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METHOD OF SILICONIZING
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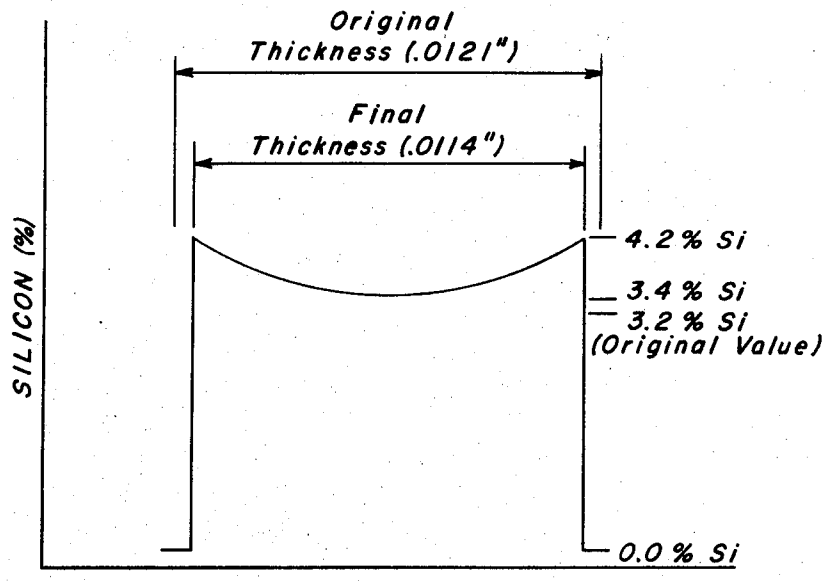



FIG. 1.

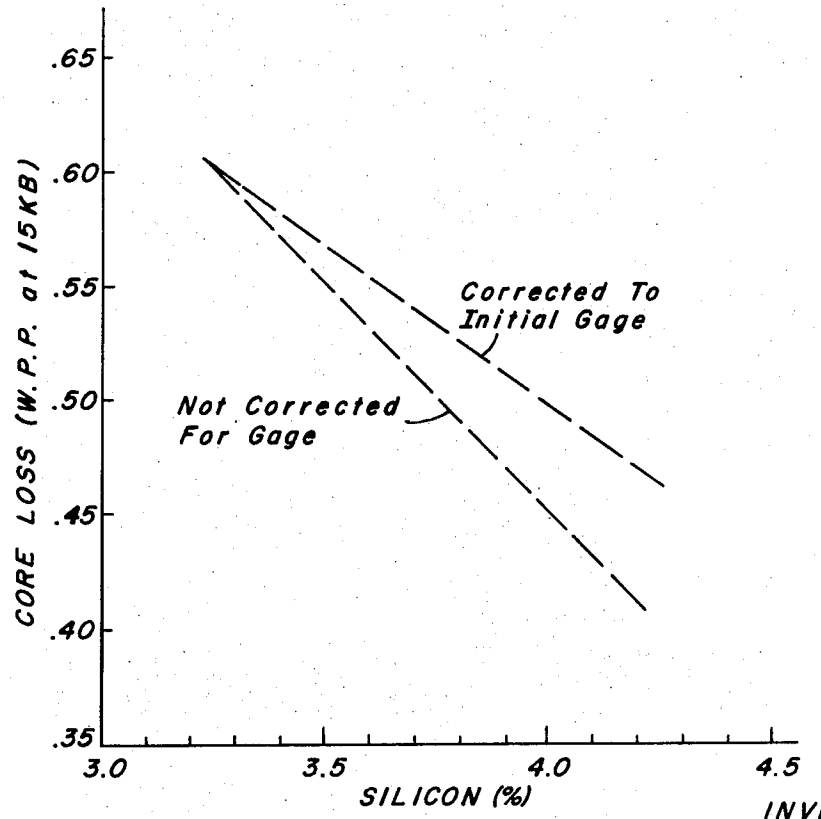



FIG. 2.

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# METHOD OF SILICONIZING

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Continuation-in-part of application Ser. No. 811,873, Apr. 1, 1969. This application Mar. 25, 1971, Ser. No. 128,161

Int. Cl. H01f 1/16

U.S. Cl. 148—113 9 Claims

## ABSTRACT OF THE DISCLOSURE

A method of treating grain oriented silicon steel, which comprises the steps of: heating grain oriented silicon steel at a temperature of from about 1900° F. to about 2300° F.; subjecting the steel to an acidic atmosphere which preferentially removes iron, thus enriching the member with silicon, for a period of time sufficient to increase the total proportion of silicon in the steel by about 0.4 to 4 wt. percent; and homogenizing the steel at a temperature and for a time sufficient for the silicon to disperse itself substantially uniformly therein.

This application is a continuation-in-part of copending application Ser. No. 811,873 filed Apr. 1, 1969, and now abandoned.

The present invention relates to a method for improving the properties of grain oriented silicon steel.

