

1

3,379,581

## DESULFURIZING COATING FOR FERROUS MATERIAL AND METHOD OF USING IT

Dale M. Kohler, Middletown, and Victor W. Carpenter, Franklin, Ohio, assignors to Armco Steel Corporation, Middletown, Ohio, a corporation of Ohio  
No Drawing. Filed Dec. 21, 1964, Ser. No. 420,091  
4 Claims. (Cl. 148—113)

### ABSTRACT OF THE DISCLOSURE

An inorganic coating for desulfurizing ferrous materials consisting essentially of magnesium oxide and from about 2% to about 10% of calcium oxide by weight, and a method of desulfurization comprising the steps of annealing a strip of ferrous metal for several hours at a temperature of about 2000° F. to 2300° F. in a dry hydrogen-bearing atmosphere while the surfaces of the strip are covered with the above described coating.

This invention relates to the manufacture of oriented silicon-irons in which the majority of the (100) planes or cube faces are oriented substantially parallel to the sheet surface, broadly called "cube-on-face," and also more narrowly to oriented silicon-irons in which the cube edges are oriented in the rolling direction and at 90° thereto, generally called "cubic texture."

As is now generally known in the art, silicon-iron sheet stock having cubic texture may be produced by reducing silicon-iron to a desired final gauge in two stages of cold rolling following hot rolling to an intermediate gauge, there being an intermediate anneal between the stages. Reference is made to U.S. Patent No. 3,130,094 in the names of D. M. Kohler and M. F. Littmann. The condition of the material after the second stage of cold rolling and after a primary recrystallization will be such that a number of cubically oriented nuclei will have formed therein. Under suitable conditions of secondary recrystallization, the grains produced from the nuclei can be caused to grow at the expense of grains having other orientations until substantially the entire silicon-iron sheet stock is characterized by the cubic orientation. The orientation contemplated is primarily an orientation in which the cube faces are substantially parallel to the surface of the sheet stock, four of the cube edges being oriented in the direction of rolling. The orientation is classified as (100) [001] by Miller's Indices.

It has also hitherto been known that the silicon-iron sheet stock at the time of the secondary recrystallization must be "clean," i.e., it should not contain oxide inclusions in an amount greater than about .0035%. The elimination of oxide inclusions may be accomplished in various ways. It is most conveniently accomplished by precautions taken during the production of the silicon-iron alloy, e.g., by vacuum melting or by treating the molten metal in the furnace, ladle, or mold. Oxide inclusions may also be reduced by a prolonged annealing in hydrogen. Carbon and sulfur should be removed before the final box anneal if the material is to be annealed under equilibrium conditions, such as in tightly wound coils of wide width where access to the annealing atmosphere is limited. The reduction of carbon to a low enough value is most easily accomplished by known processes of wet gas decarburization, for example, that set forth in U.S. Patent No. 2,287,467. It is to the elimination of sulfur that the teachings of the present application are primarily addressed; and it is a basic object of this invention to provide a method for carrying the sulfur content down to at most about 6 parts per million prior to the final anneal.

The secondary recrystallization required is one which

2

proceeds in accordance with the phenomenon of surface energy. For the conditions of such an anneal, reference may be made to U.S. Letters Patent 3,130,095 issued Apr. 21, 1964, in the names of Dale M. Kohler and John M. Jackson. The secondary recrystallization there set forth involves the use in the annealing atmosphere of minute quantities of a polar substance which affects the surface energy of the grains and causes cubically oriented grains to assume the lowest energy position. Although the polar substance may be and in most instances is sulfur, hydrogen sulfide, or another dissociable sulfur compound (used within the range of substantially 20 to 250 parts per million), the fact remains that no large quantity of residual sulfur can be tolerated in the steel. If steel containing more than 6 parts per million of sulfur is annealed in wide widths of tightly wound coils, the atmosphere adjacent to the surfaces will contain more than 250 parts per million of sulfur when equilibrium has been reached and good cubic texture or cube-on-face stock cannot be obtained. Moreover, the surfaces of the silicon-iron sheet stock must be free of continuous overlying adherent films of material, including annealing separators and glassy derivatives therefrom, so that the grains will have exposed "clean" surfaces at the surface of the sheet stock. It is an important object of this invention to provide a method of lowering sulfur in the steel itself which does not result in the formation of any adherent coating on the surfaces of the stock or any coating which is difficult to remove by ordinary acid pickling.

