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SILICONIZING OF ELECTRICAL SHEET STEEL BY DIFFUSION

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No Drawing. Filed Nov. 21, 1962, Ser. No. 239,340
Claims priority, application Germany, Nov. 29, 1961, L 40,575

15 Claims. (Cl. 148—113)

The present invention relates to a method of treating sheet metal for the purpose of improving its magnetic characteristics, particularly iron sheets used as laminations in electrical machinery and containing, in addition to the iron, 4.5% or even only up to 3.5% silicon, depending on whether the sheets are to be only hot-rolled or whether, after the hot-rolling, they are still to be cold-rolled.

It is generally desirable to improve the good magnetic characteristics of sheet iron, which are obtained in the case of cold-rolled sheets and which are related with the formation of special crystal textures, by increasing the silicon content above the customary level. It is known that with increasing silicon contents, firstly, the specific electric resistance increases, as a result of which that portion of A.C. field losses which is due to eddy currents is decreased, and secondly, the magnetostriction is reduced, i.e., the changes of length of the ferromagnetic substance in the magnetic field become smaller, it being these changes in length, for instance, which cause the undesired noise produced by transformer laminations. If, however, the sheets are to be cold-rolled, the starting material cannot contain more than about 3.5% silicon, because a silicon content above this percentage renders the material too brittle to allow it to be cold-rolled.

It is, therefore, an object of the present invention to provide a method by means of which the silicon content can be increased above the customary limit despite the fact that such a material cannot, for all practical purposes, be cold-rolled.

With the above object in view, the present invention resides in a method of improving the magnetic characteristics of sheets for use in electrical apparatus, wherein sheets of customary silicon content which have been put through the cold-rolling process are thereafter additionally siliconized by annealing in a SiCl_4 -containing non-oxidizing protective gas, after which the sheets are subjected to a homogenizing treatment carried out by means of a second annealing step.

While it has been suggested to react the sheets with silicon so as to provide the sheets with a protective (Fe_3Si) layer containing about 14% silicon, the sheets as a whole are not, in this way, homogeneously siliconized. Even if the surface of the sheets, which have been enriched to a silicon content of 14%, are then homogenized by annealing at high temperature, the sheets will not have the desired good magnetic characteristics.

The method according to the present invention is able to raise the silicon content of the sheets to approximately 7%, this silicon content being distributed evenly over the entire cross section of the sheets. It has been found that this is possible by annealing, i.e., heat treating the sheet metal in a SiCl_4 -containing protective gas atmosphere

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which has but a relatively small proportion of silicon tetrachloride, preferably only up to 4% by volume. The protective carrier gas may, for instance, be nitrogen or argon. The same should be sufficiently pure so that no oxide layer is formed at the surface of the sheets, because such an oxide layer would impede a homogeneous siliconization. For this reason, the sheets to be siliconized should first have any oxide layers removed. During the siliconization, the sheets are preferably kept at a temperature of between 1100 and 1250° C. Expressed in other words, the silicon is diffused into the sheet metal and, so long as the proportion of silicon tetrachloride is kept no greater than 4% by volume and the temperature at which the siliconization—this term being used throughout the instant specification to refer to a diffusion rather than a plating process—takes place is kept within the above-mentioned limits, the rate at which silicon is deposited is less than the rate at which iron silicide (Fe_3Si) is formed, so that there is no opportunity for any iron silicide layer to be formed in the first place, instead, the silicon will diffuse into the metal. It is in the course of this annealing step, then, that the silicon is deposited and diffused into the sheet metal.

Even though the above-described process will produce what is for all practical purposes an even siliconization throughout the entire cross section of the sheets, it has been found expedient to subject the siliconized sheets to a homogenizing process by annealing at temperatures of between 1150 and 1300° C.

Finally, the magnetic characteristics can be improved even further by heating the homogenized sheets to a temperature of about 800° C. and thereafter cooling them in a magnetic field. The magnetic field should have a field strength of more than 10 oersteds and be applied in such a manner as to be oriented in the preferred magnetic direction as dictated by the desired crystalline structure, i.e., the lines of flux of the magnetic field should be so oriented as to produce the desired crystalline and hence magnetic anisotropy of the sheets. The sheets can be cooled at a rate of for example 100° C. per minute.

The siliconization can be carried out in a furnace which surrounds a gas-tight tube. The strip of sheet metal to be siliconized is passed through the tube while there flows through this tube a gas mixture composed of the silicon tetrachloride and the protective carrier gas, e.g., nitrogen or argon. The amount of SiCl_4 which is drawn out of the silicon tetrachloride reservoir, the latter being kept at a constant temperature, depends on the temperature and speed of the gas, and can be adjusted to any desired amount by changing these variables. In practice, it will be most expedient to keep the proportion of the silicon tetrachloride under 4% by volume.

