USE OF SILICON STEEL ALLOY HAVING A CRITICAL SULFUR RANGE TO INSURE CUBE-ON-FACE ORIENTATION

Fig. 1.

A - CUBE ON EDGE OR SINGLE ORIENTATION
B - CUBE ON FACE OR DOUBLE ORIENTATION

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

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Fig. 6.
USE OF SILICON STEEL ALLOY HAVING A CRITICAL SULFUR RANGE TO INSURE CUBE-ON-FACE ORIENTATION

Fig. 7.

Fig. 8.

Fig. 9.
ELIMINATION OF SULFUR FROM 12 MIL THICK SHEET AT 1200°C IN VACUUM
Fig. II.

PERCENT CUBE GROWTH AS A FUNCTION OF SULPHUR CONTENT

PERCENT CUBE GROWTH

ANEALING TEMPERATURE -1200°C

H₂ ATMOSPHERE

100 90 80 70 60 50 40 30 20 10 0

PERCENT CUBE GROWTH
Fig. 12.

HOT ROLL INGOT TO STRIP 40 TO 150 MILS THICK

ANNEAL 700°C TO 1100°C NON-OXIDIZING ATMOSPHERE

COLD ROLL STRIP TO 5 TO 20 MILS (IN ONE OR MORE STAGES)

INTERMEDIATE ANNEAL AT TEMPERATURE UP TO 1300°C BETWEEN COLD ROLLING STAGES (IF MORE THAN ONE COLD ROLLING STAGE EMPLOYED)

FINAL ANNEAL 1100°C TO 1400°C SULFUR CONTENT 0.00003 TO 0.00006% OXYGEN CONTENT UP TO 0.0035 %

Fig. 13.
USE OF SILICON STEEL ALLOY HAVING A CRITICAL SULFUR RANGE TO INSURE CUBE-ON-FACE ORIENTATION


Filed Oct. 21, 1964, Ser. No. 405,562

11 Claims. (Cl. 140--112)

This application is a continuation-in-part of application Serial No. 154,803, filed November 24, 1961, which was itself a continuation-in-part of application Serial No. 85,432, filed January 27, 1961, and both are now abandoned.

This invention relates to double oriented iron-silicon magnetic alloy sheets and to processes for producing double oriented magnetic sheet material from the alloys. Magnetic sheets of iron-silicon alloys have been produced heretofore wherein the texture is such that the grains have a preferred orientation in only one direction, usually the direction of rolling. This grain texture is of the "cube-on-edge" type, or, as it is designated in Miller Indices, the (110) [001] orientation. As is well known to those skilled in the art, the permeability and other magnetic properties of alloys so oriented are outstanding in the rolling direction, or the (100) direction, which is parallel to the cube edges, since this is the direction of easiest magnetization of the grains of iron and iron alloys. However, in any other direction, as, for example, the transverse direction of the sheet, the magnetic properties are greatly inferior because the magnetization is not parallel to the cube edges of the crystal.

Single oriented magnetic sheets of the type described in the previous paragraph have achieved great commercial success and magnetic cores made therefrom are sold under the trade name "Hipersil." A wide variety of transformer cores for various applications made from single oriented iron-silicon alloy sheet material are presently available.

It has long been the goal of metallurgists in the field to produce double oriented iron-silicon sheets in which the grains have the cube-on-face orientation, or "cube" texture, which is designated as the (100) [001] type in Miller Indices. If sheets of a cube-on-face or double oriented grain texture were available so that a high proportion of the volume of the sheet comprised grains having their cube faces in the plane of the sheets with cube edges parallel both to the rolling direction and to the cross-wise direction of the sheet, the magnetic properties of the sheet would be outstanding both in the rolling direction of the sheet and in the transverse direction of the sheet.

Some success has been obtained previously in producing iron-silicon magnetic sheets in thin gauges of from 1 to 4 mils having a major proportion of cube texture grains, by secondary recrystallization annealing. Despite the great desirability and advantages of the (100) [001] texture material, a reliable, commercially acceptable process for the consistent development of a high volume of cube texture in relatively thick sheets of 8 mils and greater thicknesses of iron-silicon alloys has so far eluded the efforts of numerous skilled metallurgists.

The difficulties besetting the path of investigators have been most perplexing. For example, it has been recognized for some time that cube oriented steel may be obtained by a secondary recrystallization process which has as its basis an increase in the grain growth driving force for selected crystal nuclei based on surface energy. For that reason, much attention has been devoted to the surface condition of the sheets being treated. However, it has often been observed that even when exceptional steps are taken to insure a good surface condition, such as electro-polishing of the sheets before and during annealing; when the annealing atmosphere is such as to give a clean bright surface as by use of hydrogen of a low dew point of --50 °C. or lower, or a high vacuum which causes all surface films to disappear, cube grain growth may not occur at all or at most it amounts to just a few percent of the sheet volume. Thus, it is concluded that while the above conditions relative to the sheet surfaces are necessary to the production of highly cube oriented steels, they are not sufficient to insure a successful process for commercial use.

Also, the known processes for producing cube texture material have not received commercial acceptance because these processes tend to be expensive as a result of the multiple handling and treatments required, and because the processes often depart from recognized commercial practices in the art and require excessive care in their execution. Furthermore, and even more basically, the known processes are not sufficiently reliable in giving reproducible results in that they fail to yield a consistently high volume of cube texture in the sheet product. Another difficulty which has arisen with certain of the prior art processes is that due to the plurality of reduction passes required, and to the severity of each reduction step (often 60% to 80% reduction), the final cube texture sheet material obtained is necessarily thin, generally below 5 mils in thickness. The great volume of magnetic sheet used in the electrical industry is above 10 mils in thickness.

One process for producing double oriented iron-silicon magnetic material is disclosed in U.S. Patent No. 3,078,198, issued February 19, 1963, to G. W. Wiener, entitled "Process for Producing Oriented Silicon Steel." This patent discloses a cyclic treatment involving cleaning and reannealing of the magnetic strip. The cleaning in this case means etching or electrolytic polishing of the surface of the specimen between repeated annealing treatments. It will be appreciated that, while this is reasonably effective in producing a high volumetric percentage of cube texture, the process is inherently costly. Even so, there are cases where it will not produce cube texture exceeding 60% of the sheet volume.

Another method for developing the cube texture comprises cold rolling and annealing a grain-oriented ingot or a slab cut therefrom, in which ingot columnar grains are produced to have a preferred orientation with a cube direction essentially parallel with the columnar axis. Such grain-oriented ingots are obtained by slow and careful unidirectional solidification of the ingot metal in a specially designed ingot mold, to which precisely controllable heating and cooling devices have been attached. This process is more of a laboratory than a commercial technique.

It is clear that the above processes require special complex treatment, and critically controlled conditions.
It has now been discovered that there are certain interrelated critical factors influencing the formation of double oriented or cube texture in iron-silicon magnetic alloys, these being the influence of:

1. Composition, including the amount and distribution of inclusions, and the sulfur and oxygen content.
2. Surface energy conditions, including the influence of impurities.
3. Rolling schedule, including severity of working and rolling temperature.
4. Annealing conditions, including the time, temperature, and atmosphere.

Previous lack of understanding of the complex interrelationships of the above factors has resulted in complex processes, low yield of double oriented material, and variability of the quality of the product produced not only from lot to lot, but in sheets of the same batch.

One of the problems involved in attaining the desired tube texture grain growth is the establishment of a sulfur content within a critical range in the sheet alloy during the secondary recrystallization phase of the final anneal. It has been discovered that conventional analytical techniques have been erratic and often in serious error in indicating the actual sulfur content when present in amounts below 0.0015% of the sheet alloy. We have also discovered that it is approximately at the level at which previous analytical techniques failed that the critical sulfur content occurs. Due to the inability to accurately measure sulfur content at these low levels, the process was not amenable to control, and cube texture secondary grain growth was often defeated by reason of the presence of either no significant amounts or excess sulfur in the previously unmeasurable small quantities. To achieve control of the process, new analytical techniques have been developed for determining the sulfur content relatively accurately down to amounts of as low as 0.00001% by weight, and even less.

