United States Patent [19]

Foster et al.

[11] **3,833,431**

[45] **Sept. 3, 1974**

[54] **PROCESS FOR CONTINUOUSLY ANNEALED SILICON STEEL USING TENSION-PRODUCING GLASS**

[75] Inventors: **Karl Foster**, Pittsburgh; **Jack W. Shilling**, Monroeville, both of Pa.

[73] Assignee: **Westinghouse Electric Corporation**, Pittsburgh, Pa.

[22] Filed: **Dec. 9, 1971**

[21] Appl. No.: **206,511**

[52] **U.S. Cl.** **148/113,** 148/112, 148/122

[51] **Int. Cl.** **H01f 1/04**

[58] **Field of Search** 148/113, 112, 111, 121, 148/122, 110, 31.5, 6

[56] **References Cited**

UNITED STATES PATENTS

2,351,922	6/1944	Burgwin	148/110
2,818,360	12/1957	Porter	148/31.5
2,913,361	11/1959	Fitz	148/110
3,021,237	2/1962	Henke	148/113
3,132,056	5/1964	McQuade	148/113
3,396,044	8/1968	Satterfield	148/6
3,496,506	2/1970	Seidel et al.	148/113
3,522,108	7/1970	Yamamoto et al.	148/113
3,522,114	7/1970	Knuppel et al.	148/112
3,582,409	6/1971	Kohler	148/113
3,671,337	6/1972	Kumai et al.	148/113

OTHER PUBLICATIONS

Rawson, H.; Inorganic Glass-Forming Systems; London, 1967, pp. X & XI.

Primary Examiner—Walter R. Satterfield
Attorney, Agent, or Firm—R. T. Randig

[57] **ABSTRACT**

A process is described for producing silicon steel containing nominally 3.25 percent silicon, by a continuous annealing process. The magnetic characteristics exhibited by the fully processed steel approach those of commercially available silicon steel but without the necessity of extensively desulfurizing the steel from that sulfur content which is usually obtained employing a commercial process. Essentially, the process consists of selecting a cold worked, decarburized semiprocessed silicon steel which is thereafter subjected to a continuous strand annealing at a temperature in the range between about 1,000°C and about 1,100°C in order to substantially completely recrystallize the steel by a secondary recrystallization process and the application of a tensile stress of at least 200 psi to the underlying steel for producing improved watt losses over that material having substantially the same sulfur content but which was manufactured by regular commercial processes.

9 Claims, No Drawings

PROCESS FOR CONTINUOUSLY ANNEALED SILICON STEEL USING TENSION-PRODUCING GLASS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of producing cube-on-edge oriented silicon steels which are characterized by exhibiting magnetic characteristics similar to those steels in commercial production today but without the use of an expensive desulfurization process which the commercially produced steels in use today are subjected to during normal commercial manufacture.

2. Description of the Prior Art

The present commercial practice for producing cube-on-edge orientation in nominally 3.25 percent silicon steel usually comprises a long time high temperature box anneal which develops both the orientation or texture of the material and removes sulfur to a value below about 50 ppm for optimum magnetic quality. This long time high temperature box anneal usually requires a programmed cycle for heating the material in slow stages to a temperature of about 1,200°C, maintaining the steel at this temperature for periods of time usually of about 24 hours or more and thereafter a programmed cooling of the material in order to obtain the desired magnetic characteristics in the final product.

By contrast, a continuous annealing practice for the final anneal could be quite attractive for the manufacture of power transformer laminations since a continuous strip furnace would have the capacity of a large number of box annealing furnaces and in addition, a flattening operation would not be required prior to shearing of the strip or sheet into laminations of desired configuration. Some of the major factors in the economic feasibility of a continuous annealing process are the time and temperature required. Previous investigations have shown that essentially complete grain texture development can be obtained in as short a time as 5 minutes at about 1,050°C which would indeed make a continuous annealing process quite attractive. Unfortunately, however, annealing at 1,050°C results in essentially no sulfur removal and the amount of sulfur, usually about 250 ppm normally contained in semi-processed silicon-iron, is detrimental to the ultimate magnetic quality exhibited by the alloy.

