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[54] **METHOD FOR PRODUCING NONORIENTED SILICON ELECTRICAL SHEET STEEL**
2 Claims, 6 Drawing Figs.

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117/22, 148/6, 148/112
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C23f 7/00
[50] Field of Search..... **148/110,**
111, 112, 113, 6, 12.1; 117/22

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ABSTRACT: A nonoriented electrical sheet steel containing not more than 0.03 percent carbon and from about 0.5 percent to about 4.5 percent silicon and a process for manufacturing said electrical sheet steel. The process includes preparing low carbon sheet steel by conventional methods of melting, pouring and rolling, coating the surfaces of the sheet steel with a layer of silicon-containing powder, compacting the powder onto the sheet and heat treating the composite thus formed in a protective environment to cause a solid-state diffusion of silicon into the sheet steel. The core losses of electrical sheet steel thus prepared are equivalent to or better than electrical sheet steel of the same silicon content and gage prepared by additions of silicon to the steel while it is in a molten state.

Fig. 1

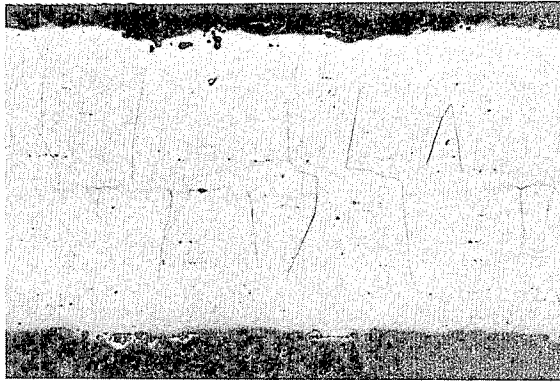


Fig. 2

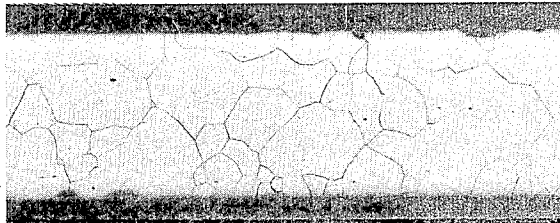
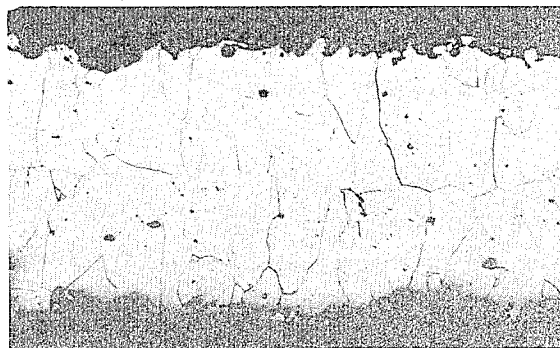


Fig. 3



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Fig. 4

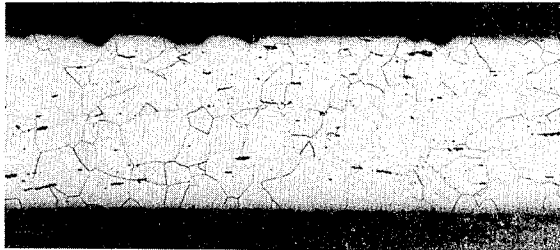
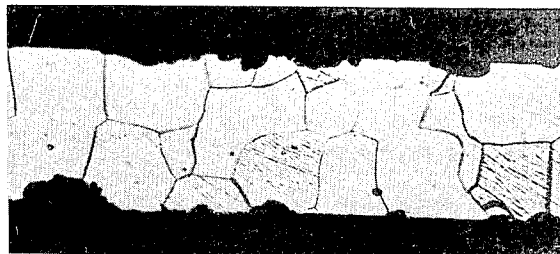