Based on these new analytical techniques, it was found that the values for sulfur content set forth in the parent application Serial No. 85,432 were unreliable in the lower ranges and subsequently application Serial No. 154,803 was filed to set forth the more correct sulfur data necessary to the satisfactory practice of the invention.

The object of the present invention is to provide iron-silicon alloys having a critically controlled composition uniquely suitable for consistently producing, by commercially acceptable processes, magnetic sheets having a high volume fraction of cube-on-face or double oriented grain texture.

Another object of the invention is to provide a process for producing predominantly cube-on-face or double oriented grain texture magnetic sheets of a thickness of up to 30 mils from an iron-silicon alloy having critically controlled sulfur content and a low oxygen content, by suitable commercially acceptable rolling and annealing steps resulting in substantially complete secondary recrystallization in the sheets.

Still further objects of the invention is to provide a process including the step of melting and processing an iron-silicon alloy so as to maintain the sulfur content within a critical range at the time secondary recrystallization occurs, and to reduce the oxygen content of the alloy in the sheets of the final gauge to an extremely low level which alloy lends itself in a highly favorable manner to the production of cube texture magnetic sheets by rolling and annealing under specified easily maintained conditions.

Other objects of the invention will in part be obvious and will in part, appear hereinafter. For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawings in which:

FIGURE 1 is a schematic view in perspective illustrating the grain orientations discussed herein;
FIG. 2 is a plan view of a ring magnetic lamination;
FIG. 3 is a plan view of laminated punchings made from a sheet;
FIG. 4 is a plan view of an L punching;
FIG. 5 is a plan view of an E punching;
FIG. 6 is a schematic showing of one method of melting the alloy of this invention;
FIG. 7 is a graph in which percent cube texture is plotted against annealing time in hours for alloys containing various amounts of oxygen;
FIG. 8 is a graph of percent cube texture plotted against annealing time in hours for stacks of strips, each stack consisting of alloy strips containing the same amount of oxygen;
FIG. 9 is a graph of the rate of cube transformation plotted against the percent oxygen for strips annealed individually and for strips annealed in stacks;
FIG. 10 is a graph in which the sulfur content of strips annealed individually and in stacks is plotted against time in hours;
FIG. 11 is a graph in which the amount of cube texture in percent is plotted against weight percent of sulfur for a plurality of samples;
FIG. 12 is a graph in which the amount of cube texture is plotted against parts per million hydrogen sulfide in the atmosphere and weight percent sulfur in the steel; and
FIG. 13 is a flow diagram illustrating a process in accordance with the invention.

In the descriptive matter which follows below, a practical method for consistently obtaining cube texture sheets from an iron-silicon alloy of novel composition on a commercial scale, is fully set forth.

Referring to FIG. 1 of the drawing, there is illustrated a sheet of ferrous metal in which are schematically depicted a cube A which represents the crystal lattice form of a cube-on-edge or single oriented grain, and a cube B which represents the crystal lattice form of a cube-on-face or double oriented grain. The cube A, it will be noted, stands on one edge with respect to the plane of the rolled surface of the sheet. Four edges of the cube A are aligned parallel to the rolling direction of easiest magnetization of the grain is along the cube edge or [001] direction. Therefore, the direction of easiest magnetization of the sheet is essentially in the direction of rolling when it comprises predominantly grains oriented in the manner of cube A. It will be noted, however, that the magnetization in a cross-wise or transverse direction of the edge or rolling direction of the sheet proceeds along the face diagonal or [110] direction of cube A. As is well known, the [110] direction is much inferior magnetically to the [100] direction. Cube B, on the other hand, has four cube edges oriented in the direction of rolling and four cube edges oriented in the cross-wise direction, and best magnetic properties are obtained in both directions because the easiest direction of magnetization of the grains is in a direction parallel to these edges. Consequently, a sheet comprising all cube-on-face grains B will exhibit highest magnetic properties in both the direction of rolling and in direction transverse thereto.

The double oriented iron-silicon magnetic sheets of this invention can be employed to great advantage in electrical apparatus, such as motors, generators and transformers. As illustrated in FIG. 2 of the drawing, a stator lamination 10 for a motor or generator core may be provided from a sheet or strip of the double oriented sheet. The lamination 10 comprises slots 12 into which a winding may be applied, and teeth 14 which carry a high magnetic
flux. The back or peripheral portion 16 of the lamination carries magnetic flux in service. The arrows 18 indicate the two easiest directions of magnetization of the magnetic sheet. Therefore, the teeth 14 directly above arrows 18 will be readily magnetized to high flux densities while the periphery also carries magnetic flux easily.

As illustrated in FIG. 3, magnetic steel sectors 26 for use in large generators and motors, may be punched out of the large strip 20 so that the teeth 24 defining core slots 30 will be essentially parallel to the direction of rolling of the sheet and therefore nearly parallel to one of the directions 22 of the easiest magnetization, while the back 32 extends generally parallel to the other direction 24 of the easiest magnetization. Therefore, outstanding magnetic properties will be obtained during use of the magnetic sheet sectors 26.

As shown in FIG. 4, L-punchings 40 suitable for use in transformer cores are cut from a sheet so that one leg 42 is parallel to one easiest direction 46 of magnetization while the other leg 44 is parallel to the other easiest direction 48 of magnetization. Consequently, the L-punching will possess outstanding magnetic properties.

An E-punching 50 as shown in FIG. 5 suitable for use in transformer cores, is so cut from the double oriented sheet that the back 52 is parallel to the one easiest direction 60 of magnetization while the legs 54, 56 and 58, are parallel to one another but perpendicular to the E-punching 50. It will be apparent that lamination configurations and core structures other than those illustrated in FIGS. 2 to 5 may be prepared to obtain maximum benefit from the double oriented magnetic sheets of this invention.

Important discoveries have been made with respect to the composition of iron-silicon alloys which particularly favors the development of a predominantly (100) [101] or cube grain texture. The most critical factor in composition, hitherto unknown and unappreciated, is that a rigid control of the sulfur content within the critical range of 0.0003 to 0.0006 is indispensably necessary if a high volume proportion of grains having a (100) [001] orientation is to be obtained.

It is desirable that at least 70% of the volume of the sheet comprise cube texture grains, that is (100) [001] orientation, with the cube faces of such grains being parallel to the sheet surface within approximately 5°, and the cube edges being within 15° of the direction of rolling.

The phenomena of secondary cube grain growth during final anneal in silicon steel is dependent primarily on the sulfur content being within such critical range and only secondarily on the oxygen content. If the sulfur is outside of the range of 0.0003 to 0.0006 then secondary cube grain growth is virtually impossible. The lower the oxygen the more rapid is the cube grain growth. Oxygen content affects the rate at which the secondary cube grains will grow, though beyond a level of oxygen depending on the sheet thickness, in no event exceeding about 0.0035% oxygen for sheets thicker than 5 mils, the retarding effect of oxygen will be so great that cube grain growth is virtually impossible. In particular if a substantially continuous oxide film is present on the surface of a silicon steel sheet cube grains cannot grow inasmuch as the selective energy necessary for such growth is derived from the surface. Outside of the drastic deterring effects of relatively high levels of oxygen, sulfur is the controlling factor in growth of secondary (100) [001] grains in silicon steel. Expressed in another way, oxygen deters cube grain growth in direct proportion to the amount thereof, while sulfur must be present in the critical range of from 0.0003 to 0.0006 in order for cube grains to grow regardless of what the oxygen content is.