There exist substantially two reasons for the presence of sulfur in cold worked 3.25 percent silicon-iron. Initially, the sulfur is present as an impurity in the melt and is quite difficult if not substantially totally impractical to reduce the sulfur content to a value of less than about 150 ppm. The second and the most important reason for the presence of sulfur, is that sulfur combines with the manganese to form manganese sulfide inclusions which are considered to be the major factor in the secondary grain growth kinetics which are exhibited by the oriented silicon steels as commercially produced today. Consequently, the mere removal of the sulfur in the melt to a low level say about less than 100 part per million could raise the cost of the material significantly yet the end result would be that the material would not respond to the final high temperature annealing for the texture development. Following texture development by secondary recrystallization, sulfur can be removed by continuous annealing at a higher temperature, that is a temperature of about 1,200°C, and the material must be maintained at such temperature for about 20 minutes. The additional annealing time and the high temperature involved are quite disadvantageous both from a technical as well as economic point of view.

The present invention alleviates some of the shortcomings of the prior art through the use of the higher sulfur containing silicon steel material and imparting a residual tensile stress to the material. This results in the final material exhibiting magnetic characteristics comparable to those of material which is presently commercially produced through a high temperature desulfurization box anneal as part of the final heat treatment process.

SUMMARY OF THE INVENTION

The present invention employs a steel containing nominally about 3.25 percent silicon as the starting composition. This steel is melted, hot rolled, cold worked in one or more operations to the desired finished gauge and then subjected to a decarburizing anneal. Thereafter, the steel is subjected to a continuous anneal in which a strand of the material is passed through a furnace and the strand is heated to a temperature within the range between 1,000°C and about 1,100°C for a time period sufficient to substantially completely secondarily recrystallize the structure to obtain the desired orientation. The secondarily recrystallized steel is then subjected to the application of a tensile stress which produces a stress in the steel within the range between about 200 psi and about 800 psi. By thus processing the steel in the manner set forth, the residual sulfur content is not appreciably changed from that exhibited by the steel in its cold rolled decarburized condition, which is always in excess of 75 ppm, and in most cases, in excess of about 150 ppm. The magnetic characteristics exhibited by the alloy thus produced are comparable to the magnetic characteristics exhibited by the otherwise similar silicon steel material subjected to a high temperature box annealing heat treatment for the purpose of developing the texture and reducing the sulfur content.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of the present invention contemplates the use of a steel containing nominally about 3.25 percent silicon. It will be understood however that the process is applicable to steels containing anywhere between about 2 percent and about 6 percent silicon so long as the steel is capable of having developed therein an orientation which is characterized by a cube-on-edge orientation or (110) [001] in Miller Indices.

The steel having the requisite chemical composition is melted, preferably cast into ingots, hot worked and then cold worked in one or more operations with one or more intermediate anneals interposed therebetween until the steel has been cold reduced to finished gauge thickness. These operations are all well known in the art for producing, for example type M-5 grain oriented silicon steel. The steel of final gauge is thereafter subjected to a decarburizing heat treatment for example by a wet hydrogen anneal, in order to remove the carbon content to a sufficiently low value to prevent both magnetic as well as mechanical aging during use. For convenience the material of finished gauge dimension which has been subjected to a decarburizing anneal, is referred to herein as semiprocessed grain oriented silicon steel having a potential cube-on-edge orientation.

The semiprocessed silicon steel is usually obtained in large coils ready for additional processing. In this respect the prior used practices include the application of a separator insulation coating which is applied to the surfaces of the steel strip which are thereafter recoiled and the coil is thereafter set on edge in a box annealing furnace. A programmed heat treatment is applied to the silicon steel coil in the presence of a dry hydrogen atmosphere and upon heating to a temperature of 1,200°C the steel is substantially completely secondarily recrystallized and by holding at said elevated temperature for a time period of about 24 hours, the residual sulfur content is reduced so that the optimum magnetic characteristics may be developed in the steel.