These and other objects of the invention which will be set forth hereinafter, or will be apparent to one skilled in the art upon reading these specifications, are accomplished in those procedures of which certain exemplary embodiments will now be described.

It has hitherto been understood that certain substances capable of use as annealing separators have a tendency to desulfurize the silicon-iron. This is true of magnesia and calcium oxide. But, certain difficulties have been encountered. For example, if the silicon-iron is subjected to wet gas decarburization in accordance with the above noted patent, the conditions during the decarburization anneal are reducing toward iron, but oxidizing toward silicon and carbon. The stock will be decarburized, and the oxidation products of carbon will pass off in the form of gases. But, silicon will be oxidized to silica at and near the surfaces of the stock; and if a magnesia separator is used in a subsequent high temperature anneal, some of the magnesia will fuse with the silica forming a tightly adherent thin glass layer. Such a layer is valuable in silicon-irons having the cube-on-edge orientation because it gives good interlamination resistivity in magnetic cores; but it is difficult to remove, and so long as it is present it interferes with secondary recrystallization by surface energy.

Furthermore, calcium oxide when used as an annealing separator tends to combine with carbon dioxide from the air or from other sources to form calcium carbonate. During a subsequent high temperature anneal, the calcium carbonate will dissociate to form calcium oxide and carbonaceous gases. The carbonaceous gases themselves dissociate, and there is a strong tendency to recarburize the silicon-iron. Such recarburization causes magnetic aging. This application is premised on the discovery that the above disadvantages may be obviated by the use of an annealing separator containing both calcium oxide and magnesia in critical proportions. The calcium oxide should constitute about 2% to about 10% of the total weight of the separator. The preferable range is from about 4% to 6% if the initial sulfur is about .025%. In many instances the magnesia will make up the balance of the separator; but other substances may be present as hereinafter set forth. The use of less than about 2%

calcium oxide is not desirable for various reasons including the fact that magnesia is a less effective material for desulfurization. With pure magnesia, for example, it is not possible to reduce the sulfur level in the silicon-iron to a value below the range of about 7 to 10 p.p.m. within a reasonable time and under conditions in which the contact of the annealing gas atmosphere with the surfaces is limited. On the other hand, the use of more than about 10% of calcium oxide does not further the desulfurization effect and increases the danger of carburization during the coating, drying, and coil handling process as above explained. The use of a mixture of calcium oxide and magnesia within the range set forth permits the lowering of the sulfur content to at most about 6 p.p.m. with commercial certainty.

It is contemplated that the mixture set forth herein will be used as an annealing separator in an intermediate anneal, which is a box anneal at 2000° to 2300° F. preferably about 2200° F. in dry hydrogen having an inlet dew point of -25° F. or less. Several hours are required to accomplish the purification. Depending upon the initial sulfur content, the time may be as much as 30 hours or more. By "intermediate anneal" is meant an anneal in the routing other than the final anneal in which the ultimate conversion of the product to the cubic texture is accomplished under conditions of surface activity. Usually, therefore, the anneal in which the mixture of calcium oxide and magnesia is used is an anneal located between two stages of cold rolling. In its broader aspect, the invention is not so limited, and may be practiced at any stage in the routing excepting the final secondary recrystallization. Also it may be pointed out that the invention is of value in the formation of silicon-iron sheet having orientations other than the cubic orientation above described. For example, it can be employed in the manufacture of any cube-on-face orientation, wherein the cubic crystals are so oriented that certain faces of the crystals lie parallel to the surfaces of the sheet stock while the cube edges which bound these faces may be randomly oriented, as in U.S. Patent No. 3,130,090 issued Apr. 21, 1964, or aligned in any direction. It should be kept in mind that desulfurization throughout the body of the stock is easier and takes less time the closer the stock is to the final gauge. Moreover, the present invention is applicable to various modes of producing stock having cubic texture, e.g., the procedures set forth in Patent No. 3,130,094 issued Apr. 21, 1964, in the names of Kohler and Littmann Patent No. 3,130,093 issued Apr. 21, 1964, in the name of Kohler and Patent No. 3,130,092 issued Apr. 21, 1964 in the names of Kohler and Littmann.