More specifically, with respect to the sulfur content of the alloy sheets before the final anneal, a minimum of 0.002% and preferably about 0.015% of sulfur is normally satisfactory in the sheets for commercially acceptable final annealing. Such relatively large amounts are necessary at this point because sulfur rapidly escapes from the sheets during the high temperatures of the final anneal in the usual furnace atmospheres so that when the secondary recrystallization begins the sulfur concentration is below a critical value before the bulk of the sheet has undergone transformation. A maximum of about 0.03% sulfur can be tolerated, but an excess quantity of sulfur in the magnetic steels which are the subject of this invention may prevent the desired secondary recrystallization; the critical sulfur content must be controlled through appropriate heat treatment and atmosphere. The minimum sulfur content of 0.002%, stated above, is the lowest which can usually be relied upon on a practical basis in annealing processes of a commercial type.

While the above indicated range of sulfur control in the sheets before they undergo final anneal has been found to be practical in that it results in cube texture grain growth, the actual critical sulfur content in the alloy sheets during the stage of secondary grain growth is far smaller and basically more important. Actually, the basic requirements with respect to sulfur is that it be present in a critical range of from about 0.00035% to 0.0006% at the time secondary growth begins and extending substantially throughout the secondary cube grain growth anneal. Under equilibrium conditions, in which there is no loss of sulfur, cube growth will occur and be sustained when the sulfur content is in this critical range. It has been observed that when the sulfur content in the sheet exceeds 0.0006%, or is less than about 0.00005%, during the secondary grain growth phase of the final anneal, cube-on-edge or (110) [011] texture tends to develop preferentially. This critical sulfur range is independent of sheet thickness.

Under most practical annealing conditions, sulfur loss occurs to such an extent that to maintain in the strip during the secondary recrystallization an effective amount of sulfur in the range of from about 0.00005% to 0.0006%, the practical lower sulfur limit in the cold rolled strip before anneal is 0.002%. Thus, for such conditions, by setting the lower limit of sulfur at a value of 0.002% we are, in effect, assuring that an effective amount of sulfur is present in the steel as the anneal proceeds. Under conditions in which the loss of sulfur is minimal, such as in stacks of very wide sheets (thirty-six inches or more), or where external additions of sulfur are made to the furnace atmosphere, sulfur content in the cold rolled strip below 0.002% are acceptable.

The oxygen content of the alloys which is of importance in the context of this invention is that oxygen which is in the form of small oxide inclusions essentially uniformly distributed throughout the magnetic sheet. After primary recrystallization some of these oxide inclusions are situated within the body of the crystal grains while others are located at the grain boundaries. The inclusions at the grain boundaries of the primary grains tend to "pin" or inhibit the growth of secondary grains during the transformation anneal. The higher the oxygen content, the greater the number of oxide inclusions, and the greater the danger that the process will fall short of complete secondary cube transformation. Therefore, the best practice is one that reduces the oxygen content to as low a level as is reasonably practical.

As is well known, a few gross inclusions of oxides may occur as the result of melting practice, entrapment of furnace refractory or for other reasons and thereby yield a high overall oxygen analysis, while the small inclusions have an oxygen content well within the required limits. Such large local concentration of oxides do not seriously affect the transformation to cube texture of the main
sheet and should be excluded in determining the oxygen content of the operative part of the invention. The thickness of the magnetic sheet affects the tolerance of the process to oxygen content. As a broad statement of this relationship, it may be said that the amount of oxygen which can be tolerated is roughly inversely proportional to the sheet thickness. This so-called "thickness effect" can be explained in a simplified manner as follows.

In a thick sheet of an alloy having a given oxygen content, there will be a certain number of inclusions per unit volume which tend to pin or restrain cube grain growth; i.e., act as a retarding force. In a thinner sheet having the same total number of inclusions per unit volume, the primary grains are smaller since their size is determined by the sheet thickness. Most of the driving force for secondary cube grain growth comes from the primary grains and is inversely related to the size of the primary grains. This driving force is decreased by the retarded growth of the primary grains, which is in turn determined by the number of such inclusions per unit volume. The net driving force necessary for cube grain growth can therefore exist with a higher inclusion or oxygen content in the thinner sheets where the grain size is smaller and the related driving force consequently greater.

The above discussion suggests that for each thickness of sheet there is a critical oxygen content above which the desired transformation will not occur or occur so slowly that it is impractical. As a practical matter essentially the same critical upper limit of oxygen content applies for the rather broad range of sheet thicknesses from 5 to 20 mils. Thus, it has been found that in magnetic sheets which, in accordance with usual commercial practices, either are stacked for a final anneal to effect secondary recrystallization, or coiled for the final annealing, the oxygen content of the iron-silicon alloy should not exceed 0.0035%, by weight, at the time the sheets begin to undergo the final anneal when the magnetic sheets have a thickness of 12 to 15 mils and that this critical level is also approximately correct for sheet thicknesses from above about 5 mils to 20 mils. For optimum rates of grain growth, the oxygen content of the sheets in this 5 to 20 mil range of thickness should not exceed about 0.0015% by weight.

For sheet thicknesses of less than 5 mils the tolerance for oxygen rises with decreasing thickness, so that sheets 2 or 3 mils thick will fully transform although containing two or three times the indicated critical upper limit of 0.0035% of oxygen for the thicker sheets.

In summary, a maximum oxygen content of 0.0035% by weight will permit the desired rapid secondary recrystallization cube growth to occur in stack or coil anneals in all commercial gauges of silicon-iron alloy sheets and this limit is particularly critical in sheets of from about 5 mils to 20 mils.

For magnetic sheets which are to be individually annealed, either as punching strips or a continuous strip, the permissible upper limit of oxygen content may be somewhat higher since a small amount of oxygen may be removed during final anneal, but in no case should the oxygen content exceed 0.005% by weight, at the time the final annealing is initiated. However, it is not usual commercial practice at present to anneal individually iron-silicon sheets to effect secondary recrystallization thereof.

It will be understood that the iron-silicon alloys having sulfur and oxygen contents within the critical amounts specified may be transformed to cube texture with appropriate processes which includes at least one cold rolling step to effect a total reduction of at least 30%, an intermediate anneal at a temperature up to 1300°C, if more than one cold rolling step is employed, and a final anneal at a temperature between 1100°C and 1400°C in a highly reducing atmosphere and for a sufficient time to effect substantially complete secondary recrystallization, providing certain annealing conditions are maintained as will be set forth. When a plurality of cold rolling steps are employed usually each stage of cold rolling will effect a reduction of at least 30%, smaller reductions may be employed but are not economical.

The following theory is set forth to explain the results obtained in practicing the invention. It has been recognized that the growth of grains having a particular crystal lattice orientation is basically determined by the relative driving energy available to promote the development of the desired orientation. Thus, it is known that the grain boundary energy conditions affect the preferential growth of grains having certain lattice orientations. More recently, it has been found that surface energy conditions are particularly important in the growth of cube-on-face grains. It has been established that impurities materially alter the surface energy conditions and thereby affect the growth of cube-on-face grains. It has been found that surface films which constitute impurities, drastically inhibit development of cube-on-face grain growth. However, it is hardly conceivable that the presence or absence of seemingly infinitesimally small amounts of sulfur and oxygen in the body of the alloy would have such a large effect upon the surface energy conditions controlling grain growth in magnetic alloy sheets. It is now established that the conditions for cube-on-face grain growth are critically determined by the presence of a few thousandths of 1% of oxygen, and in some cases, as the limit of oxygen tolerance of a particular strip sample is approached, a variation of several ten thousandths of 1% of oxygen is the difference between good cube-on-face grain growth and very little growth of such grains. The velocity of cube-on-face grain growth is reduced by the presence of small amounts of oxygen. The presence of sulfur in the effective amounts specified is fundamentally necessary to produce the transformation of the metal to the cube texture.