Silicon steels are widely used in electrical equipment because of their superior electrical and magnetic properties. These properties are dependent upon the percentage of silicon contained therein. As the silicon content is increased, resistivity increases, magnetostriction decreases, magnetic anisotropy decreases, and core loss decreases. At approximately 6.25% silicon, the magnetostriction is essentially zero. This is of primary importance in the design of power transformers as magnetostriction is considered to be the source of audible noise which must be controlled. If noise is not below acceptable limits, it must be dampened by a process which is both costly and inconvenient. From the increased resistivity results lower eddy current losses in alternating magnetic fields and from the decreased magnetic anisotropy comes a lessening of the difference in effort necessary to magnetize a hard and soft direction in textured steel.

The manufacture of silicon generally involves cold rolling. As a result, a certain degree of ductility must be possessed by the steel leaving the melt. Since ductility decreases with increased silicon, it has been the practice in the past to restrict silicon steels to a maximum silicon level of from about 3% to about 4%. Hence, improved properties which could be realized from increased silicon, i.e., up to about 7% silicon for electrical steels, have not always been available. In order to produce high silicon steels, an alternative approach, siliconizing, has been proposed. Siliconizing is concerned with silicon enrichment of the steel strip at final gage rather than by alloying in the melt. A method of siliconizing is described in Pat. No. 3,423,253, issued Jan. 21, 1969, in the names of Stuart L. Ames and William R. Bitler. It is a gaseous siliconizing process and involves a reaction between a heated strip and a siliconizing atmosphere which contains a nonreactive gas and a thermally decomposable silicon compound such as silicon tetrachloride.

We have discovered a method for "siliconizing" silicon steel wherein the steel is reacted with an acidic atmosphere. The atmosphere preferentially removes iron thus enriching the steel with silicon and simultaneously reduces its gage. Both the increased silicon and the gage reduction



lower the steel's core loss and accordingly provide a superior electrical steel.

It is accordingly an object of this invention to provide a method of improving the properties of grain oriented silicon steel.

The foregoing and other objects of the invention will be best understood from the following description, reference being had to the accompanying drawings wherein:

FIG. 1 is a plot showing an electron microprobe trace of the silicon content of grain oriented silicon steel treated according to this invention, prior to homogenization; and

FIG. 2 is a plot of core loss versus silicon content for homogenized grain oriented silicon steel.

According to the present invention, grain oriented silicon steel is heated at a temperature between about 1900° F. and about 2300° F., preferably between about 2050° F. and 2150° F., and subjected to an acidic atmosphere, preferably an atmosphere comprising hydrogen chloride vapor, which preferentially removes iron thus enriching the steel with silicon, i.e., increasing the proportion of silicon, while simultaneously reducing its gage. Subjection to the acidic atmosphere is for a period of time sufficient to increase the total proportion of silicon in the steel by about 0.4 to 4 wt. percent. No specific range can be set for the time period as it varies with such interrelated variables as the temperature at which the steel is heated and the concentration of acidic vapors within the acidic atmosphere.

The steel can be heated while it is within the siliconizing chamber or prior to its entry therein. A minimum temperature of about 1900° F. is employed. At temperatures below about 1900° F. the diffusion of silicon into the steel does not proceed fast enough so as to preclude the buildup of excessive silicon at the surface and the inherent formation of severe compositional gradients. Such buildup and gradient formation is detrimental as it can destroy the soundness of the steel's microstructure and result in undesirable magnetic properties, i.e., the microstructure becomes porous and/or cracked. A maximum temperature of about 2300° F. is observed because surface melting becomes a problem at higher temperatures.

The acidic atmosphere must contain acidic vapors which preferentially remove iron rather than silicon. An exemplary group of acidic materials are hydrogen chloride, hydrogen bromide and hydrogen iodide, with hydrogen chloride being preferred. The vapors can be used straight or mixed with non-oxidizing gases. Suitable non-oxidizing gases include inert gases such as nitrogen and argon and reducing gases such as hydrogen. Nitrogen is a preferred non-oxidizing gas for dilution. The atmosphere can be static or flowing. When a flowing atmosphere is employed it is preferred that flow be in a direction counter to strip movement although it can be in the same direction.

FIG. 1 shows the silicon gradient of grain oriented silicon steel treated in accordance with a preferred embodiment of the invention. Since it is necessary to achieve a chemically homogenous product the steel must be subjected to a homogenizing treatment. This homogenizing treatment can be accomplished immediately after the silicon content is increased to the desired level or at some subsequent time. It can even be performed after delivery of the steel to a purchaser. The homogenization is a solid state diffusion process wherein the silicon disperses itself substantially uniformly throughout the steel. It is time and temperature dependent as are other diffusion processes. As the temperature is increased the time is shortened and as the temperature is decreased the time is extended. A suitable, but not limiting time period is from about 0.25 hour to 24 hours with the temperature within the range of from about 1800° F. to about 2300°

F. Preferred conditions are a time period of from about 1 hour to about 16 hours with the temperature within the range of from about 2050° F. to about 2200° F.