The following are several examples of the present invention. The starting material was constituted by sheets usable for transformer laminations, which sheets, after being cast, were cold-rolled to a thickness of 0.32 millimeter. The silicon content was 3.2%. Previously formed oxide layers were removed by etching in diluted hydrochloric acid with bromide admixed.

During the siliconization, the furnace was moved at a constant speed along the sheet web. The annealing zone was 5 centimeters long, the temperature was approximately 1150° C.

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The following chart shows the final silicon content as a function of the speed of the furnace with respect to the web, and also as a function of the silicon tetrachloride content of the protective gas, the carrier of the latter being constituted by nitrogen. The gas was passed through the annealing tube at a rate of 140 liters per hour. The silicon content was determined analytically and from the electrical resistance.

Percent by volume of SiCl_4 in N_2	Speed of the furnace, centimeters per hour	Silicon content, percent by weight
0.75	51	4.2
1.34	35	6.5
3.64	51	7.3

The siliconized sheets were then rendered homogeneous by annealing for 10 hours at 1200° C. in a hydrogen atmosphere, and thereafter cooled to room temperature. The sheets were then again heated to 800° C., from which temperature they were cooled to room temperature at a rate of approximately 100° C. per hour, this cooling being done in a magnetic field having a strength of approximately 200 oersteds.

By means of a strip measuring apparatus, the following values for the magnetic reversal losses at 10 kg. (V_{10}) at 50 c.p.s. were measured in the case of non-siliconized and siliconized sheets, both with and without cooling in the magnetic field.

Silicon content, percent by weight	Without cooling in magnetic field V_{10} , W/kg.	After cooling in magnetic field V_{10} , W/kg.
3.2	0.41	0.39
4.2	0.59	0.39
6.5	0.52	0.36
7.3	0.37	0.34

It will be seen from the above that the V_{10} -value is decreased by increasing the silicon content and thereafter cooling the sheets in the magnetic field. With the latter step, the silicon contents has to be approximately 7% before the V_{10} -value is reduced.

The minimum magnetostriction saturation was found in sheets having a silicon content of approximately 6%.

It will be understood from the above that, thanks to the present invention, sheets of relatively high silicon contents are obtained without it being necessary, however, to forego the cold-rolling process for making the sheets. This is accomplished, as described above, by first completing the cold-rolling process of the sheet metal having a silicon content sufficiently low to allow the sheet metal to have been cold-rolled in the first place, i.e., about 3.5%, and only thereafter subjecting the thus cold-rolled sheets to a treatment which raises the silicon contents to the desired level, the latter being a level above that permissible for cold-rolling.

The present invention is not limited specifically to the use of silicon tetrachloride as the volatile silicon compound, the latter term being deemed to refer to a silicon compound which is volatile at the annealing temperature during which sheet metal is siliconized. For example, the volatile silicon compound can be one of the other silicon halides, namely, SiF_4 , SiBr_4 , and SiI_4 , or silicon tetraacetate, silicon sulfide dibromide (SiSBr_2), or silane (SiH_4) or one of the substituted silanes, e.g. SiCl_2H_2 , or silicon tetrathiocyanate ($\text{Si}(\text{SCN})_4$).

As stated above, if the silicon compound is silicon tetrachloride, the proportion of such silicon tetrachloride will be no greater than 4% by volume; this, it will be

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appreciated, means that, with the atomic weight of Si being 28 and the atomic weight of Cl being 35.5, the total silicon contents in the mixture is no greater than

$$\frac{28}{28 + (4 \times 35.5)}$$

of 4%, or $\frac{28}{170}$, it being this percentage, rather than the percentage of SiCl_4 as such, which is of primary significance insofar as volatile silicon compounds in general are concerned.

It will be understood that the above description of the present invention is susceptible to various modifications, changes, and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

For instance, the siliconized sheets need not be cooled to room temperature after being rendered homogeneous by annealing, but may be cooled to approximately 800° C., from which temperature they are cooled to room temperature in a magnetic field as described above.

What is claimed is:

1. A method of improving the magnetic characteristics of cold-rolled sheet metal having a silicon content sufficiently low to allow said sheet metal to have been cold-rolled, said method comprising the step of subjecting the sheet metal to a temperature of between 1100° and 1250° C. in an atmosphere of a gas mixture composed of a non-oxidizing carrier gas and a volatile silicon compound, wherein the total silicon contents in said gas mixture is no greater than $\frac{28}{170}$ by volume of the total gas, to diffuse silicon into the sheet metal to a level above that permissible for cold-rolling; and homogenizing the diffused silicon by annealing the sheet metal.