It is believed that the difference in surface energy which has been found to exist between the (100) planes and other crystallographic planes in iron-silicon sheets having the required low sulfur content is such as to make the (100) plane the lowest energy plane. However, during vacuum or hydrogen annealing of low oxygen alloy sheet it has been observed that the energy of the (100) plane was unstable, changing with time, with the result that growth of textures other than the cube texture may be favored, and cube texture growth ceases or even may retrogress. It now appears that the change in energy is due to a loss of sulfur from the alloy sheet. In the annealing furnace, with a hydrogen atmosphere or in vacuum, and the sheet entirely exposed to the furnace atmosphere, sulfur is removed from the surface of the steel at a surprisingly rapid rate, and, if the sulfur content is below 0.002% when the annealing treatment is begun, the sulfur content may be reduced in the course of the annealing treatment to substantially less than the critical value of about 0.00003%. However, in annealing tight stacks of sheets and coils the reaction rate is much decreased, and lower initial sulfur contents can be tolerated, and may in fact, be preferable. On the other hand, even if adequate sulfur is present, iron-silicon sheets of over 5 mils which contain above 0.0035% oxygen, when placed in stacks or coils, will not grow an appreciable amount of cube texture grains in any reasonably annealing time during the final anneal. The volumetric rate of cube texture grain growth decreases rapidly to approach zero as the oxygen content increases materially above 0.0035% for stack anneals, and at slightly above 0.005% oxygen the growth rate of cube-on-face grains approaches zero even for individually annealed sheets of the alloy.

Iron-silicon alloys of the following composition range have been successively converted, repeatedly and con-
sistantly, to an extremely high volume proportion of cube texture in accordance with this invention:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.001 to 0.1</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.02 to 0.20</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.2 to 7</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.001 to 0.015</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.0005 to 0.03</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0005 to 0.0035</td>
</tr>
<tr>
<td>Iron</td>
<td>Balance</td>
</tr>
</tbody>
</table>

All of the above analyses are in weight percent of the alloy immediately prior to final anneal. Sulfur is relatively fugitive and the quantity thereof in the sheets drops significantly during annealing, as will be detailed hereinafter. The sulfur and oxygen ranges described herein have been established to be absolutely necessary for stack or coil annealing of the silicon-Iron. It will be understood that both sulfur and oxygen may depart upwards from these necessary ranges during intermediate cold-rolling and annealing, for instance. Normally, in order to prevent loss of sulfur below the critical lower limit, sulfur may be introduced into the furnace atmosphere so as to maintain a high sulfur level at the sheet surface. For example, if the sulfur content of the sheet tends to be too low, it may be replenished or augmented by suitable additions, to the annealing atmosphere such as by adding some hydrogen sulfide. In some cases, the added sulfur may be introduced as a component of the refractory separator material between the sheets, the latter technique being set forth in detail in a pending patent application Serial No. 88,276, filed February 10, 1961, now Patent No. 3,157,900. Other means may be employed to supply sulfur to the area adjacent the sheet surface. Usually, any significant reduction of the oxygen content of the sheets, if the oxygen content is excessive, is not practical during the final anneal, particularly when the oxygen is present as inclusions within the body of the alloyed sheets. However, oxide films on the sheet surface can be removed by using a high vacuum or a very dry hydrogen of from about 50°C to 70°C dew point, for instance. For single sheets or extremely loose coils a slightly higher oxygen content may be tolerated, but in no event should the oxygen content exceed 0.005%.

It will be recognized that slight departures from the sulfur content may be made if the annealing conditions are changed by using either extremely tight stacks or coils or if the flow rate of hydrogen is very slow. Tight stacks or low hydrogen flow rate could result in a negligibly small rate of sulfur loss.

Some comment on certain of the other elements which are present in the alloys of this invention is in order at this point. The silicon content of these alloys may range from 2% to 7%, but it is preferred to hold the silicon content within the more restricted range of from 2.25% to 3.5%. The carbon content immediately prior to final anneal should be low; i.e., not exceeding 0.01% and preferably below 0.005%, which is consistent with present day good magnetic steel practice, to produce stable, low loss silicon steel sheets. The carbon content of the alloy ingot or slab may be as high as 0.05%, but the carbon content falls as the result of subsequent processing. The manganese may range upward to as much as 0.5%, but is usually held to no more than 0.2%. The amount of titanium and boron, elements considered detrimental in these alloys, will be below 0.005%, essentially the same as that present in alloys made in accordance with good commercial practice. For best results in these alloys, the aluminum content should not ordinarily exceed 0.006%, but may be present in amounts up to about 0.015%. Alloys containing aluminum in amounts of 0.02% or even 0.03% will undergo transformation, but other difficulties render such high aluminum content undesirable. Nitrogen should not exceed 0.01%.

Employing an iron-silicon ingot in the range of alloy compositions described above, relatively thick magnetic sheet having a high volume percentage of cube texture can be produced by the process described below and illustrated in the flow diagram of FIGURE 13:

1. Hot rolling the ingot to a strip of a thickness of the order of 40 to 150 mils,

2. Annealing the hot rolled strip in a nonoxidizing atmosphere at a temperature of from 700°C to 1100°C,

3. Reducing the thickness of the strip to a final gauge of between 5 and 20 mils by at least one cold rolling step,

4. Intermediate annealing the resultant sheet after each cold rolling step at a temperature up to 1300°C, and

5. Final annealing the sheet following the final cold rolling step at a temperature between 1100°C and 1400°C in a highly reducing atmosphere causing surface films to disappear, for a period of time sufficient to enable substantially complete secondary recrystallization of the grains.

The principal purposes of the various steps of the process outlined above may be summarized as follows:

(a) The hot rolling helps achieve a uniform microstructure in the strip and reduces the thickness of the strip to a convenient size for subsequent cold working,

(b) Annealing the hot rolled strip achieves any necessary recrystallization of the hot worked texture,

(c) Cold rolling further reduces the strip thickness and develops a preferred orientation texture in the sheet,

(d) Intermediate annealing of the cold rolled sheet reduces the sulfur content of the alloy sheet and further produces a texture which when cold rolled yields a high permeability product capable of sustaining the growth, under appropriate annealing conditions of grains having the (100) [001] orientation, and

(e) Final annealing promotes the growth by secondary recrystallization of grains having the (100) [001] orientation, large grains having the desired orientation thus supplanting grains having other orientations.

Broadly then, the invention resides in the discovery that cold rolled sheets of iron-silicon alloys having small amounts of sulfur and oxygen therein and comprising, by weight, from 2% to 7% silicon, up to 0.05% carbon, less than 0.015% aluminum and the balance iron except for small amounts of impurities, can be transformed to magnetic sheet having a high volumetric proportion of grains having a (100) [001] orientation by a process including the steps of finally annealing the cold-rolled sheet at a temperature between 1100°C and 1400°C in a reducing atmosphere which is capable of reducing the oxide films on the sheet surface and is further capable of maintaining the oxygen content of the sheet at a level not exceeding 0.0015%, by weight, and the sulfur content of the sheet between 0.00005% and 0.00006% by weight during secondary recrystallization, for a period of time to cause substantially complete secondary recrystallization of the sheet whereby at least 70% by volume of the sheet is composed of grains having the (100) [001] orientation.

More comprehensively, the invention relates to a process for providing a magnetic sheet having a high percentage by volume of cube texture grain structure, the steps comprising, (1) hot rolling to a strip having a thickness of the order of 40 to 150 mils a slab of an alloy composed, by weight, of from 2% to 7% of silicon, up to 0.05% carbon, not in excess of about 0.5% manganese, up to 0.01% nitrogen, not in excess of about 0.015% aluminum, the balance iron except for small amounts of impurities (2) annealing the hot rolled strip in a relatively non-oxidizing atmosphere at a temperature of from 700°C to 1100°C, and pickling the hot rolled strip to remove scale, (3) cold rolling the strip at least once to reduce the thickness thereof to a final gauge preferably between 5 and 20 mils, though thicker intermediate gauges may be produced, and subjecting the resultant strip after each cold rolling step to an intermediate anneal at a temperature up to 1300°C, if a plurality of cold
rolling steps are employed, and (4) subjecting the sheet, which should now have an oxygen content not exceeding 0.0035%, by weight, and a sulfur content from 0.002% to 0.03%, by weight, to a final stack anneal following the final cold rolling step at a temperature in the range from 1100°C to 1400°C, for a period of time sufficient to effect substantially complete secondary recrystallization of the grains in an atmosphere capable of causing surface films to disappear whereby at least 70% of the volume of the sheet comprises cube grains.

