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ELECTRIC ALLOY STEEL CONTAINING VANADIUM AND SULFUR

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This application is a continuation in-part of my copending application, Serial No. 178,578, filed March 9, 1962, now Patent No. 3,239,332.

This invention relates to sheet steel for use in magnetic cores of electrical apparatus and relates to steel manufacturing methods. The invention particularly concerns the production of silicon steel having a high degree of preferred orientation and highly directional magnetic properties.

Grain oriented silicon steel in sheet form is widely used in the electrical manufacturing industry in large tonnage. Desirable magnetic properties with a grain orientation of approximately 80% have been achieved by alternate heating and cold rolling of suitable hot rolled strip. Suitable procedures are described in the original Goss Patent No. 1,965,559.

Numerous efforts have been made to effect further improvement in grain orientation and to reproduce such results reliably; and 90% grain orientation has long been a goal in the industry.

The sheet materials to which my invention is related are usually referred to in the art as "electrical" silicon steel or, more properly, grain oriented silicon and containing relatively minor amounts of impurities such as sulfur, manganese, phosphorous and very low carbon content.

It has been found from experience in the production of commercial grain oriented silicon steel that while all the grains are oriented in the (110) [001] direction, some deviation from the ideal exists. This deviation may be as much as 10 degrees from the ideal. This reduces the apparent orientation, and makes it appear that the grains are only 80% oriented. In testing many specimens by means of the torsion magnetometer, it was found that the apparent orientation varies from 78% to 82% in the best grain oriented silicon steel produced at the present time.

An object of the invention is to cause a high percentage of the grains comprising the material to have their crystal space lattices arranged in a substantially identical relationship to the plane of the sheet and to the direction of rolling. More specifically, in the finished strip the grains are oriented with the (110) [001] direction coinciding with the rolling direction. The term "grain orientation" in the specification and claims is employed to indicate the percentage of the grains having their (110) [001] direction coinciding with the rolling direction.

An object of the invention is to obtain increased permeability at flux densities of 15,000 gauss or more. Furthermore, it is an object to achieve more nearly perfect crystal structure and grain boundaries and orientation exceeding 85%, as well as grain size control. Moreover, it is an object to accomplish reduction in watt loss and hysteresis at over 15,000 gauss.

The unit cells or body-centered unit cubes comprising these materials each have a high degree of magnetic anisotropy with respect to the crystallographic planes and directions of the unit cube, and hence, each grain or crystal comprising a plurality of such unit cells exhibits a similar anisotropy. More particularly, crystals of the silicon-iron alloys to which this invention is directed are known to have their direction of easiest magnetization parallel to the unit cube edges, that is, the (110) [001] orientation. It is, therefore, desirable to find processing

procedures and chemical compositions which enhance this desired texture.

Heretofore by following suitable procedures of heat treatment and cold rolling as described reasonably good orientation as high as 80%, e.g., was achieved by using high sulfur steel, over .009 and ordinarily between .015 and .025%. The sulfur content is objectionable in the finished steel, however, and the excess sulfur must be driven out by a high temperature final anneal, which adds to the expense and causes deterioration of the properties of the steel in other respects. One of the objects of the invention, therefore, is avoidance of a high temperature final anneal.

A further object is attainment of favorable magnetic properties without the use of steel having a high initial sulfur content.

I have succeeded in achieving a grain orientation of 90%, that is, of the (110) [001] texture in low sulfur steel, by introducing into the alloy an additive consisting of vanadium alone, or in combination with other suitable elements. The use of such additives has also made less critical than heretofore the processing procedures employed in order to obtain the desired preferred grain orientation, has reduced the cost of manufacture and increased the yield of acceptable magnetic sheet steel.

It was found that by adding small amounts of certain elements to clean low-sulfur 3% silicon steels, the orientation could be improved; that is, the grains could be more perfectly aligned in the direction of rolling. For example, by adding about 0.04% vanadium one increased the orientation so that 90% orientation was measured. It was found that by increasing the orientation from 80% to 90%, a marked improvement resulted in the permeability at a flux density of 15,000 gauss and over. With other additives included these results were accomplished with between 0.005% and 0.02% vanadium.