Fig. 5



Fig. 6



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METHOD FOR PRODUCING NONORIENTED SILICON ELECTRICAL SHEET STEEL

BACKGROUND OF THE INVENTION

It is well known that the addition of silicon to iron decreases the core losses which occur during electrical excitation of the iron. Much of the sheet used today for electrical applications is iron alloyed with from about 0.5 percent to about 6.0 percent silicon. It is also known that the core losses of the sheet are adversely affected by interstitial elements, carbides, nitrides, nonmetallic inclusions, grain boundaries and stresses induced in the sheet by cold working. Modern technology for manufacturing sheet steel for electrical applications consists of careful selection of raw materials to be charged into the melting furnace, melting the charge with utmost care to prepare a molten bath as low in carbon, manganese, phosphorus, sulfur and other impurities, such as oxygen and nitrogen, as technically and economically possible, and adding silicon-containing alloys to the molten bath to obtain a desired final silicon content.

Sheet steel of up to about 2.00 percent silicon content may be processed without undue difficulty, however, steels having above 2.00 percent silicon content are brittle and difficult to work, requiring heavy mill equipment, low drafts per pass and frequent annealing steps.

The primary object of this invention is to provide a process whereby the silicon content of sheet steel may be increased by a solid-state diffusion of silicon therein to produce a sheet steel which may be used in electrical apparatus.

It is an object of this invention to provide a silicon electrical sheet steel containing not more than 0.03 percent carbon and from about 0.5 percent to about 4.5 percent silicon without the need for heavy equipment and complicated rolling and heat treatment procedures heretofore required.

It is an object of this invention to provide a silicon electrical sheet steel containing not more than 0.03 percent carbon and from about 0.5 percent to about 4.5 percent silicon in which the core losses are equivalent to or better than conventionally melted and fully processed silicon electrical sheet steel of the same silicon content and gage.

SUMMARY OF THE INVENTION

Broadly, the invention comprises solid-state diffusion of silicon from a silicon-containing powder compacted on the surfaces of a conventionally melted and rolled low carbon sheet steel to produce an electrical sheet steel in which the core losses are equivalent or better than silicon electrical sheet steel of the same silicon content and gage and conventionally prepared.

DESCRIPTION OF THE DRAWINGS

The FIGS. are reproductions of photomicrographs of cross sections of sheet steel of the invention at 100 magnifications.

FIG. 1 is a reproduction of a photomicrograph of a cross section of a sheet steel in the as-diffused condition showing silicon diffusion through 90 percent of the sheet.

FIG. 2 is a reproduction of a photomicrograph of a cross section of the sheet steel of FIG. 1 after it has been cold reduced and annealed.

FIG. 3 is a reproduction of a photomicrograph of a cross section of a sheet steel in the as-diffused condition showing silicon diffused uniformly through the thickness of the sheet.

FIG. 4 is a reproduction of a photomicrograph of a cross section of the sheet steel of FIG. 3 after it has been cold reduced and annealed.

FIG. 5 is a reproduction of a photomicrograph of a cross section of a sheet steel in the as-diffused condition showing silicon diffused uniformly through the thickness of the sheet.

FIG. 6 is a reproduction of a photomicrograph of a cross section of the sheet steel of FIG. 5 after it has been cold reduced and annealed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the one method of the invention, a low carbon steel is refined in a conventional manner, for example in an electric furnace, basic oxygen furnace or basic open-hearth furnace, and is rolled to a desired gage and annealed if desired. The steel may contain a maximum of about 0.10 percent carbon, a maximum of about 1.00 percent manganese and a maximum of about 2.00 percent silicon, the remainder substantially iron and incidental impurities such as phosphorus, sulfur, aluminum, and dissolved gases, for example, nitrogen and oxygen. It is preferred to use a steel containing:

Carbon	not more than 0.05%
Manganese	not more than 0.4%
Phosphorus	not more than 0.015%
Sulfur	not more than 0.03%
Silicon	not more than 0.01%
Aluminum	not more than 0.010%
Nitrogen	not more than 0.005%
Oxygen	not more than 0.03%