Because the oxygen content can be so critical in the production of double-oriented steel, a reliable method for determining oxygen content is necessary. The method chosen in this case is the vacuum fusion technique and all the analyses reported herein have been obtained in this way. The vacuum fusion method for the oxygen determination is capable of reproducibly converting substantially all oxygen normally found in silicon steels to carbon monoxide. The alloy sample is melted in a graphite crucible and then superheated to 1650°C, which is several hundred degrees above the melting point of carbon-saturated silicon iron, while under a high vacuum of less than a micron absolute pressure the carbon monoxide so evolved is quantitatively converted to carbon dioxide and the latter gas is frozen out in a trap, and then the trap is heated to cause the carbon dioxide to volatilize and allowed to expand into a measuring device. The volume and pressure of the carbon dioxide are measured and the oxygen may be readily calculated therefrom.

Since the critical limit for oxygen content in the alloy sheets of commercial gauges of this invention is that it not exceed 0.0035%, and preferably be below 0.0015%, the melting procedure used to produce the alloy is extremely important. The lower the oxygen content of the iron-silicon ingot, the less difficulty in reaching a low level in the sheet at the time when it is undergoing the final anneal. Under ideal conditions, it is well known that the percent oxygen at 1600°C in equilibrium with SiO2 in silicon-iron containing 3% silicon is about 0.0035%. Such低碳 conditions are seldom attained in actual practice with the result that the oxygen present in the alloys produced is much higher. Standard open hearth practice yields an alloy containing so much oxygen that it cannot be materially reduced to lower values during subsequent hot rolling, annealing, and so on, and therefore the alloy cannot be consistently converted to cube texture.

Since the maximum oxygen specified for commercial use in the alloys of this invention is 0.0035% by weight, the open hearth is capable on some occasions of yielding a product which will barely meet the minimum requirements specified herein. A study of a number of open hearth heats have shown their oxygen content to range from 0.0033% to 0.01% oxygen. Only the heat having 0.0033% oxygen of those studied had an oxygen content low enough to enable successful double oriented iron-silicon sheets to be produced by the process of this invention.

Experience has shown that the oxygen content of the iron-silicon alloy in the ingot is not materially reduced during subsequent processing. For example, extensive annealing of open hearth alloy sheets having 0.005% oxygen content increases the oxygen content by 0.005% for times up to 50 hours is not sufficient to reduce the oxygen content to the required value. Therefore, it may be concluded that for commercial operation, where reproducible results are mandatory, the conventional open hearth practice must be modified, or other melting processes used, to produce ingots of the low oxygen iron-silicon alloy of this invention. Much success has been obtained by using a vacuum in melting.

In the vacuum process the melting is carried out in the absence of a silica-rich slag and this results in highly satisfactory low-oxygen content. Even with low carbon content, the iron-silicon alloy may be completely deoxidized by the following reaction:

$$\text{Si-O (oxygen dissolved in iron)} \rightarrow \text{SiO}$$

The vacuum causes rapid elimination of silicon monoxide from the molten metal.

In vacuum this reaction proceeds quantitatively and rapidly, and carbon is not required for the deoxidation reaction. Open hearth iron-silicon alloy is therefore suitable as a starting material for vacuum treatment in the production of the prod.-of double-oriented steel. Several manufacturing processes using vacuum may be employed for obtaining the desired low oxygen iron-silicon alloys. Among them are remelting using a vacuum consumable arc furnace, or vacuum induction melting, or vacuum degassing of the melt in the ladle, stream, or mold, or a double pouring operation in which the silica-rich slag is removed in the first stage while the atmosphere above the molten metal is replaced by an inert atmosphere.
into the deoxidation chamber 90, and when the liquid level in the ladle has reached a level such that a relatively thin layer of molten metal and substantially all the slag remain in the ladle, the stopper 84 is closed.

In order to show the effect of the oxygen content in the alloys to be processed in accordance with this invention, a variety of iron silicon alloys was selected, the analyses of the alloys being given below in Table I, at the stage of processing indicated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
<th>Total</th>
<th>Al</th>
<th>O</th>
<th>N</th>
<th>Source of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-4</td>
<td>0.007</td>
<td>0.019</td>
<td>0.005</td>
<td>3.11</td>
<td>0.048</td>
<td>0.009</td>
<td>0.008</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>8080</td>
<td>0.000</td>
<td>0.070</td>
<td>0.034</td>
<td>2.28</td>
<td>0.007</td>
<td>0.006</td>
<td>0.007</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>8064</td>
<td>0.000</td>
<td>0.085</td>
<td>0.019</td>
<td>3.19</td>
<td>0.072</td>
<td>0.003</td>
<td>0.028</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>7138</td>
<td>0.000</td>
<td>0.019</td>
<td>0.022</td>
<td>3.04</td>
<td>0.004</td>
<td>0.002</td>
<td>0.049</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>7128</td>
<td>0.000</td>
<td>0.019</td>
<td>0.022</td>
<td>3.18</td>
<td>0.004</td>
<td>0.002</td>
<td>0.029</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>7101</td>
<td>0.000</td>
<td>0.019</td>
<td>0.022</td>
<td>3.12</td>
<td>0.002</td>
<td>0.006</td>
<td>0.011</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>8103</td>
<td>0.010</td>
<td>0.065</td>
<td>0.006</td>
<td>2.76</td>
<td>0.019</td>
<td>0.006</td>
<td>0.001</td>
<td>Hot Band, Forged Slab.</td>
<td></td>
</tr>
<tr>
<td>8069</td>
<td>0.005</td>
<td>0.070</td>
<td>0.005</td>
<td>3.13</td>
<td>0.005</td>
<td>0.004</td>
<td>0.008</td>
<td>Cold Rolled Sheet.</td>
<td></td>
</tr>
</tbody>
</table>

In the alloys, iron formed the balance, except for incidental impurities. Analysis at the termination of the anneal indicated very little change in the composition, and in particular no significant change in the oxygen and sulfur content of the alloy was observed in the final cold rolled sheet prior to the final anneal.

The alloys listed in Table I were made according to the following melting practices.

BD-4—Prepared from pressed briquettes of electrolytic iron and 80 mesh low aluminum grade silicon powder. The briquettes were cylindrical sections which were welded together to form an electrode. The electrode thus formed was melted at a high rate in a vacuum arc furnace.

8080—Vacuum arc melt of a standard commercial grade open hearth heat.

8664—Selected open hearth ingot with specifically low oxygen content.

7128—Selected open hearth heat.

Acc-1—Open hearth heat.

7130—Vacuum induction melt to open hearth heat.

7130—Vacuum arc melt of open hearth ingot.

8103B.

Samples BD-4, 8080 had been forged into slabs to break up all ingot solidification structure. Samples 8664, 7128, 7130 and Acc-1 had been slabbed and processed according to usual steel mill practice.

The alloys of Table I were each processed in accordance with the following examples:

**EXAMPLE I**

Ingot BD-4 was forged to a slab and hot rolled at 1050°C to a band of a thickness of 0.050 inch. The hot rolled band was annealed for 2 hours at 1050°C in hydrogen and after annealing thoroughly pickled to remove all traces of scale. The band was then cold rolled in one stage to a sheet of 0.012 inch thickness. The cold rolled sheet was then finally annealed in vacuum of 10^-3 mm Hg at 1200°C for various times to produce a secondary recrystallized texture. The 0.012 inch sheet was given a final anneal, both as a single strip and stacked with dry aluminum oxide as a separator between several sheets to prevent sticking during the final anneal.