In contrast thereto, the present invention subjects the semiprocessed silicon steel to a continuous strand annealing by uncoiling the material and passing a single strand of the semiprocessed steel through a continuous annealing furnace. Of course, a plurality of non-contacting paralled strands can be processed simultaneously. While not necessary to do so the steel is hung usually in an essentially horizontal catenary form suspended from each end of a horizontally disposed furnace and continuously moves through the furnace at a predetermined rate. In the process of the present invention, the steel strand is subjected to a heat treatment wherein the steel is rapidly heated to a temperature of from 1,000° to about 1,100°C and maintained at such temperature for a period of usually between about 5 minutes and about 10 minutes. Thus each segment of steel strand upon entering the furnace is heated to a minimum temperature of 1,000°C and up to a maximum of about 1,100°C and preferably at a temperature of about 1,050°C. While continuously moving through the furnace at this elevated temperature, the speed of the material is regulated so that each segment of the steel is maintained at this temperature for a time period of between about 5 minutes and about 10 minutes. In this respect, shorter times at the higher enumerated temperature of 1,100°C while at the lower temperatures, that is about 1,000°C, the longer time may be employed, optimum results are obtained when the steel is heated to about 1,050°C for a time period of 5 to 10 minutes or until the material has been secondarily recrystallized substantially completely.

The sulfur which is bound up, usually in the form of manganese sulfides, and distributed throughout the matrix of this steel acts as a grain growth inhibitor at low temperatures, and the dissolution of the small MnS particles at 1,000° to 1,100°C allows complete secondary recrystallization and grain growth to occur without appreciably changing the sulfur content from that of the material in its semiprocessed condition. In carrying out the recrystallization heat treatment, the sulfur content usually runs anywhere between about 200 and 250 parts per million but may be as low as 150 ppm but seldom lower than about 75 ppm. Usually the steel will have a sulfur content within the range between 150 ppm and about 250 ppm, which sulfur content will not be appreciably altered during the term of the secondary recrystallization heat treatment as described hereinbefore.

Preferably, during such secondary recrystallization heat treatment, the material undergoing the continuous strand annealing is subjected to a protective atmosphere, particularly good results being obtained using hydrogen having a dew point of less than about −40°C. It is preferred to maintain this protective atmosphere in order to not unduly scale the material which would adversely affect the magnetic characteristics ultimately exhibited by the material in its finished form.

Following the secondary recrystallization heat treatment the steel is next subjected to a process by means of which a residual tensile stress between about 200 psi and about 800 psi is applied to the steel. This is most advantageously accomplished by means of applying to the surface of the steel a slurry of a glass which has a coefficient of thermal expansion substantially less than that exhibited by the underlying steel and usually of the order of less than about 8.5×10^{-6} in./in. per degree centigrade. By applying a proper thickness of the slurry of a glass to the surface of the steel sheet or strip and thereafter fusing the glass at a low temperature, for example, 700°–850°C, the steel upon cooling to room temperature will be placed in tension usually within the range between about 200 psi and about 800 psi.

When lesser stresses then 200 psi have been produced the resultant magnetic characteristics exhibited by the steel have not been improved sufficiently to make them comparable to commercially produced 3-¼ percent grain oriented silicon steel as produced by the box annealing method described hereinbefore. When higher stresses than 800 psi have been employed, no appreciable improvement in the observed watt loss, coercive force or magnetostriction has been observed in such processed steel.

The glass slurry coating is preferably fused to the surface of the steel by heating the steel to a temperature within the range between about 750°C and 800°C, the same occurring either by means of a box anneal with the glass slurry in place thereon or by means of another continuous strand heat treatment in which an individual strand of the material is passed through the furnace and the material is heated to this temperature in order to fuse the glass of the slurry onto the surface of the steel. When the coated steel is cooled to room temperature, the difference in coefficient of thermal expansion between the glass and the steel coordinated with their relative thicknesses is sufficient for placing the steel in tension to effect a stress of at least 200 psi and preferably between about 400 psi and about 800 psi. During the subsequent heat treatment fusing the glass to the surface of the steel a non-reducing atmosphere can be employed and a slightly oxidizing atmosphere is preferred. In order to provide for the proper stacking factor, when the material is ultimately used, for example, in a lamination of a power transformer core, the glass is limited to a thickness in the range between about 0.25 mil and about 1.0 mil in total thickness, the greater thickness being used with thicker sheet steel, for example 1 mil glass on a 13 mil thick sheet, and the 0.25 mil glass coating on a 3 to 6 mil thick sheet. Such thickness is sufficient to exerting the proper degree of tensile stress without unduly reducing the stacking factor.