Both sides of the sheet are now coated with a layer of silicon-containing powder. A convenient way of applying the powder is to first coat both sides of the sheet with a thin film of liquid, such as tridecyl alcohol. The liquid should have such viscosity, volatility and tackiness characteristics as to render it suitable as a temporary bonding agent for the subsequent applied powder. A silicon-containing powder such as substantially pure silicon, a mixture of substantially pure iron and silicon powder or ferro-silicon alloy powder is then applied to the sheet. The silicon in the powder must be in a form which will permit it to be diffused into the sheet steel. The powder is compacted onto the sheet by rolling. A roll pressure sufficient to cause an elongation of about 1 percent to about 5 percent in the sheet will produce satisfactory compaction. The powder may have a silicon content of about 15 percent to about 100 percent, not more than 0.40 percent carbon, and the balance iron. In the diffusion treatment, hereinafter described, a dual solid-state diffusion occurs. The silicon in the powder diffuses into the sheet steel and iron diffuses from the sheet steel to the powder. Carbon may diffuse in either direction depending upon the carbon content of the constituents of the composite. Since the final product should have a carbon content not greater than 0.03 percent, the carbon content of the powder should be such that either carbon will diffuse from the sheet to the powder or the diffusion of carbon into the sheet will be a minimum. It has been found that if the sheet contains about 0.04 percent to 0.10 percent carbon, the powder may contain not more than 0.20 percent carbon. On the other hand, sheet containing less than 0.04 percent carbon may be coated with a powder containing not more than 0.40 percent carbon. In any event, we prefer to use a ferroalloy powder containing not more than 0.20 percent carbon and about 70 percent to about 90 percent silicon, the remainder iron. Although the particle size of the powder is not critical, the powder should be of a size which will allow an amount to be compacted on the sheet steel to obtain the sufficient weight per area to thereby attain the desired diffusion of the silicon therein. We have found that the powder may have a particle size of -60, +325 mesh Tyler Sieve Size to achieve efficient diffusion of silicon into the sheet steel.

The composite thus formed is subjected to a diffusion treatment in a protective environment at a temperature and for a time sufficient to cause a solid-state diffusion of silicon from the powder into the sheet throughout at least 50 percent of the thickness of the sheet and to cause carbon diffusion from the sheet to the powder if the sheet contains more than 0.03 percent carbon and to keep carbon diffusion at a minimum into the sheet if the carbon is near or at the desired 0.03 percent. The composite may be annealed in flat sheet form or in coil form. If in coil form, either a tight coil or an open coil may be used. A nonoxidizing, reducing or neutral furnace atmosphere may be used. Dry hydrogen and NH gas are each satisfactory

as a furnace atmosphere for open coil annealing. For tight coil annealing, NH gas is preferred because it prevents sticking, which may occur when hydrogen is used. NH gas may be defined as a mixture of gaseous nitrogen and hydrogen, for example, 96 percent nitrogen and 4 percent hydrogen or 82 percent nitrogen and 18 percent hydrogen. A diffusion temperature of at least 1,600° F. is required, with a preferred range being 1,700° to 1,900° F. Actually, there is no upper limit for diffusion temperature other than that which may be dictated by practical considerations. The time may satisfactorily be 120 hours at 1,600° F. but at higher temperatures the satisfactory time required will be lowered in an inverse manner. Variations in the composition and amount of the powder, the diffusion temperature and the time at temperature result in variations in the silicon content of the sheet and the extent to which the silicon is diffused throughout the thickness of the sheet.

In the diffusion treatment, a brittle outer layer of iron-silicon intermetallic compounds may be formed on the surface of the sheet. The brittle outer layer may easily be removed by wire brushing and/or by flexing the sheet.

The solid-state diffusion treatment above described results in the formation of coarse ferritic columnar grains in the sheet steel. Grains ranging in size from 30 grains per square inch to 10 grains per square inch when viewed at 100 magnifications according to ASTM E-112 may be formed.

As noted above, the as-diffused sheet steel of the invention may be cold rolled to any desired gage and annealed to obtain improved core loss properties and permeability.