**EXAMPLE II**

Ingot 8080 a single vacuum remelt of a standard open hearth ingot was forged to a slab and hot rolled at 1050°C to a band of a thickness of 0.050 inch. The hot rolled band was annealed for two hours at 1050°C, pickled, and then cold rolled to a final gauge of 0.012 inch in one stage and then annealed according to the process outlined in Example I.

**EXAMPLE III**

The open hearth ingots 8664, 7128, and 7130 were slabbed on a slabbing mill and hot rolled to a band of 60 mils thickness. The bands were annealed at 1050°C for two hours in hydrogen, pickled and cold rolled in one step to 12 mil sheets. The cold rolled material was then annealed as described in Example I.

**EXAMPLE IV**

A part of open hearth ingot 7130 was remelted in a vacuum induction furnace, the remelted ingot being identified as 7130R. Ingot 7130R was hot rolled at 1000°C to a band 0.050 inch thick. The hot rolled band was annealed at 1050°C for two hours in hydrogen and pickled. The band was cold rolled in one stage to a final gauge of 0.012 inch thickness. The cold rolled sheet was annealed at 1200°C in a vacuum of below 10^-3 mm. Hg pieces thereof being stacked together with dry aluminum oxide as a separator to prevent sticking.

**EXAMPLE V**

Ingot 8103 was forced to a slab and hot rolled following a commercial steel mill practice to a thickness of 135 mils. The hot rolled strip was pickled and open annealed 7 minutes at 950°C in hydrogen. The strip was then cold rolled to 50 mils, recrystallized for 20 minutes at 840°C in wet hydrogen and heat treated (intermediate anneal) 10 hours at 1200°C in dry hydrogen (—50°C dew point). The annealed 50 mil sheet was pickled and cold rolled to 12 mils. The cold rolled strip was then cut into sheets and they were annealed as single strips for 15 hours at a temperature of 1200°C in a vacuum of below 10^-3 mm Hg.

The alloy samples designated 8103B were treated at 8103 above except that the intermediate anneal or heat treatment was carried out for one hour at 1100°C.

**EXAMPLE VI**

Alloy Acc-1 was slab rolled and hot rolled to 0.150 inch. The band was open annealed at 900°C and their cold rolled to 0.050 inch. At this stage it was box annealed for 100 hours at 1200°C in a dry hydrogen (—50°C dew point) atmosphere. It was then cold rolled to 0.012 inch. Samples were annealed as in Example I.

In Table II is listed, for the various alloys of Table I processed as described in the above examples, the volume percent of transformation to cube texture at selected times of anneal. Table II refers only to the steels annealed as a single strip. For convenience the oxygen content is given in parenthesis next to each sample. The rate of transformation clearly decreases with increasing oxygen content. The criticality of the 0.0035% oxygen limit is quite apparent.
Table II—Volume percent cube texture in single strip annealing

<table>
<thead>
<tr>
<th>Sample</th>
<th>O₂</th>
<th>1 Hr.</th>
<th>8 Hrs.</th>
<th>14 Hrs.</th>
<th>20 Hrs.</th>
<th>30 Hrs.</th>
<th>40 Hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-4</td>
<td>.0009</td>
<td>71</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>8800</td>
<td>.0009</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>8644</td>
<td>.0044</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>AcF-3</td>
<td>.0027</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>7128</td>
<td>.0005</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>81033</td>
<td>.0035</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>AcS-6</td>
<td>.0001</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>7128</td>
<td>.0001</td>
<td>71</td>
<td>95</td>
<td>85</td>
<td>65</td>
<td>45</td>
<td>25</td>
</tr>
</tbody>
</table>

In Table III is listed the volume percent of transformation for the alloys when annealed in a stacked condition with aluminum oxide as a separator.

Table III—Volume percent cube texture in stack anneals

<table>
<thead>
<tr>
<th>Sample</th>
<th>O₂</th>
<th>1 Hr.</th>
<th>4 Hrs.</th>
<th>8 Hrs.</th>
<th>30 Hrs.</th>
<th>40 Hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-4</td>
<td>.0009</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>8800</td>
<td>.0009</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>8644</td>
<td>.0044</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>AcF-3</td>
<td>.0027</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>7128</td>
<td>.0005</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>81033</td>
<td>.0035</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>AcS-6</td>
<td>.0001</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>7128</td>
<td>.0001</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

It is of importance to understand in interpreting the data of Tables II and III that, since the effect of varying the oxygen content of the alloys was under study, it was necessary to prevent the sulfur content of the samples from dropping below a value of about 0.00003% weight percent during annealing. Thus, the annealing stage was carried out in an iron-base alloy tube that had a substantial proportion of sulfur in the composition thereof. At the elevated temperatures employed, sulfur from the furnace tube maintained a level of sulfur in the environment sufficient to prevent the sulfur content of the samples from dropping below the critical value.

From both Tables II and III, it will be noted that the oxygen content is very critically related to the volume percent of cube texture grain growth, and that the best results both in rapidity of cube texture growth and total volume of cube texture grains, are secured in the lowest oxygen content samples. Furthermore, when the oxygen content materially exceeded 0.0033% no significant transformation could be obtained in stacked annealed samples, and when materially above 0.0041% no significant transformation could be observed even in single strip annealed samples.

The alloys of Table I have also been as successfully annealed in dry hydrogen as in a vacuum. For example, alloys BD-4 and 8808 will transform nearly completely to cube texture after 24 hours at 1200 °C. in a hydrogen atmosphere of 60 °C. dew point. Generally for pure hydrogen anneals the oxygen content, both as O₂ and H₂O in the hydrogen must be held below 0.002% by volume thereof.

The above examples are illustrative, but not limiting, of both the melting methods and the processing techniques which may be successfully followed. It will be recognized that other vacuum or inert atmosphere treatments will be suitable for obtaining a low oxygen iron-silicon alloy. It will be understood that the subsequent processing of the alloy should be directed to maintaining therein a low oxygen content, and preferably in the direction of reducing the oxygen content if it is at the higher permissible levels. Thus care should be had not to employ excessively long wet hydrogen anneals, which anneals in conventional iron-silicon reductions, since such anneals introduce oxygen into the sheets.

The critical effect of the oxygen content on the cube texture secondary grain growth for thick sheet of the iron-silicon alloys of this invention is dramatically illustrated by the curves shown in FIGS. 7, 8 and 9. The data from which FIG. 7 was plotted were obtained from annealing tests of single strips of 12 mils thickness of silicon iron strips, each of the strips were carefully encapsulated in a jacket of the same composition steel so that the strip is essentially in equilibrium with its environment. The annealing temperature was 1200 °C. The sample contained oxygen about 0.0033% and so rapidly a transformation to cube texture that more than 50% by volume of sample was transformed to cube texture in one hour. The transformation is essentially linear so that 100% would be attained in 2 hours. In the sample containing 0.0033% oxygen, the rate of transformation is considerably reduced so that only about 80% of the volume transformed in the first hour, but, even so, over 80% of the volume was transformed to the cube texture in four hours. On the other hand, the sample containing 0.0042% oxygen exhibits so sharply reduced a rate of transformation that only about 15% of the volume was cube texture after four hours annealing. The sample containing 0.0059% oxygen showed no appreciable cube texture growth, and substantially no transformation was evident after four hours of annealing.

