur and, of special importance, from 0.010 to 0.065 percent acid soluble aluminum, the balance being iron and mixed impurities. After hot rolling and pickling, the silicon steel is reduced to final gauge by one or more stages of cold rolling. Aside from the melt composition, it is critical that the last stage of cold rolling produces a reduction of 81 to 95 percent and that before the final cold rolling step the silicon iron be subjected to a high temperature anneal such that aluminum nitrides are formed in the steel sheet in such quantity that more than 0.0020 percent nitrogen is present as aluminum nitride.

While the magnetic properties of the cube-on-edge oriented silicon iron produced in accordance with U.S. Pat. No. 3,287,183 are excellent, the process does involve certain drawbacks. For example, pickling cannot be as readily accomplished as in other routings by virtue of the presence of the aluminum. The process requires that the anneal immediately prior to the final stage of cold rolling be a high temperature anneal followed by a relatively rapid cool or quench. Finally, by virtue of the presence of aluminum oxide on the surface of the silicon steel, an ordinary insulative mill glass is difficult to form thereon.

United States Letters Pat. No. 3,700,506 teaches the use of a particular annealing separator in the process of the above mentioned U.S. Pat. No. 3,287,183. In accordance with this teaching, a magnesium oxide separator is used to which a titanium compound and a maganese compound have been added. To the annealing separator boron or a boron compound is additionally added together with sulfur or a sulfur compound or selenium or a selenium compound. The patent teaches that the boron or boron compound when added with sulfur or selenium results in an improved core loss in the final product and in the formation of a thin, uniform glassy film on the silicon steel. In this patent the boron or boron compound is used to control secondary grain growth during the final anneal, the aluminum nitrides being relied upon to control grain growth during theprimary grain growth stage of the final anneal.

The present invention is directed to the production of a cube-on-edge oriented silicon steel having excellent magnetic characteristics including a permeability at H=10 oersteds of greater than about 1,820 and up to 1,900 or more. No unusually high temperature anneal is required prior to the final anneal; pickling may be readily accomplished in the usual manner; boron and nitrogen additions are made to control grain growth during the primary grain growth stage of the final anneal; and a conventional insulative mill glass may be formed on the silicon steel as a part of its regular processing.

SUMMARY OF THE INVENTION

The present invention contemplates the addition of boron and nitrogen in critical amounts to a conventional melt composition for cube-on-edge oriented silicon iron. The melt may also contain up to 0.008 aluminum.

Any suitable melt process may be employed. The melt can be either cast as ingots or continuously cast slabs. Prior to hot rolling, the silicon steel is heated to a temperature of from about 2,300° to about 2,550° and thereafter hot rolled to hot band. Following hot rolling, the silicon steel is annealed within a temperature range of from about 1,500°F to about 2100°F and the annealing temperature used bears an inverse relationship to the final gauge of the silicon steel. The anneal is followed by conventional pickling and cold rolling to final gauge in one or more stages.

The cold rolled material is conventionally decarburized and coated with a magnesia (MgO) annealing separator. While not required, to achieve optimum permeability values in the final product an inhibitor may be provided in the environment of the silicon iron during the primary grain growth stage of the final anneal. For example, from about 1 percent to about 6 percent by weight of sulfur may be added to the magnesia annealing separator.

The decarburized and coated material is then subjected to a final anneal in a dry hydrogen atmosphere at a temperature of from about 2,000°F to about 2,300°F. Again, while not so limited, to achieve optimum permeability values the heat-up portion of the final anneal may be conducted in a nitrogen atmosphere, the temperature being raised at the rate of less than about 125°F per hour and preferably about 50°F per hour.

The cube-on-edge oriented silicon iron of the present invention is characterized by a permeability greater than about 1,820 and up to 1,900 or beyond.

DESCRIPTION OF THE PREFERRED EMBODIMENNTS

The melt contemplated by the present invention may be produced by any suitable and known method such as by an openhearth furnace, a converter, an electric furnace, a vacuum melting furnace or the like.