As an alternative embodiment of the present invention, it will be appreciated that it is possible to start with the semiprocessed silicon steel and apply directly to the surface thereof a slurry of a coating containing a glass having the suitable coefficient of thermal expansion so as to exhibit the required tensile stress in its fused condition. To carry this out, a slurry of the glass is applied to the semifinished silicon steel and the steel is thereafter continuously strand annealed at a temperature in the range between 1,000° and 1,100°C for a time period of between about 5 minutes and about 10 minutes. It is preferred to employ a non-reducing atmosphere while firing said glass to the surface of the steel. During such heat treatment the underlying steel will be substantially completely secondarily recrystallized with the requisite grain growth and at the same time, the slurry which has been applied to the surface of this steel will be fused and upon cooling the same to room temperature, the differences in the relative coefficients of thermal expansion between the glass and the metal will result in placing the underlying steel in tension sufficient to exert a tensile stress between about 200 psi and about 800 psi.

In order to more clearly demonstrate the method of the present invention, reference may be had to the following processing schedule which demonstrates the observed magnetic properties which are attributable to the material having a high sulfur content and a glass coating as opposed to substantially an identical steel with a low sulfur content and no glass coating.

Epstein strips of 12 mil thickness semiprocessed silicon steel containing about 3.25 percent silicon and in the cold rolled and decarburized condition were continuously annealed to obtain substantially complete secondary recrystallization and grain growth but without any appreciable sulfur removal. The final sulfur content in each instance was above 200 ppm. The following Table I lists the magnetic properties of this sample together with the catalog properties for a commercial type M-5 silicon steel which is presently marketed and employed in the manufacture of power transformers.

TABLE I

Sample	Hc (Oe)	B_{10} (G)	Pc 15/60 (W/lb)
Continuously annealed (no glass)	0.172	18000	0.63
Fully processed	0.10	18000	0.57

From Table I it is seen that the continuously annealed material has a higher coercive force and a higher watt loss than the catalog properties of the fully processed M-5 type material. While the B_{10} values are substantially unchanged, nonetheless the watt loss is high and the coercive force is high. This very clearly demonstrates the adverse effect of the high sulfur content since the continuously annealed material had a sulfur content in excess of 200 ppm whereas the fully processed type M-5 material has a sulfur content of less than about 75 ppm.

In order to demonstrate the effect of applying tension to the steel, the continuously annealed sample was thereafter tested employing varying amounts of tension applied thereto. The results are set forth hereinafter in Table II.

TABLE II

Applied Tension (psi)	Hc (Oe)	B_{10} (G)	Pc 15/60 (W/lb)
0	0.172	18000	0.63

TABLE II-Continued

Applied Tension (psi)	Hc (Oe)	B_{10} (G)	Pc 15/60 (W/lb)
100	0.163	18000	0.61
400	0.138	18000	0.58
800	0.131	18000	0.57
1200	0.132	18000	0.57
1600	0.136	18000	0.57

As can be seen from Table II, the application of up to 400 psi to the steel is effective for substantially reducing the coercive force and the observed watt loss without substantially changing the B_{10} values. The improved magnetic characteristics became evident with as little as 200 psi applied tensile stress. Further increases in the tensile strength above 800 psi do not materially affect the observed magnetic properties and, in particular, when the tensile stress applied to the steel exceeds about 800 psi substantially no further improvement has been noted in the coercive force as well as the observed watt loss characteristics. By comparison with the data set forth in Table 1, it becomes readily apparent that the applied tension to the high sulfur containing steel results in the steel exhibiting magnetic characteristics closely approaching those of the commercially fully processed 3-¼ percent silicon steel of the M-5 type.

Since it is desirable to have the tension applied continuously so as to maintain the steel in tension throughout its use, additional samples of the material were coated with a glass identified as LX101. This glass had a composition which included 8 percent SiO_2, 20 percent B_2O_3, 60 percent ZnO and 12 percent PbO and exhibited a coefficient of thermal expansion of about 4.6 $\times 10^{-6}$ per degree centigrade. In order to improve the adhesive of the glass to the steel, samples were first treated by the application of a thin coating of aluminum thereto. The coating thickness was about 2,000 A. The glass, in a slurry form, was applied to the aluminized surface of the continuously annealed sample and thereafter fired at a temperature of 760°C. After cooling to room temperature, the as annealed material was tested together with the glass coated material, the latter employing the teachings of the present invention the test results are set forth in Table III.