Sheet steels of the invention in their as-diffused condition have core losses (watts per pound when tested at 60 cycles) equivalent to or better than those of conventional fully processed sheet steel of the same silicon content and gage. However, the permeability of the steel sheets of the invention is not always as good as the conventional fully processed steel sheet. After cold-rolling and annealing, the core losses and permeability of the steel sheet of the invention are equivalent to or better than conventional semiprocessed sheet steel of the same silicon content and gage. The core losses and permeability of two tests lots of silicon electrical steel sheets of the invention are compared to conventional silicon electrical sheet steel of the same silicon content and gage in the following table No. 1.

TABLE 1

Sample	Core losses (watts per pound— tested at 60 cycles), kilogausses		Permeability (μ), kilogausses	
	10	15	10	15
Test Lot 1—2.84% Si as-diffused 24 gage..	1.00	1.83	1,400	430
M-27 grade—2.80% Si typical fully-processed 24 gage.....	1.00	2.35	4,000	600
Test lot 1—2.84% Si cold-rolled and annealed 20 gage.....	0.38	0.91	17,000	4,500
M-27 grade—2.80% Si typical semi-processed 24 gage.....	0.81	1.90	7,200	800
Test lot 2—3.20% Si as-diffused 24 gage.....	0.84	1.80	7,060	1,920
M-19 grade—3.25% Si typical fully-processed 24 gage.....	0.88	2.00	4,500	700
Test lot 2—3.20% Si cold-rolled and annealed 20 gage.....	0.59	1.60	9,000	3,720
M-19 grade—3.25% Si typical semi-processed 20 gage.....	0.66	1.60	9,000	600

A conventional nonoriented silicon electrical sheet steel is a steel in which the silicon content is obtained by additions to the molten bath, hot rolled from ingot form to an intermediate gage followed by conventional processing steps. A conventional fully processed silicon electrical sheet steel is a sheet steel in which the desired gage and specified core losses are

developed by the producer in a complicated decarburization—cold rolling—annealing sequence which may require more than one cold rolling and annealing step. The sheet steel is skin-passed prior to shipment to the consumer. The required parts are stamped out of the sheet steel and are used as is by the consumer. A conventional semiprocessed silicon electrical sheet steel is a sheet steel in which the desired gage is developed by the producer in a complicated decarburization—cold rolling and annealing sequence which usually requires several anneals during cold rolling. The specified core losses are developed in a high temperature anneal by the consumer after he has stamped the required parts from the sheet steel.

The process of the invention may have several variations. The sheet steel may be treated by a tight coil or an open coil diffusion treatment. The sheet steel may be decarburized prior to diffusion treatment or may be decarburized during the diffusion treatment step.

EXAMPLE 1

As a specific example of the above described invention, a low carbon steel was refined in a basic oxygen furnace to the following chemical composition:

Carbon	0.041%
Manganese	0.35%
Phosphorus	0.005%
Sulfur	0.012%
Silicon	0.01%
Aluminum	0.005%
Nitrogen	0.0019%
Oxygen	0.017%

The steel was hot rolled to an intermediate gage, cold-rolled to a thickness of 0.024 inch (24 gage) and annealed. Several flat sheets were processed according to the invention. A thin layer of tridecyl alcohol was applied to both surfaces of each sheet. They were coated on both sides with a ferrosilicon powder having a chemical composition of:

Silicon	85.0%
Carbon	0.16%
Iron	Remainder

and a particle size of 94 percent —60, +325 mesh Tyler Sieve Size and 6 percent —325 mesh Tyler Sieve Size. The amount of the powder coating was 24 grams per square foot of sheet surface. The powder was compacted onto the surfaces of the sheet by rolling. The sheets were clamped together to form a tight bundle and were diffusion treated at 1,850° F. for 60 hours in an atmosphere of dry hydrogen. The brittle surface layer of iron-silicon intermetallic compounds formed in the diffusion treatment, was removed by brushing. FIG. 1 is a reproduction of a photomicrograph showing the cross section of the product in its as-diffused condition. The sheets had a carbon content of 0.004 percent, a bulk silicon content of 0.79 percent. Silicon diffusion had occurred in all but the center 10 percent of the original thickness of 0.024 inch. A ferritic grain size of 25 grains per square inch when viewed at 100 magnifications according to ASTM E-112 was developed in the sheet steel. The core losses of the sheets of the invention are compared to the typical and maximum specified core losses of fully processed M-45 Grade electrical sheet steel of the same gage and typically containing 1.05 percent silicon in table 2 below:

TABLE 2

	Core Losses (Watts per Pound) (Tested at 60 cycles)	
	10 kilogausses	15 kilogausses
As-diffused	1.30	2.55
M-45 (Fully Processed Typical)	1.70	3.60

M-45 (Fully Processed Maximum)	1.74	4.00
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The as-diffused sheets were cold rolled to a thickness of 0.014 inch (29 gage). Several sheets were annealed at 1,450° F. for 4½ hours in a dry hydrogen atmosphere. FIG. 2 is a reproduction of a photomicrograph showing the cross section of the product. The grain size was found to be 8 grains/square inch when viewed at 100 magnifications according to ASTM E-112. The core losses of the sheets are compared to the maximum specified core losses of semiprocessed M-45 grade electrical sheet steel of the same gage in table 3 below:

TABLE 3

	Core Losses (Watts per Pound) (Tested at 60 cycles)	
	10 kilogausses	15 kilogausses
Cold Rolled and Annealed M-45 (Semiprocessed Maximum)	0.77 1.28	1.53 2.90

EXAMPLE 2

As another example of the invention, a 6,000 lb. coil of sheet steel having a thickness of 0.024 inch (24 gage) and containing:

Carbon	0.002%
Manganese	0.30%
Phosphorus	0.007%
Sulfur	0.022%
Silicon	0.04%
Aluminum	0.004%
Nitrogen	0.003%

was coated on both surfaces with 20 grams per square foot of a ferrosilicon powder containing 90 percent silicon, 0.16 percent carbon, remainder iron, and having a particle size 98.5 percent -100, +325 mesh and 1.5 percent -325 mesh Tyler Sieve Size. After compacting the powder on the sheet, the coil was placed in a furnace in a tight coil condition and was diffusion treated at 1,750° F. for 120 hours in a dry hydrogen atmosphere. The brittle surface layer of iron-silicon intermetallic compounds was removed by brushing. FIG. 3 is a reproduction of a photomicrograph showing the cross section of the product. The sheets had a carbon content of 0.03 percent, a silicon content of 3.20 percent diffused throughout the entire thickness of the sheets and a grain size of 9/10 grains per square inch at 100 magnifications. The core losses of the sheets of the invention are compared to the typical and maximum specified core losses of fully processed M-22 grade electrical sheet steel of the same gage and typically containing 3.20 percent silicon in table 4 below:

TABLE 4

	Core Losses (Watts per Pound) (Tested at 60 cycles)	
	10 kilogausses	15 kilogausses
As-diffused	0.84	1.80
M-22 (Fully Processed Typical)	0.95	2.20
M-22 (Fully Processed Maximum)	0.98	2.23

Several as-diffused sheets were cold-rolled to a thickness of 0.015 inch (29 gage) and were then annealed at 1,450° F. for 4 hours in a dry hydrogen atmosphere. FIG. 4 is a reproduction of photomicrograph showing the cross section of the

product. The grain size was found to be 25 grains per square inch when viewed at 100 magnifications. The core losses of the sheets of the invention are compared to the typical and maximum specified core losses of 29 gage, M-22 grade electrical sheet steel and typically containing 3.20 percent silicon in table 5 below:

TABLE 5

	Core Losses (Watts per Pound) (Tested at 60 cycles)	
	10 kilogausses	15 kilogausses
Cold Rolled and Annealed M-22 (Semiprocessed Typical)	0.59 0.70	1.60 1.70
M-22 (Semiprocessed Maximum)	0.76	1.82

EXAMPLE 3

As another example of the invention, sheet steel containing:

Carbon	0.037%
Manganese	0.30%
Phosphorus	0.005%
Sulfur	0.04%
Silicon	0.01%
Aluminum	0.003%
Nitrogen	0.002%

was cold rolled to a thickness of 0.024 inch and decarburized in an 18% H₂-82% N₂ atmosphere having a dewpoint of 80° F. to reduce the carbon to 0.002 percent. Flat sheets of the material were coated with a ferrosilicon alloy powder containing 90 percent silicon, 0.16 percent carbon, remainder substantially iron, and having a particle size of 100 percent, -100, +200 mesh Tyler Sieve Size. The amount of the coating was 24 grams per square foot of sheet surface. After compacting the coating onto the sheets by rolling, the sheets were placed in a furnace with spacers between them. The sheets were diffusion treated at 1,800° F. for 72 hours in a dry hydrogen atmosphere. The brittle surface layer of iron-silicon intermetallic compounds formed in the diffusing treatment was removed by brushing. FIG. 5 is a reproduction of a photomicrograph showing the cross section of the product. After diffusion, the sheets contained 0.005 percent carbon and 1.7 percent silicon diffused throughout the entire thickness of the sheets. The sheets had a grain size of 10 to 15 grains per square inch at 100 magnifications. The core losses of the as-diffused sheets of the invention are compared to the typical and maximum specified core losses of 24 gage, M-43 gage electrical sheet steel of the same gage and typically having a silicon content of 1.5 percent in table 6 below:

TABLE 6

	Core Losses (Watts per Pound) (Tested at 60 cycles)	
	10 kilogausses	15 kilogausses
As-Diffused	0.75	1.49
M-43 (Fully Processed Typical)	1.35	3.00
M-43 (Fully Processed Maximum)	1.45	3.35

The as-diffused sheets were cold rolled to a thickness of 0.014 inch (29 gage) and were annealed at 2,000° F. for 24 hours in dry H₂.

FIG. 6 is a reproduction of a photomicrograph of a cross section of the cold-rolled and annealed product. The grain size

was found to be 15 grains per square inch when viewed at 100 magnifications. The core losses of the sheets of the invention are compared to the typical and maximum specified core losses of 29 gage M-43 grade electrical sheet steel in table 7 below:

TABLE 7

	Core Losses (Watts per Pound) (Tested at 60 cycles)	
	10 kilogausses	15 kilogausses
Cold Rolled and Annealed M-43 (Semiprocessed Typical)	0.54	1.16
M-43 (Semiprocessed Maximum)	1.02	2.30
	1.11	2.52

Whenever percentages are referred to in this specification and claims, such percentages are by weight.

The core loss values and permeabilities of the sheet steels of the invention were compared to the Industry accepted values for the various grades of silicon electrical sheet steel as set forth in the U.S. Steel Corporation publication entitled, "Nonoriented Silicon Electrical Sheet Steel."

- We claim:
1. A process for manufacturing electrical sheet steel comprising:
- a. coating the surfaces of a sheet steel containing not more

- than 0.10 percent carbon, not more than 1.00 percent manganese, balance iron and incidental impurities, with a powder containing not less than 15 percent silicon and not more than 0.40 percent carbon, balance iron,
- b. compacting the powder on the sheet steel,
- c. heating the sheet steel in a protective environment for a time and at a temperature sufficient to cause diffusion of silicon through at least 50 percent of the thickness of the sheet and to thereby produce a sheet steel containing not more than 0.03 percent carbon and from about 0.5 percent to about 4.5 percent silicon,
- d. cold rolling the product of step (c), and
- e. annealing the cold rolled product.
2. A process for manufacturing electrical sheet steel comprising:
- a. coating the surfaces of a sheet steel containing not more than 0.01 percent carbon, not more than 1.00 percent manganese, balance iron and incidental impurities, with a powder containing not less than 25 percent silicon and not more than 0.40 percent carbon, balance iron.
- b. compacting the powder on the sheet steel,
- c. heating the sheet steel in a protective environment for a time and at a temperature sufficient to cause diffusion of silicon through at least 50 percent of the thickness of the sheet and to thereby produce a sheet steel containing not more than 0.03 percent carbon and from about 0.5 percent to about 4.5 percent silicon,
- d. cold rolling the product of step (c), and
- e. annealing the cold rolled product.

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