The initial melt composition is conventional for the production of cube-on-edge oriented silicon iron with respect to silicon, maganese, carbon and sulfur. However, to this melt composition critical amounts of boron and nitrogen are added. The melt composition may be stated in weight percent as follows: from about 2 percent to about 4 percent silicon, from about 0.01% to about 0.15 percent (and preferably from about 0.03 percent to about 0.15 percent) manganese, from about 0.02 percent to about 0.05 percent carbon, from about 0.01 percent to about 0.03 percent sulfur, from about 0.002 percent to about .012% (and preferably from about 0.003 percent to about 0.010 percent) boron, from about 0.003 percent to about 0.010 percent (and preferably from about 0.004 percent to about 0.008percent) nitrogen, the balance being iron and those impurities incident to the mode of manufacture. While not required, aluminum may be present in the above stated melt composition (as a deoxidizer or impurity) in an amount up to about 0.008 percent. The optimum amount of boron is believed to be 0.007 percent and the optimum amount of nitrogen is believed to be 0.007 percent.

The boron content of the initial melt can be achieved in any suitable and well known manner, including the addition to the initial melt of a boron-containing compound such as ferroboron. The nitrogen content of the initial melt can similarly be achieved by any suitable and well known means. For example, nitrogen may be added in the form of a nitrogen compound such as nitrided manganese. Nitrogen may also be added by blowing. Finally, the desired nitrogen content may be provided through the use of a melting process which normally results in an appropriate nitrogen content, as for example the use of the electric furnace to produce a low carbon melt.

The silicon melt may be cast either as ingots or continuously cast slabs. If the steel is cast into ingots, the ingots can be either directly hot rolled to hot band, or alternatively, they can be rolled to slabs of intermediate thickness, which slabs are subsequently reheated and hot rolled to hot band. When hot rolling slabs formed from ingots or slabs from a continuous caster, the slabs should be reheated prior to hot rolling to a temperature in the range of from about 2,400°F to 2,550°F (and preferably about 2,500°F) in accordance with the above mentioned U.S. Pat. No. 2,599,340. The final hot band will normally have a thickness of from about 0.050 to about 0.10 inch.

After hot rolling to hot band, the silicon steel is annealed at a temperature of from about 1,500°F to about 2,100°F, and preferably from about 1,700°F to about 2,000°F for about 3½ minutes in any appropriate atmosphere such as air, products of combustion, etc. It has been determined that to obtain optimum permeability values the temperature of this anneal bears an inverse relationship to the desired final thickness of the silicon steel. Thus, when thinner final sheet stock is to be produced, the temperature of this anneal should fall within the upper portions of the above stated ranges. Similarly, when thicker sheet stock is to be produced, the temperature of this anneal should fall within the lower portion of the above stated ranges. The annealed, hot rolled silicon steel may be spray quenched or air cooled. The silicon steel is thereafter conventionally pickled and cold reduced in a single stage (or in two or more stages with intermediate anneals) to final gauge.

The cold reduced silicon steel is decarburized in a wet hydrogen atmosphere at a temperature of about 1,500°F and a dewpoint of about 135°, in accordance with the above mentioned U.S. Pat. No. 2,287,467.

After the decarburization step, the silicon steel is provided with an appropriate annealing separator such as magnesia, alumina, calcium oxide or mixture of these. When it is desired to have a mill glass formed upon the finished product, a magnesia annealing separator can be used in accordance with the above noted U.S. Pat. No. 2,906,645. The magnesia separator may be applied to the silicon steel in any of the conventional and well known ways.

The silicon steel, having been provided with an annealing separator, is subjected to a final box anneal at a temperature of from about 2,000°F to about 2,300°F, and preferably about 2,200°F for a period of time of from about 8 to about 30 hours. This anneal, designated herein as the "final anneal" for purposes of clarity, is that anneal during the secondary grain growth stage of which the cube-on-edge orientation is achieved. The anneal is conducted in a dry hydrogen atmosphere.