The manner in which the annealing separator is applied to the sheet stock is not a limitation upon the invention. The calcium oxide and magnesia in finely powdered form may be thoroughly mixed and applied electrostatically as in Patent No. 3,000,752 issued Sept. 19, 1961, in the names of Jackson and Macklin. The powdered substances may be mixed with water and applied as a slurry to the surfaces of the strip stock and metered by rubber rolls to provide a thin and uniform coating. Where a water slurry is used, the coating is ordinarily dried by heating the strip to a low temperature following the coating operation.

In the practice of this invention, under some circumstances, a thin film may be formed on the silicon-iron sheet stock during the high temperature box-anneal. The formation of a glass film will be largely avoided by the use of a "non-hydrating" magnesia. A thick glass film and one which will be oxidizing to the iron is avoided by using calcium oxide rather than calcium hydroxide. In any event any coating which is formed upon the silicon-iron should be removed therefrom prior to the final anneal for secondary recrystallization, and will ordinarily be removed before any subsequent cold rolling. Any glass left by the use of the mixture of the present invention is characterized by less continuity and a lesser tend-

ency to adhere to the surfaces of the stock. The coating or annealing separator may contain additional substances which facilitate the removal of any film which is formed. In the practice of this invention any film which forms is easily removed by pickling, or abrasion.

Certain examples of the practice of the invention will now be given, it being understood that these are illustrative only and are not intended as limitations on the invention.

#### Example A

Silicon-iron containing 2.82% silicon, .071% manganese, .024% sulfur and .023% carbon was hot rolled to .110 inch in thickness and then subjected to an open anneal at 1675° F.

The hot rolled coil, 32 inches wide and weighing about 10,000 lbs., was then cold rolled to a thickness of .025 inch. It was decarburized in a strip or continuous anneal at about 1500° F. in wet hydrogen until the total carbon content was no greater than about .006% and preferably less than .003%. Next, the stock was coated with a mixture of magnesia containing 4% by weight of calcium oxide. The mixture was formed into a slurry with water, brought to a uniform thickness on the surfaces of the sheet stock by means of rubber rolls, and then dried by passing the stock through a continuous oven.

After the annealing separator had dried on the surfaces of the stock, the stock was coiled and box-annealed for 30 hours at 2200° F. in dry hydrogen having an inlet dew point of -25° F. or less. In this treatment the sulfur was brought down to a level of 3 p.p.m. in the stock.

The stock was then pickled and cold rolled to .011 inch in thickness. After being coated with alumina as an annealing separator, the stock was recoiled and box-annealed for 24 hours at a temperature of 2200° F. During the heat-up a primary recrystallization was effected in the material after which and at the high temperature set forth, secondary recrystallization by surface energy occurred. The final box-annealing was carried on under the conditions described in Patent No. 3,130,095 above mentioned; and the final product contained more than 90% of grains having the cubic texture.

#### Example B

Another silicon-iron material containing 2.94% silicon, .049% manganese, .023% sulfur and .024% carbon was hot rolled to a thickness of .090 inch and open annealed at 1675° F. After pickling it was cold rolled to a thickness of .025 inch.