The material to which this invention relates is silicon steel having a silicon content in general of about 2.8% to 3.4% and preferably in the range of about 3.0% to 3.3%. A typical preferred range and a typical specific analysis for such a steel is as given in the following table:

Table I

	Percent by Weight of Ingot Used in Grain Oriented Strip Steels	
	Average Range	Specific
Silicon	3.00–3.30	3.15
Carbon	.020–.030	.025
Manganese	.035–.10	.050
Sulfur	.003–.006	.005
Phosphorous	.005–.020	.008
Aluminum	.01 max.	.005
Copper	.050–.09	.080
Nickel	.030–.15	.050
Tin	.005–.020	.010
Chromium	.01 –.03	.02

A silicon steel may be employed having silicon content up to 3.3% and satisfactory results are obtained by employing a silicon content of approximately 3.00%. In accordance with one example, an additive was employed consisting of approximately 0.04% vanadium which had been introduced into the melt during ladling prior to the pouring of the ingot in the form of ferro vanadium. In other examples, as little as .008% vanadium was employed. As much as .05% vanadium may be employed, but for economic reasons the vanadium content is preferably limited and favorable results have been obtained with the minimum content of vanadium. The vanadium content may be reduced as the steel is made cleaner, and when combined with copper in excess of residual copper.

Grain oriented silicon steel strip including the principles of this invention may be produced by following this procedure:

(1) Heat ingot which has been poured from a clean low sulfur melt containing the vanadium additive as described above for a minimum of five hours at a temperature over 2250° F. To remove scabs and to make structure homogeneous and reduce micro segregation may require flash heating to 2450° F. for a short time.

(2) Roll on blooming mill to produce slab having a thickness of 5 to 8 inches and finish at a temperature above 2000° F., care being exercised to avoid development of laminations and the like.

(2*a*) Condition surface of slab if required.

(3) Re-heat slab to over 2275° F. and hold to homogenize and reduce slab to a thickness of ¾ to 1½ inches. Such reduction is at a fast rate and preferably accomplished in 3 passes on a single stand reversing mill, so that temperature drop is slight.

(4) The partially reduced slab then enters the six stand finishing mill and is rapidly reduced to strip with a thickness of 0.070 to 0.090 inch and at a speed to insure a temperature not more than 1700° F. at front and back end of strip.

(5) Open anneal the hot strip at 1600° F. to 1700° F. followed by a descale operation.

(6) Cold roll the annealed strip to an intermediate gauge thickness of 0.022 to 0.026.

(7) Open anneal the cold rolled strip at a temperature between 1600° F. and 1850° F. in a controlled atmoshere of low dew point.

(8) Cold roll to final thickness usually in the range of 0.012 to 0.014.

(9) Open anneal cold rolled strip in decarbonizing atmosphere to reduce carbon below 0.005% in a wet reducing gas at a temperature substantially between 1450° F. and 1500° F. Time required is usually 2 to 4 minutes. The strip is then considered semi-processed.

(10) Coat with inorganic material which acts as a spacer material during final anneal and provides an insulating film. The spacer material permits free flow of dry hydrogen during final anneal.

(11) Since a low sulfur steel is employed the final anneal need not be at high temperature to drive off sulfur and continuous anneal at 1650° to 1700° F. may be employed.

Low sulfur content in the melt employed is accomplished in the manner described in the copending application of Shozo Watanabe, Ko Kumai, Seizo Tsuda and myself, Serial No. 280,908 or 280,906 or preferably the application of Shozo Watanabe, Hideo Watanabe and myself, Serial No. 280,906 filed May 16, 1963. Into the ladle from which the ingot was poured streams of molten metal and addition agents are simultaneously directed in accordance with one purifying process so that the stream of metal and the stream of purifying agents impinge at the same point on the molten metal surface in the ladle. The stream of purifying material consists of finely divided solid particles of desulfurizing and deoxidizing agents such as thoroughly mixed calcium silicide, soda ash, fluorspar, calcium fluoride, sodium hydroxide, magnesium hydroxide and ferro manganese. The desired alloying material may also be introduced into the stream of solid particles and may consist of material selected from the group comprising silicon, molybdenum, tungsten, chromium, nickel, vanadium, titanium, copper and compounds thereof.