TABLE III

Condition	Hc (Oe)	B_{10} (G)	Pc 15/60 (W/lb)
As annealed	0.172	18000	0.63
coated with glass LX 101	0.133	17900	0.58

From the test results set forth in Table III it is noted that there is an improvement in the coercive force substantially of the same magnitude as that resulting from applying tension as set forth in Table II. While the B_{10} value is slightly lower, it is not significantly changed from that of the as annealed material whereas the watt loss exhibited by the material shows a substantial improvement and is of the same magnitude as that of the commercially fully processed type M-5 material.

From the foregoing, it is seen that the process of the present invention is effective for producing commercial quality oriented cube-on-edge type silicon steel without the necessity of substantially completely desulfurizing the material. Such processing is effective for continuously secondarily recrystallizing the microstructure and by the application of a tensile stress thereto the steel will exhibit magnetic characteristics similar to those of commercially processed type M5 material. In addition to the improved coercive force and the watt loss exhibited by the materials processed in accordance with this invention other magnetic characteristics are also improved, noteworthy among which is the magnetostriction exhibited by the steel. Magnetostriction is materially reduced. There characteristics are of prime importance to users of the material especially where the material is used as a core in a power transformer.

We claim as our invention:

1. In the process for producing silicon steel having a cube-on-edge orientation employing a continuous annealing process in which the final sulfur content is in excess of 75 ppm and in which the steel is melted, hot worked, cold worked in one or more operations to the desired finish gauge and decarburized, the steps comprising continuously annealing as a single thickness the decarburized steel at a temperature within the range between about 1,000°C and 1,100°C for a time period sufficient to develop the cube-on-edge texture and to effect substantially complete secondary recrystallization and grain growth, the final sulfur content of the steel being in excess of 75 ppm and fusing a coating on the surface of the steel of a silicate glass having a coefficient of thermal expansion of the order of less than about 8.5×10^{-6} in./in. per degree centigrade which will effect a tensile stress in the steel of at least 200 psi while not adversely affecting the other properties of the treated steel.

2. The process of claim **1** in which the steel is continuously annealed at a temperature of about 1,050°C for a time period of between about 5 minutes and about 10 minutes.

3. The process of claim **1** in which the steel is annealed in an atmosphere of hydrogen having a dew point of less than −40°C.

4. In the process for producing silicon steel having a cube-on-edge orientation employing a continuous annealing process in which the sulfur content is in excess of 150 ppm and in which the steel is melted, hot worked, cold worked in one or more operations to the desired finish gauge and decarburized, the steps comprising applying to the surface of the steel a coating of a slurry of a silicate glass having a coefficient of thermal expansion of the order of less than about 8.5×10^{-6} in./in. per degree centigrade which will effect a tensile stress within the range between about 200 psi and 800 psi when the glass is fused to said surface of the steel, said glass not adversely affecting the other properties of the steel and continuously annealing the coated steel as a strand at a temperature within the range between about 1,000°C and 1,100°C to fuse the glass to the steel surface and for a period of time sufficient to develop the cube-on-edge orientation and to effect substantially complete secondary crystallization and grain growth in the steel without any appreciable desulfurization.

5. The process of claim **4** in which the fused glass has a total thickness within the range between 0.25 mil and 1.0 mil in thickness.

6. The process of claim **4** in which the annealing takes place in a non-reducing atmosphere.

7. In the process for producing silicon steel having a cube-on-edge orientation in which the final sulfur content is in excess of 75 ppm and in which the steel is melted, hot worked, cold worked in one or more operations to the desired finish gauge and decarburized, the steps comprising, continuously annealing the decarburized steel as a strand at a temperature within the range between 1,000°C and 1,100°C in a dry, reducing atmosphere for a time period sufficient to develop the cube-on-edge orientation and to effect substantially complete crystallization and grain growth without an appreciable change in the sulfur content applying to the surface of the recrystallized steel a slurry of a silicate glass having a coefficient of thermal expansion of the order of less than about 8.5×10^{-6} in./in. per degree centigrade when when fused to the surface of the steel exerts a tensile stress in the steel within the range between about 400 psi and about 800 psi and thereafter fusing the glass to the surface of the steel at a temperature within the range between about 750°C and 800°C, said fused glass not adversely affecting the other properties of the steel.

8. The process of claim **7** in which the glass has a total thickness within the range between about 0.25 mil and about 1.0 mil.

9. The process of claim **7** in which the strand annealing for recrystallization takes place in a protective reducing atmosphere and the fusing of the glass to the surface of the steel takes place in a non-reducing atmosphere.

* * * * *