FIG. 8 is a graph derived from data obtained in tests based on a process which closely approximates the presently employed commercial process for production of magnetic steels, in that the allloy sheets are arranged in stacks containing from 3 to 5 strips separated by calcined alumina to prevent welding of the strips. The annealing was carried out at 1200 °C. in a vacuum of 10⁻⁸ mm. Hg. As a result of this treatment the strips in the stack composed of alloy having 0.001% oxygen transformed on the average, to an extent greater than 60% by volume of cube grain texture in eight hours. The alloy sheets containing 0.0033% oxygen required 30 hours to transform to the same extent. The stack containing strips composed of alloy having 0.0042% oxygen and 0.0059% oxygen, respectively, both failed to transform above 5% by volume in 30 hours. These last two would not warrant consideration for commercial purposes.

FIG. 9 is of particular interest in that it shows the effect of oxygen content on the rate of secondary cube texture grain growth both for individually annealed samples and for stack annealed samples. The curves show the fraction of the volume of the sheets that transforms to cube-on-face grains at 1200 °C. per hour in a vacuum at 10⁻⁸ mm. Hg. For higher annealing temperatures the rate curves pivot at the zero axis, being steeper at higher temperatures. The rate of change of cube grain growth decreases more rapidly for the individually annealed samples.

FIG. 9 perhaps explains to some extent why, in the past, laboratory test results, which usually are derived from experiments with single sheets in a metal capsule, have not been reproduced when applied in the stack anneal processes in pilot plant or commercial scale annealing of magnetic steels, in efforts to obtain double oriented material. In fact, the erratic, and usually much inferior results obtained in pilot plant runs had been puzzling and disconcerting. Nevertheless, curve II, for the stack annealing, shows that if the oxygen content is sufficiently low, the rate of cube grain growth transformation is such as to bring desirable results close to the point of commercial feasibility.

One difficulty which was met and overcome in defining the critical sulfur range, was the progressively greater inadequacy of the conventional methods for determining sulfur content as the amount of sulfur involved falls below 0.0015%. With the conventional analytical methods relying on consistent precision or interpretation of results in terms of sulfur content at these low levels proved almost impossible. Therefore, an entirely new analytical method of extremely high reliability and capable of measuring sulfur contents in parts per million, and even in tenths of a part per million, was devised. Briefly, the analysis for sulfur in accordance with this new method the ("Methylene Blue") method involves
the following procedure: The sample to be tested is dissolved in hydrochloric acid and the hydrogen sulfide produced then is distilled under non-oxidizing conditions. The distilled hydrogen sulfide is absorbed in zinc acetate and an indicator, methylene blue, is added to develop the color. The intensity of the color is then measured by means of a spectrophotometer and compared to a standard curve. The accuracy of the method was verified by radioactive tracer techniques.

With this improved analytical technique, the upper limit of the critical sulfur range was determined with high accuracy. A plurality of alloy samples having an oxygen analysis of 0.0015% and an initial sulfur analysis of 0.01% were finally annealed at 1200°F in a dry hydrogen atmosphere capable of depleting the sulfur content of the alloy sample. At intervals during the anneal, samples were removed from the furnace and examined for the amount of cube texture and then analyzed for the sulfur content. The results of this experiment are plotted in FIGURE 11, in which it is clear that transformation to cube texture is not initiated in alloy samples having more than 0.0006% sulfur.

A careful study was made of alloys having low oxygen content and varying amounts of sulfur therein, under conditions in which no special effort was made to prevent the loss of sulfur which ordinarily occurs in the usual annealing furnace atmosphere. In Table IV below, the carbon, sulfur, and oxygen analyses of certain of the alloys of Table I are shown, after the first anneal and the cold rolling stage or stages has been carried out. The intermediate treatments of the samples are the same as that previously described. The amount of other elements in the alloys is not affected by the treatment and the values for those elements given in Table I are essentially correct.

Table IV.—Chemical composition of alloys (in part) weight percent

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>S80</td>
<td>0.027</td>
<td>0.019</td>
<td>0.009</td>
</tr>
<tr>
<td>S83</td>
<td>0.022</td>
<td>0.009</td>
<td>0.005</td>
</tr>
<tr>
<td>BD-4</td>
<td>0.01</td>
<td>0.009</td>
<td>0.001</td>
</tr>
</tbody>
</table>

1 Verified by Methylene Blue method.

The oxygen content of the alloys of the table are clearly at a satisfactorily low level for transformation to cube texture. However, when sample BD-4, with 0.0006% sulfur at the start was anneal as a single sheet, less than 50% by volume of the sheet transformed to cube texture. On the other hand, sample S80, with 0.019 sulfur to start, transformed to 90% by volume cube texture on final annealing as a single sheet.

The samples of Table IV were also finally annealed in stacks of several superimposed sheets with Al2O3 separator in a dry hydrogen (—60°C. dew point) or vacuum atmosphere (less than 1 micron) at 1200°F. For from 17 to 24 hours. Results are presented in the following table:

Table V.—Relationship of cube texture to sulfur content

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Percent S</th>
<th>Hydrogen Annealed Percent Cube</th>
<th>Vacuum Annealed Percent Cube</th>
</tr>
</thead>
<tbody>
<tr>
<td>S80</td>
<td>0.019</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>S83</td>
<td>0.009</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>BD-4</td>
<td>0.009</td>
<td>50-90</td>
<td>90</td>
</tr>
</tbody>
</table>

This indicates that the sulfur content necessary in the sheets is determined by the annealing conditions and should be sufficient to compensate for losses during annealing. It is thus seen that sufficient initial amount is required to yield a product having the critical sulfur content during the secondary recrystallization phases of the anneal which reliably causes growth of cube texture comprising at least 70% by volume of cube grains having the cube plane within 5° of the rolling plane. The degree of transformation to cube texture accordingly depends largely on the amount of sulfur initially in the sheet prior to final anneal. A high, but not excessive, initial sulfur content insures that sufficient sulfur will be present in the sheet throughout the course of the annealing period so that interruption of the process of transformation will not occur.

From a comparison of results obtained with sample BD-4 under the conditions of Tables II and III, and under the conditions of Table V, it may be stated that insofar as sulfur is concerned the composition of this particular sample is borderline, if complete transformation to cube texture is the objective. If the atmosphere of the annealing furnace is such that conditions approaching equilibrium as to sulfur are established, a high volume percentage of cube texture grains can be obtained, but, in processes of the commercial type, in which equilibrium conditions do not prevail, and the close control necessary to establish such conditions is not practical, the transformation performance of alloys with such a low sulfur content will be highly variable and may provide no more than 50% by volume of cube texture grains or even less.

In FIG. 10 graphically illustrated are the non-equilibrium conditions prevailing in the 1200°F. anneal of sulfur-containing iron-silicon alloys in the form of sheet, and the rapid rate of removal of sulfur from the alloy. The curves demonstrate that the rate of removal of sulfur depends to a substantial extent upon whether the anneal is carried out on a single sheet or on stacked sheets, with the single sheet anneal reducing the sulfur content more drastically.

In a further experiment, stacks of alloy sheets having sulfur contents substantially above the critical maximum of 0.0006% and being otherwise suitable for transformation to cube texture were annealed to produce secondary recrystallization. After annealing one such stack for four hours the stack was removed from the furnace and was analyzed and examined for cube grains. The individual sheets of the stack had sulfur contents ranging from 0.0003% to 0.00007% and partial transformation to cube texture had taken place in the sheets to an extent ranging from 20% to 40% by volume. Thus, one sheet in the stack contained 0.00015% by weight of sulfur and had 35% by volume of cube grains. The stack was then replaced in the furnace and annealed for an additional 16 hours. The individual sheets of the stack, one at a time, and anneal ranged from 0.00015% to 0.00002% by weight of sulfur and were composed of 100% by volume of cube texture grains. One of these sheets analyzed 0.00008% by weight of sulfur and was 100% transformed to cube texture grains. It will be understood that depletion of sulfur may continue after the cube texture is fully established.