The following examples are illustrative of several embodiments of the invention. Silicon steel members were heated to a temperature of 2100° F. and passed through a 12 inch long siliconizing chamber having an acidic atmosphere. The members originally had a silicon content of 3.2%, a gage of 0.0121 and a core loss of 0.606 W.P.P. at 15 kb. The acidic atmosphere employed was $2N_2$:1 HCl. It was delivered to the siliconizing chamber at a flow rate of ½ cubic foot per hour. The exposure time was determined by the line speed which was varied between 0.5 inch per minute and 2.4 inches per minute. The line speed for each member can be found in Table I along with other given data.

TABLE I

| Steel | Line speed (inches/minute) | Temperature (° F.) | Initial silicon content (percent) | Initial gage (inches) | Core loss (60ν W.P.P. at 15 kb.) |
|---|---|---|---|---|---|
| A | 2.4 | 2,100 | 3.2 | 0.0121 | 0.606 |
| B | 1.2 | 2,100 | 3.2 | 0.0121 | 0.606 |
| C | 1.2 | 2,100 | 3.2 | 0.0121 | 0.606 |
| D | 0.89 | 2,100 | 3.2 | 0.0121 | 0.606 |
| E | 0.89 | 2,100 | 3.2 | 0.0121 | 0.606 |
| F | 0.69 | 2,100 | 3.2 | 0.0121 | 0.606 |
| G | 1.50 | 2,100 | 3.2 | 0.0121 | 0.606 |

After passing through the siliconizing chamber the members were homogenized by holding at a temperature of 2100° F. for a period of 16 hours.

Found below in Table II are the final silicon content, final gage and final core loss for the members processed as described above.

TABLE II

| Steel | Final silicon content (percent) | Final gage (inches) | Core loss (60ν W.P.P. at 15 kb.) | |
|---|---|---|---|---|
| | | | As measured | Corrected to 0.0121 gage |
| A | 3.6 | 0.0110 | 0.592, 0.577 | 0.619, 0.604 |
| B | 3.6 | 0.0114 | 0.516 | 0.534 |
| C | 3.7 | 0.0114 | 0.525 | 0.543 |
| D | 3.8 | 0.0104 | 0.475 | 0.518 |
| E | 3.9 | 0.0104 | 0.478 | 0.521 |
| F | 3.9 | 0.0099 | 0.463, 0.447 | 0.492, 0.503 |
| G | 4.2 | 0.0093 | 0.400 | 0.470 |

The homogenized members were found to have a final silicon content ranging from 3.6 to 4.2% silicon and a final gage ranging from 0.0114 to 0.0093 inch. Those with the higher silicon content and lower gage were processed at a slower line speed and hence had longer exposure times. They also had a lower core loss due to the fact that core loss as stated earlier decreases with increasing silicon and with decreasing gage. Since the decrease in core loss was attributable to both these factors, a column is provided in Table II wherein the core loss corrected to initial gage is given. The values were adjusted using a 0.025 W.P.P. correction factor for each mil change in gage. This conversion factor has been derived from statistics on minor gage variations in 0.011 inch production silicon steel. The corresponding correction factor for 0.014 inch production silicon steel is 0.035 W.P.P. per mil. By subtracting the as-measured core loss from the corrected core loss, that portion of the core loss decrease attributable to the smaller gage can be obtained. That portion attributable to increased silicon can be obtained by subtracting the as-corrected core loss from the original core loss. FIG. 2 shows core loss as a function of silicon content for the members as measured and as corrected to gage.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific examples thereof will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific examples of the invention described herein.

We claim:

1. A method of treating grain oriented silicon steel, which comprises the steps of: heating grain oriented silicon steel at a temperature of from about 1900° F. to about 2300° F.; subjecting said silicon steel to an acidic atmosphere which preferentially removes iron, for a period of time sufficient to increase the total proportion of silicon in said steel by about 0.4 to 4 wt. percent; and homogenizing said steel at a temperature and for a time sufficient for the silicon to disperse itself substantially uniformly therein.

2. A method according to claim 1 wherein said silicon steel is heated to a temperature of from about 2050° F. to about 2150° F.

3. A method according to claim 1 wherein said acidic atmosphere comprises acidic vapor from the group consisting of hydrogen chloride vapor, hydrogen bromide vapor, and hydrogen iodide vapor.

4. A method according to claim 3 wherein said acidic atmosphere comprises hydrogen chloride vapor.

5. A method according to claim 1 wherein said acidic atmosphere comprises a mixture of non-oxidizing gas and acidic vapor from the group consisting of hydrogen chloride vapor, hydrogen bromide vapor, and hydrogen iodide vapor.

6. A method according to claim 5 wherein said acidic atmosphere comprises a mixture of hydrogen chloride vapor and non-oxidizing gas.

7. A method according to claim 1 wherein said silicon steel is heated to a temperature of from about 2050° F. to about 2150° F. and wherein said acidic atmosphere comprises a mixture of hydrogen chloride vapor and nitrogen.

8. A method according to claim 1 wherein said homogenizing is performed at a temperature of from about 1800° F. to about 2300° F. for a period of time of from about 0.25 hour to about 24 hours.

9. A method according to claim 1 wherein said homogenizing is performed at a temperature of from about 2050° F. to about 2200° F. for a period of time of from about 1 hour to about 16 hours.

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