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[54] **PROCESS FOR DIFFUSING SILICON INTO SHEET STEEL**
10 Claims, 3 Drawing Figs.

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148/113, 148/12.1

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C21d 7/02, C23c 9/00

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111, 112, 113, 31.5, 31.55, 39, 12.1, 14;
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ABSTRACT: A process for solid-state diffusion of silicon into sheet steel containing not more than 0.05 percent carbon, the process including preparing sheet steel by conventional methods of melting, pouring and rolling, coating the surfaces of the sheet steel with a layer of powder containing about 15 percent to about 95 percent silicon and the remainder substantially calcium, iron and incidental impurities, compacting the powder onto the sheet and heat treating the composite thus formed in a protective environment to cause a solid-state diffusion of the diffusible silicon into the sheet steel.

Fig. 1

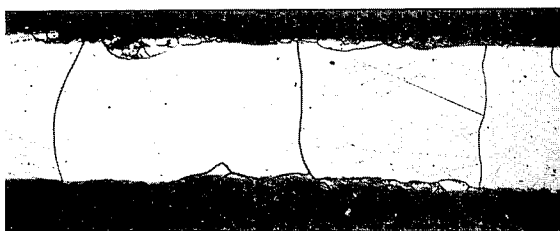


Fig. 2

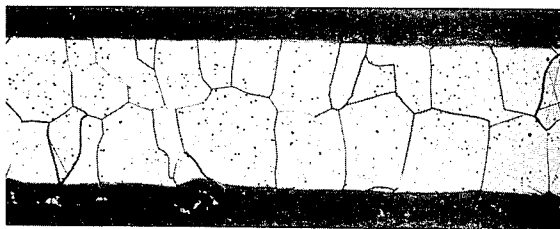


Fig. 3



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PROCESS FOR DIFFUSING SILICON INTO SHEET STEEL

BACKGROUND OF THE INVENTION

The object of the invention is to provide a process whereby silicon may be diffused into a sheet steel by solid state diffusion and the powdery surface layer of iron-silicon intermetallic compounds which forms can be easily and effectively removed.

Another object of this invention is to provide a process whereby silicon and calcium in powder form are applied to the surface of steel and during a high temperature treatment the calcium combines with carbon, nitrogen, oxygen and other impurities in the powders, gas atmosphere, and base steel making the silicon diffusion into the base steel more effective.

SUMMARY OF THE INVENTION

Broadly, the invention includes solid-state diffusion of a diffusible substance into sheet steel from a calcium-containing powder compacted on a conventionally melted, poured and rolled sheet steel.

DESCRIPTION OF THE DRAWINGS

The FIGS. are reproductions of photomicrographs of sheet steel prepared by the process of the invention viewed at 100 magnifications.

FIG. 1 is a reproduction of a photomicrograph of a transverse section of a sheet steel in the as diffused condition showing silicon diffused uniformly through the thickness of the sheet.

FIG. 2 is a reproduction of a photomicrograph of a transverse 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 transverse section of a sheet steel after it has been diffusion treated, sheared into test specimens, and stress-relief annealed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In 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 in a conventional manner to a desired gage. The sheet steel may be 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 phosphorous, sulfur, aluminum, nitrogen and oxygen. It is preferred to use a steel containing:

Carbon	not more than 0.05%
Manganese	not more than 0.40%
Phosphorous	not more than 0.015%
Sulfur	not more than 0.03%
Silicon	not more than 0.01%

A thin layer of a vehicle such as tridecyl alcohol is applied to the surfaces of the sheet steel and powder containing calcium and silicon is applied thereto. The powder is compacted onto the sheet by rolling. The powder may have a silicon content of about 15 percent to about 95 percent, and the remainder calcium, iron and incidental impurities.

The powder may be a mixture of calcium and silicon powders, a mixture of calcium, silicon, and iron powders, calcium silicon alloy, a calcium silicon iron alloy or combinations thereof.