It was decarburized in an open anneal at a temperature of about 1500° F. in wet hydrogen, having a dew point of about 100° F. It was thereupon coated with a slurry of annealing separator containing about 6% calcium oxide the balance being magnesia. The coating was dried and the strip was coiled.

The strip was box annealed at 2200° F. in dry hydrogen (dew point of -25° F.) and for 30 hours at temperature. This resulted in a total sulfur content in the silicon-iron of not greater than 2.5 p.p.m.

The desulfurized material was pickled, cold rolled to .011 inch, coated with alumina as an annealing separator and coiled, whereupon it was box-annealed at 2200° F. for 24 hours in an atmosphere containing not over about 250 p.p.m. of hydrogen sulfide. This material also had cubic texture grains occupying more than 90% of its volume.

The conditions under which the final anneal is conducted are well known and are not a part of this invention. For example, the temperature may vary from about 1900° F. to 2300° F. and the time may be more or less than 24 hours. Also, the sulfur catalyst may be derived from many known sources.

Although the process of the invention has found particular utility in the manufacture of silicon-iron having a final cube-on-face texture, it will be understood that the magnesia and calcium oxide mixture may be useful in

reducing the sulfur content of any ferrous material to very low levels.

By silicon-iron is meant a material containing from about 2.5 to 4.0% silicon, an initial carbon content of not more than .040%, an initial sulfur content of not more than about .030%, manganese in the range of about .02 to about .10% and oxide inclusions not over about .0035%, the balance being iron with such impurities as are usual in the manufacture of silicon-iron in the basic open hearth furnace, electric furnace, or the various oxygen blowing processes.

Modifications may be made in this invention without departing from the spirit of it.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An inorganic coating for desulfurizing ferrous materials consisting essentially of substantially non-hydrating magnesium oxide and from about 2% to about 10% of calcium oxide by weight, said coating being readily removable after an annealing treatment.

2. An inorganic coating for desulfurizing ferrous materials consisting essentially of substantially non-hydrating magnesium oxide and from about 4% to about 6% of calcium oxide by weight, said coating being readily removable after an annealing treatment.

3. A method of desulfurizing a ferrous metal comprising the steps of, applying a coating consisting essentially of a substantially non-hydrating magnesium oxide and from about 2% to about 10% of calcium oxide by weight, annealing said metal at a temperature of about 2000° F. to 2300° F. in a dry hydrogen bearing atmosphere while the surfaces of said metal are covered with said coating,

and removing said coating from the surface of said metal.

4. A method of making cube-on-face textured silicon-iron stock which comprises the steps of hot rolling silicon-iron stock containing substantially 2.5 to 4% silicon to an intermediate gauge, cold rolling the said stock to a thickness heavier than the desired final gauge, subjecting said stock to a decarburizing treatment, coating the stock with an inorganic coating consisting essentially of a substantially non-hydrating magnesium oxide and about 2% to about 10% of calcium oxide by weight and annealing the stock for several hours at a temperature of 2000° F. to 2300° F. in a dry hydrogen-bearing atmosphere so as to reduce the sulfur content of said stock to a value not over about 6 p.p.m., removing said coating, cold rolling the stock to final gauge, and subjecting the stock to a surface energy secondary recrystallization.

#### References Cited

##### UNITED STATES PATENTS

|    |           |         |                    |         |
|----|-----------|---------|--------------------|---------|
| 20 | 1,869,025 | 7/1932  | Seastone.          |         |
|    | 2,394,047 | 2/1946  | Else et al. ....   | 148—110 |
|    | 3,212,942 | 10/1965 | Takahashi .....    | 148—112 |
|    | 3,278,348 | 19/1966 | Foster et al. .... | 148—110 |

##### FOREIGN PATENTS

570,532 2/1959 Canada.

HYLAND BIZOT, *Primary Examiner*.

30 DAVID L. RECK, *Examiner*.

N. F. MARKVA, P. WEINSTEIN, *Assistant Examiners*.