2. A method as defined in claim 1 wherein said volatile silicon compound is silicon tetrachloride, the proportion of said silicon tetrachloride in said mixture is no greater than 4% by volume of the total gas.

3. A method as defined in claim 2 wherein said carrier gas is selected from the group consisting of nitrogen and argon.

4. A method as defined in claim 2 wherein said carrier gas is of sufficient purity to avoid the formation of an oxide layer on the sheet metal.

5. A method as defined in claim 2 wherein the annealing during said homogenizing step is carried out at a temperature of between 1150 and 1300° C.

6. A method as defined in claim 5 wherein said homogenizing step is carried out while the sheet metal is in an atmosphere of hydrogen.

7. A method as defined in claim 2, comprising the further steps of heating the sheet metal subsequent to the homogenizing step, and thereafter cooling the sheet metal while the same is exposed to a magnetic field.

8. A method as defined in claim 7 wherein the sheet metal, during the subsequent heating step, is heated to a temperature of approximately 800° C., and wherein during said cooling step the sheet metal is cooled at a rate of approximately 100° C. per minute.

9. A method as defined in claim 7 wherein the magnetic field has a strength greater than 10 oersteds.

10. A method as defined in claim 7 wherein said magnetic field has a strength of approximately 200 oersteds.

11. A method of improving the magnetic characteristics of cold-rolled sheet metal having a silicon content of not more than approximately 3.5%, said method comprising the steps of:

(a) subjecting the sheet metal to a temperature of between 1100 and 1250° C. in an atmosphere of a gas mixture composed of a nonoxidizing carrier gas and silicon tetrachloride, the proportion of silicon tetrachloride in said gas mixture being not greater than 4% by volume, to diffuse silicon into the sheet metal to a level above that permissible for cold-rolling; and thereafter

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(b) homogenizing the diffused silicon by annealing the sheet metal at a temperature of between 1150 and 1300° C.

12. A method as defined in claim 11, comprising the further steps of:

(c) heating the sheet metal to a temperature of about 800° C.; and thereafter

(d) cooling the sheet metal to room temperature at a rate of approximately 100° C. per hour while the sheet metal is in a magnetic field having a strength of approximately 200 oersteds.

13. A method of improving the magnetic characteristics of cold-rolled sheet metal having a silicon content of not more than approximately 3.5%, said method comprising the steps of:

(a) subjecting the sheet metal to a temperature of between 1100 and 1250° C., in an atmosphere of a gas mixture composed of a nonoxydizing carrier gas and silicon tetrachloride, said carrier gas being selected from the group consisting of nitrogen and argon and being of sufficient purity to avoid the formation of an oxide layer on the sheet metal, and the proportion of silicon tetrachloride in said gas mixture being not greater than 4% by volume, to diffuse silicon into the sheet metal to a level above that permissible for cold-rolling; thereafter

(b) homogenizing the diffused silicon by annealing the sheet metal for approximately ten hours at a temperature of between 1150 and 1300° C. while the sheet metal is in an atmosphere of hydrogen;

(c) after cooling of the sheet metal, re-heating the same to a temperature of approximately 800° C; and thereafter

(d) cooling the sheet metal to room temperature at a rate of approximately 100° C., per hour while the sheet metal is in a magnetic field having a strength of approximately 200 oersteds.

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14. A method of making sheet metal for use in electrical apparatus, said method comprising the steps of:

(a) manufacturing the metal with a silicon content sufficiently low to allow the metal to be cold-rolled;

(b) cold-rolling the metal;

(c) subjecting the sheet metal to a temperature of between 1100° and 1250° C. in an atmosphere of a gas mixture composed of a non-oxydizing carrier gas and a volatile silicon compound, wherein the total silicon contents in said gas mixture is no greater than 2 1/2% by volume of the total gas, to diffuse silicon into the sheet metal to a level above that permissible for cold-rolling; and

(d) homogenizing the diffused silicon by annealing the sheet metal.

15. The method defined in claim 14 comprising the further steps of:

(e) re-heating the sheet metal; and

(f) cooling the sheet metal at a rate of approximately 100° C. per hour while the sheet metal is in a magnetic field having a strength of approximately 200 oersteds.

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DAVID L. RECK, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,224,909

December 21, 1965

Klaus Sixtus et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 46, for "With" read -- Without --.

Signed and sealed this 29th day of November 1966.

(SEAL)

Attest:

ERNEST W. SWIDER

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Commissioner of Patents