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. A nonoxidizing, reducing or neutral furnace atmosphere may be used. We prefer to use a dry hydrogen atmosphere. A diffusion temperature of about 1,600° F. may be used. The time may satisfactorily be 120 hours at lower temperatures, for example 1,600° F., but at

higher temperatures less time may be required. Variations in the composition 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 hereinafter described, a dual solid-state diffusion occurs. Silicon contained in the calcium-silicon powder diffuses into the sheet steel and iron and carbon diffuse out of the sheet steel into the powder layer. The calcium atoms remain in the powder. Calcium combines with carbon from the sheet steel and that present in the powder material and with oxygen and nitrogen from the powder material and gas atmosphere. The iron which diffuses from the sheet steel combines with the silicon to form intermetallic compounds. The powdery surface layer thus formed comprises oxides, carbides, nitrides, and intermetallic compounds of iron and silicon. The powdery layer is easy to remove by surface brushing leaving the surface of the sheet steel clean and smooth. It is therefore evident that calcium is a decarburizing, deoxidizing and protecting agent in this solid state diffusion process.

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 about 1 grain to the square inch to about 25 grains to the square inch when viewed at 100 magnifications according to ASTM E-112 are formed.

The process is therefore particularly adapted to prepare silicon sheet steel suitable for use in electrical apparatus. Electrical sheet steels thus prepared have core losses in the as diffused condition better than those of conventional fully processed sheet steel of the same silicon content and gage. After cold-rolling and annealing these steels have core losses and permeabilities better than those of conventional semiprocessed sheet steel. A conventional 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 hot band, cold rolled to an intermediate gage, decarburized, and cold rolled to the final gage. Conventional fully processed silicon electrical sheet steel is a sheet steel in which the specified core losses have been developed in an anneal by the producer. The required parts are stamped out of the sheet steel and used as stamped by the consumer. A conventional semiprocessed electrical sheet steel is a sheet steel which is shipped in the cold rolled condition. The consumer stamps out the required parts and subjects the parts to a stress relief anneal prior to use to obtain the desired properties.

The as diffused sheet steel may be cold rolled to any desired gage and annealed to obtain improved core loss properties and permeability.

EXAMPLE I

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	0.044%
Manganese	0.32%
Phosphorus	0.006%
Sulfur	0.016%
Silicon	0.01%

The steel was hot rolled to an intermediate gage, cold rolled to a thickness of 0.014 inch (29 gage) thickness 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 calcium-silicon powder having a chemical composition of:

Calcium	28.0%
Silicon	67.0%
Iron	3.00%
Carbon	0.29%

and a particle size of 100 percent -100, +325 mesh Tyler Sieve Size. The amount of the powder applied was 25grams per square foot; 12.5 grams per square foot on each side. 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 1,750° F. for 60 hours in an atmosphere of dry hydrogen. FIG. 1 is a reproduction of a photomicrograph of the product in the as diffused condition. The sheets had a carbon content of 0.016 percent, a silicon content of 2.37 percent. The silicon was diffused uniformly throughout the thickness of the sheet. A ferritic grain size of less than 1 grain per square inch when viewed at 100 magnifications according to ASTM E-112 was formed in the sheets. The thickness of the sheet steel increased to 0.017 inch. The powder layer comprised of carbides, nitrides, oxides, and silicon-iron intermetallic compounds formed on the sheets during diffusion treatment was easily removed by wire brushing, leaving a smooth surface on the sheets. The core losses of the sheets compare favorably with those of M-19 Grade electrical sheet of the same gage (27 gage) containing typically 3.25 percent silicon as noted below in table 1:

Table 1

	Core Losses (watts per pound) (60 cycles per second)	
	10 Kilogausses	15 Kilogausses
As-diffused (27 gage)	0.78	1.60
M-19 (Fully Processed Maximum)	0.71	1.79

The as diffused sheets were cold reduced to 0.014 inch (29 gage) and annealed at 1,450° F. for 4½ hours in a dry hydrogen protective atmosphere. FIG. 2 is a reproduction of a photomicrograph of the product. The grain size was found to be about 25 grains per square inch when viewed at 100 magnifications according to ASTM-112. The core losses of the sheets compared favorably with those of M-19 grade silicon electrical sheet steel of the same gage and containing typically 3.25 percent silicon as shown below in table 2:

Table 2

	Core Losses (watts per pound) (60 cycles per second)	
	10 Kilogausses	15 Kilogausses
Cold Rolled Annealed (29 Gage)	0.46	1.30
M-19 (Semiprocessed Maximum)	0.69	1.68

Example 2.