While to obtain good permeability values it is not necessary, it has been determined that to obtain optimum permeability values an inhibitor should be provided in the environment of the silicon steel immediately prior to or during the primary grain growth stage ofthe final anneal. Sulfur, selenium, and their compounds will serve as excellent inhibitor material and the provision of this material in the environment of the silicon steel may be accomplished in any of those ways described by the above noted U.S. Pat. Nos. 3,333,991; 3,333,992 and 3,333,993. For example, excellent results have been achieved when the magnesia annealing separator contains from about 1 percent to about 6 percent by weight of sulfur.

While again it is not required for purposes of this invention, it has nevertheless been found that to obtain optimum magnetic properties a nitrogen atmosphere should be used during the heat-up portion of the anneal, dry hydrogen being substituted therefore during the remainder of the annealing treatment. The heat-up portion of the anneal should have a relatively slow temperature rise of less than about 125°F per hour and preferably about 50° per hour.

Examples of the present invention may be given as follows:

EXAMPLE 1

A lab melt under vacuum was prepared having the following analysis in weight percent:

C	.033%
Mn	.094%
S	.029%
Si	3.24%
B	.006%
N	.068%
Al	.002%

An ingot was cast and heated to 1,900°F. The material was thereafter hot rolled to 0.100° and annealed at 1,900°F for 3½ minutes. Following this anneal, the silicon steel was air cooled, pickled and cold reduced in a single stage to 0.012 in.

The cold reduced silicon iron was decarburized at 1,500°F in wet hydrogen at a dewpoint of 135°F. Thereafter, the silicon steel was coated with a magnesia annealing separator containing 6 percent by weight of sulfur. Finally, the coated silicon steel was box annealed in a hydrogen atmosphere at 2,200°F for 30 hours. The finished material was determined to have a straight grain permeability at H=10 oersteds of 1921.

The above example illustrates the high permeability achievable when both boron and nitrogen are added to the melt within the ranges given above and the silicon steel is processed in accordance with the present invention.

EXAMPLE 2

A laboratory heat was produced having the following analysis in weight percent:

C	.032%
Mn	.100
S	.025
Si	3.35
B	.0052
N	.0077
Al	.004

The material was cast into 1 inch thick ingots. The ingots were heated to 1,900°F and hot rolled to approximately 0.09 in. First and second samples of this material were annealed at 1,700°F for 3½ minutes. A third sample was annealed at 2,100°F for 3½ minutes. The first sample was air cooled and cold rolled to 14 mils. The second and third samples were each spray quenched and cold rolled to 10 mils.

All three samples were decarburized at 1500°F in wet hydrogen at a dewpoint of 135°. All samples were coated with a magnesia annealing separator containing 6 percent by weight of sulfur. The coated samples were box annealed at 2,200°F for 27 hours with a heat-up rate of 50° per hour. The heat-up portion of the final anneal was conducted in a nitrogen atmosphere, while the remainder of the final anneal was conducted in a hydrogen atmosphere.

The first, second and third samples were characterized by permeabilities at H=10 oersteds of 1,889, 1,864 and 1,896, respectively. Samples 2 and 3 clearly demonstrate the inverse relationship between the temperature of the anneal following hot rolling and the final gauge.

EXAMPLE 3

A laboratory heat was prepared with the following analysis in weight percent:

C	.030
Mn	.100
S	.025
Si	3.29
B	.0072
N	.0078
Al	.007

The material was cast into 1 inch thick ingots, heated to 1,900°F and hot rolled to approximately 0.09 inches. The material was annealed at 1,700°F for 3½ minutes, air cooled, pickled and cold rolled to a thickness of 14 mils. The cold rolled silicon steel was decarburized at 1,500F in wet hydrogen at a dewpoint of 135° and was coated with a magnesia separator containing 6 percent by weight of sulfur. The coated silicon steel was given a final anneal at 2,200°F for 27 hours with a heat-up rate of 50° per hour. During the heat-up portion of the final anneal a nitrogen atmosphere was used, a hydrogen atmosphere being used throughout the remainder of the anneal. The final product demonstrated a permeability at H=10 oersteds of 1,889.