According to another practice inclusions are removed from the molten steel by projecting inert material in jet form against each of six or more streams of molten metal to disintegrate the streams into particles, injecting with the inert material a purifier selected from the group consisting of sodium, magnesium, silicon, calcium, silicon calcium fluoride, cryolite, albite and allowing the metal particles to descend through a filter formed by the resultant slag layer. When the inert material is projected in jet form against the streams of molten metal the operation is carried on in a closed ladle having a tundish cover so that the full benefit of the deoxidizing effect of sodium, magnesium or the like is achieved. It will be understood that such metallic reducing agents as sodium and magnesium will be in the form of a vapor at the temperature of molten steel.

Although vanadium alone may be employed as an additive in silicon steel to achieve the improved grain orientation, I have found that other additives in addition to vanadium impart desirable results and reduce costs by permitting partial replacement of the vanadium content. In one example, both vanadium and copper were employed as additives. With a copper content in the finished steel between .1 and .25%, less vanadium could be employed and satisfactory results were obtained with as little as .008% vanadium in combination with the copper in a clean steel.

It is important that any additive added must not generate oxides, nitrides, and so forth, which are finely dispersed in the melt. Such finely divided oxide particles will precipitate into the grain boundary and impair the magnetic properties. It will be noted that the additives chosen herein are added in very small amounts in order to avoid such deleterious effects. Furthermore, any oxides which can precipitate into grain boundary affect the perfection of (110) [001] texture, and so must be avoided by using suitable deoxidation practices. The cleaner the steel the easier it is to orient the grains by means of suitable additives which tend to perfect the desirable (110) [001] texture.

It is now well established that in a properly processed oriented strip the (110) [001] direction is aligned in the rolling direction for all the grains, but this alignment is not perfect. Torque measurements indicate that in present day material about 80% of the grains are oriented due to the scatter in orientation. However, when the additives vanadium and copper are added to a clean heat, in the sense defined here, even in extremely small amounts, increased perfection in orientation is experienced. A texture which is oriented 90% can be achieved in this way. A clean heat may be defined as one in which the deoxidation products are not finely dispersed. Since it is well known that finely dispersed oxides in excess can adversely affect the magnetic properties, every effort is made to hold the oxides which may be colloidally or finely dispersed under 0.005%. This requires utilization of a suitable deoxidation practice as described herein.

The additives vanadium and copper singly or in combination can therefore only be effective when the heat is substantially free of finely dispersed oxides and so forth. A reliable measure of a clean steel is the initial permeability. Steels having an initial permeability of 1300 or more are usually considered very clean. The best results are obtained with initial permeabilities of 1300 or more. However, I have achieved orientation of 85% or more with steels having initial permeabilities in the range between 1300 or 1350 and 1450. This is an essential requirement, otherwise the additives such as vanadium and copper will not function in the manner described herein.

I have shown and particularly described certain embodiments of my invention and certain methods of operation embraced therein for the purpose of explaining its principle of operation and showing its application, but it will be obvious to those skilled in the art that many modifications and variations are possible and I aim, therefore, to cover all such modifications and variations as fall within the scope of my invention, which is defined in the appended claims.

What is claimed is:

1. Silicon steel in sheet form consisting essentially of between .008 and .05% vanadium and between approximately .003% and .009% sulfur, between 2.8% and 3.3% silicon and the balance iron and sufficiently free from in-

clusions of finely dispersed oxides to have an initial permeability of over 1450 to produce approximately 90% grain orientation.

2. Low sulfur silicon steel consisting essentially of between .003% and .01% sulfur between 2.8% and 3.3% silicon, an additive consisting of approximately .02% vanadium, and the balance iron, sufficiently free from inclusion of finely dispersed oxides to have an initial permeability over 1350 and grain orientation of over 85%.

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