In another example of the invention, a low carbon steel was refined in a basic oxygen furnace to the following chemical compositions:

Carbon	0.044%
Manganese	0.32%
Phosphorus	0.006%
Sulfur	0.016%
Silicon	0.02%

The steel was hot rolled to intermediate gage and cold rolled to 0.014 inch (29 gage) thickness and annealed. Sheets of the

base steel were coated on two sides with a thin layer of tridecyl alcohol and a coating of calcium silicon powder formed on each side of the sheet. The powder had a chemical composition as follows:

Calcium	27.8%
Silicon	67.8%
Carbon	0.29%
Iron	3.30%

The powder had a particle size of 100percent -100 , +325 mesh Tyler Sieve Size. The amount of powder coating applied was 25 grams per square foot; 12.5 grams per square foot on each side. The powder was compacted onto the surfaces of the sheet by rolling. The sheets were clamped together and were diffusion treated at 1,850° F. for 96 hours in a atmosphere of dry hydrogen. The sheets were found to have a carbon content of 0.032 percent and a silicon content of 3.90 percent. The silicon was uniformly diffused throughout the thickness of the sheet. The sheets had a ferritic grain size of 2 grains per square inch when viewed at 100 magnifications according to ASTM E-112. The thickness of the sheets increased to about 0.019 inch. The powder layer comprising carbides, oxides, and silicon-iron intermetallic compounds formed on the sheets during diffusion was easily removed by wire brushing. After removal of the layer, the surfaces of the sheets were found to be relatively smooth.

Several sheets were sheared into test specimens and stress-relief annealed at 1,450° F. for 4 hours in an atmosphere of dry hydrogen. FIG. 3 is a reproduction of a photomicrograph of a transverse section of the product after it had been sheared into test specimens and stress relief annealed. The core loss properties of the sheared as diffused sheets and stress-relief annealed sheared sheets are shown below in table 3:

Table 3

	Core Losses (watts per pound) (60 cycles per second)	
	10 Kilogausses	15 Kilogausses
As-diffused (26 gage)	0.78	1.75
Stress-relief Annealed	0.42	1.60

From the above it is evident that a simple stress-relief anneal following shearing improved the core loss properties of the silicon electrical sheet steel.

In this specification and claims wherever percentages are referred to such percentages are by weight unless otherwise noted.

We claim:

1. Process for diffusing silicon by solid-state diffusion into 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 from about 15 percent to about 95 percent silicon, and from about 5 percent to about 85 percent calcium,
- 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 the silicon through at least 50 percent of the thickness of the sheet and diffusion of carbon from the sheet to obtain a carbon content of not more than 0.05 percent therein and forming a powdery layer of intermediate compounds of silicon and iron as well as carbides, oxides and nitrides on the sheet which can be easily removed from the surface.

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2. Process as defined in claim 1 in which the sheet steel of step (a) contains not more than 0.01 percent carbon.

3. Process as defined in claim 1 in which the diffusion treatment of step (c) is carried out for a time and at a temperature sufficient to cause diffusion of the silicon substantially uniformly throughout the entire thickness of the sheet.

4. Process as defined in claim 2 in which the diffusion treatment of step (c) is carried out for a time and at a temperature sufficient to cause diffusion of the silicon substantially uniformly throughout the entire thickness of the sheet.

5. Process as defined in claim 1 including the further steps of (d) cold rolling the product of step (c), and (e) annealing the cold rolled product.

6. Process as defined in claim 2 including the further steps

of (d) cold rolling the product of step (c), and (e) annealing the cold rolled product.

7. Process as defined in claim 1 in which the diffusion treatment of step (c) is carried out at a temperature of at least 1,600° F. or a time sufficient to obtain the desired diffusion.

8. Process as defined in claim 2 which the diffusion treatment of step (c) is carried out at a temperature of at least 1,600° F. for a time sufficient to obtain the desired diffusion.

9. Process as defined in claim 1 in which the protective environment of step (c) is a dry hydrogen atmosphere.

10. Process as defined in claim 2 in which the protective environment of step (c) is a dry hydrogen atmosphere.

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