Modifications may be made in the invention without departing from the spirit of it.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of making cube-on-edge oriented silicon steel comprising the steps of preparing a silicon steel melt having a composition in weight percent consisting essentially of from about 2 to about 4 percent silicon, from about .01 to about 0.15 percent manganese, from about 0.02 to about 0.05 percent carbon, from about 0.01 to about 0.03 percent sulfur, from about 0.003 to about 0.010 percent boron, from about 0.003 to about 0.010 percent nitrogen, up to 0.008 percent aluminum, the balance being iron and impurities incident to the mode of manufacture, casting said silicon steel melt, reheating said silicon steel at a temperature of from about 2,300°F to about 2,550°F, hot rolling said silicon steel to an intermediate thickness of from about 0.050 to about 0.100 in., annealing said hot rolled silicon steel at a temperature of from about 1,500°F to about 2,100°F, pickling said annealed silicon steel and cold reducing it to final gauge, decarburizing said cold reduced silicon steel, providing an annealing separator for said decarburized silicon steel and subjecting said silicon steel to a final box anneal in dry hydrogen at a temperature of from about 2000°F to about 2,300°F for from about 8 to about 30 hours, whereby to provide a cube-on-edge oriented silicon steel having a permeability at H=10 oersteds greater than 1820.

2. The process claimed in claim **1** wherein said melt composition in percent by weight consists essentially of from about 2 to about 4 percent silicon, from about 0.03 to about 0.15 percent manganese, from about 0.02 to about 0.05 percent carbon, from about 0.01 to about 0.03 percent sulfur, from about 0.003 to about 0.010 percent boron, from about 0.004 to about 0.008 percent nitrogen, the balance being iron and impurities incident to the mode of manufacture.

3. The process claimed in claim **1** wherein said final anneal has a primary grain growth stage and a secondary grain growth stage, providing a grain growth inhibitor in the environment of said silicon steel during said primary grain growth stage, said grain growth inhibitor being chosen from the class consisting of sulfur, sulfur compounds, selenium and selenium compounds.

4. The process claimed in claim **1** wherein said annealing separator comprises magnesia containing from about 1 percent to about 6 percent sulfur by weight.

5. The process claimed in claim **1** wherein said final box anneal has a heat-up period, said heat-up period being conducted in a nitrogen atmosphere, the remainder of said box annealing being conducted in said dry hydrogen atmosphere.

6. The process claimed in claim **1** wherein said anneal following said hot rolling is conducted at a temperature of from about 1,700°F to about 2,000°F, said temperature range bearing an inverse relationship to said final gauge of said silicon steel.

7. The process claimed in claim **2** wherein said melt contains about 0.007 boron and about 0.007 percent nitrogen.

8. The process claimed in claim **2** wherein said anneal following said hot rolling is conducted at a temperature of from about 1,700°F to about 2,000°F, said last mentioned temperature range bearing an inverse relationship to said final gauge of said silicon steel, said annealing separator comprising magnesia containing from about 1 percent to about 6 percent sulfur by weight, said final anneal having a heat-up stage, said heat-up stage being conducted with a nitrogen atmosphere, the remainder of said final box anneal being conducted in said dry hydrogen atmosphere, the temperature of said heat-up stage being raised at the rate of less than about 125°F per hour.

9. The process claimed in claim **5** wherein said final box anneal has a heat-up stage, said temperature of said final anneal being raised during said heat-up stage at the rate of less than 125° per hour.

10. A cube-on-edge oriented silicon steel having a permeability at H=10 oersteds greater than 1,820 and made in accordance with the process of claim **1**.

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