The accuracy of the sulfur limits set forth herein has been generally confirmed by the work of others in which it was shown that in hydrogen sulfide atmospheres cube growth in steel occurs in a certain range of partial pressures of hydrogen sulfide, and that the partial pressures of hydrogen sulfide can be related to the sulfur content of the steel. These data are presented graphically in FIGURE 12 in which it is seen that, in these experiments, the range of sulfur contents in which cube growth occurs to a substantial degree extends from below 0.0001 to about 0.0006%.

While a single sheet may be individually annealed, normal commercial practice will dictate that an assembly for anneal be made either in coil form or from a plurality of stacked sheets. There should be interposed between the surfaces of the sheets in such assembly, a layer of an inert inorganic refractory material to prevent welding of the sheets and to allow escape of gases from
the metal and to allow the selected annealing atmospheric gases to penetrate to all the surfaces. The inert inorganic refractory may comprise a coating of fine powder sifted or otherwise applied to the surface of each sheet of the assembly. A finely divided powder such as Examples, aluminum oxide, zirconium oxide, or high purity hydrous magnesia will give good results. The refractory should be treated, as for example, by calcining at high temperature so that during annealing it will not evolve any moisture, oxygen, or other deleterious materials such as carbon dioxide or the like. Good results have been obtained by using as a sheet separator 200 to 350 mesh alumina that has been calcined or fired at 1000° C. to 1400° C. and then stored in a sealed container until ready for use.

For the final anneal, the assembly or stack of cold reduced sheets is placed in the annealing furnace and a non-carburizing atmosphere is provided which is substantially completely free from water, oxygen, or other oxidizing components, such that the sheet will not be oxidized during annealing, but rather will cause any surface oxides to be rapidly removed or to disappear. Silicon dioxide will be the main oxide on the sheet surfaces and at annealing temperatures of from 1100° C. to 1400° C. dry hydrogen or a high vacuum should be applied which will favor the reaction of the silicon dioxide with silicon in the sheet to form silicon monoxide which will evaporate from the surfaces. Cube-on-face grains will grow by secondary recrystallization in preference to other grain textures only if the surface is free from any substantial continuous films. In practice, the furnace may be flushed continually by passing a stream of very dry, high purity hydrogen therethrough. It has been found to be critical that the hydrogen have a dew point of below —60° C. or —70° C. at 1100° C. and below —40° C. at 1300° C. Good results have also been obtained with a vacuum atmosphere sufficient to maintain a uniformly bright surface. A vacuum of at least 10⁻¹ mm. of mercury is suitable at 1300° C., while a vacuum of the order of 10⁻⁴ mm. is preferred at 1100° C., though obviously, higher vacua may be employed. In general, a vacuum of 50 microns, or 50·x10⁻⁶ mm. will be satisfactory in the indicated temperature range. Low pressures of hydrogen or an essentially oxygen free inert gas such as argon may be employed for annealing. The prime requirement is that the atmosphere should be such that it will cause silica to rapidly disappear from the surfaces of the sheets at the annealing temperatures. Under these necessary conditions, the sheets will soon obtain a bright metallic surface free of continuous films.

Annealing should be carried out at a temperature of from 1100° C. to 1400° C. for a sufficient period of time at temperature to produce substantially complete secondary recrystallization. As is well known, primary recrystallization takes place rapidly in the initial phases depending on the amount of previous cold working and the temperature, such that it may be effected in most cases at temperatures of as low as 600° C. to 1000° C., but secondary recrystallization requires a far longer time at higher temperatures. At 1100° C. and higher secondary recrystallization may begin before completion of primary recrystallization. To secure cube-on-face secondary grain growth no continuous films should be present on the sheets at the time secondary recrystallization occurs. The annealing times required for complete secondary recrystallization will depend on the temperature at which the annealing is performed. In general, the higher the temperature the shorter the time. Of course, as will be observed by comparing Tables II and III, stack annealing takes far longer than single strip annealing to obtain comparable results. It will be understood that the temperature during annealing need not be constant but may be varied to some extent.

The present invention may be employed to produce double oriented iron-silicon magnetic sheet from a thickness of from 1 to 20 mils and even thicker. However, the disclosed process is especially valuable in producing magnetic sheet material in thicknesses in the range of from about 5 to 20 mils. It is particularly in this latter range of thicknesses that the processes known to the art have failed to consistently produce magnetic sheet material having over 70% of its volume composed of (100) [001] grains.

However, tests indicate that to produce electrical apparatus in which the highest benefits of cube texture magnetic sheet are evidenced, over 80% by volume of cube-on-face grains, and preferably over 90% is required. A sheet having 95% or more of its volume composed of cube texture grains will usually enable disproportionality better electrical performance to be secured than is possible with sheets having lower proportions of cube-on-face grains. Thus, there has been disclosed a new iron-silicon alloy which is especially suitable for the commercial production of double oriented iron-silicon magnetic sheet.

Also, a novel method for processing this alloy from ingot to double oriented magnetic sheet form, in sheet thickness heretofore unattainable, is described.

The magnetic sheet material, before the final anneal, is also a commercial product because, in some cases, it is preferred to stamp or punch laminations from the sheet first and thereafter anneal these. Thus, the annealing process is not critical, the sheet having been processed through the stage of final cold rolling in one plant, and then shipped in the form of coils to another plant for stamping and final annealing.

While the phenomena associated with the growth of cube texture grains in iron-silicon alloys have been explained in some detail as they are presently understood, the applicant does not wish to be bound by any particular theory, since regardless of theory, the compositions and methods of his invention will successfully produce the desired cube-on-face grain texture in iron-silicon alloys. It will be understood that the above description and drawings are illustrative and not limiting of the invention.

We claim as our invention:

1. In the process of producing a magnetic sheet having a high percentage by volume of grains having a (100) [001] orientation from an iron-silicon electrical steel alloy having a small amount of sulfur therein and small amounts of impurities including oxygen, wherein the steps of the process comprise,

   (1) Hot rolling an alloy slab to strip form,
   (2) Annealing the hot rolled strip,
   (3) Cold rolling the strip to sheet form,
   (4) Intermediate annealing the strip between successive cold rolling steps, and
   (5) Final annealing the strip to produce secondary recrystallization,

   the improvement comprising conducting the final anneal so as to subject the final cold rolled sheet, containing oxygen in an amount below 0.003% by weight, to a final annealing temperature of between 1100° C. and 1400° C., in a reducing atmosphere that will cause surface oxides to disappear and the sulfur content at the time secondary recrystallization is initiated to be within the range of from 0.0003% to 0.0006%, by weight, for a period of time sufficient to enable substantially complete secondary recrystallization of the grains so that at least 70% of the volume of the sheet comprises cube grains.

2. In the process of producing a magnetic sheet having a high percentage by volume of grains having a (100) [001] orientation wherein the preliminary processing comprises,

   (1) Hot rolling to a strip of a thickness of about 40 to 150 mils a slab of iron-silicon electrical steel alloy having small amounts of sulfur therein and small amounts of other impurities including oxygen,
   (2) Annealing the hot rolled strip in a non-oxidizing atmosphere at a temperature of from 700° C. to 1100° C.,
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(3) Removing surface oxides from the strip and cold rolling the cleaned strip to a reduction of at least 50% at containing oxygen in an amount below 0.0035%, by weight, at a final annealing temperature of between 1100° C. and 1400° C., the improvement comprising final annealing the final cold rolled sheet containing oxygen in an amount below 0.0035%, by weight, for a period of time sufficient to enable substantially complete secondary recrystallization of the grains so that at least 70% of the volume of the sheet comprises cube grains.

3. The process of claim 2 wherein the final anneal is conducted in a dry hydrogen atmosphere having a dew point of —40° C. and lower.

4. The process of claim 2 wherein the final anneal is conducted in a vacuum.

5. In the process of producing a magnetic sheet having a high percentage by volume of grains having a (100) [001] orientation from an alloy comprising, by weight, from 2 to 7% silicon, less than about 0.01% nitrogen up to about 0.015% aluminum not in excess of about 0.5% manganese, a small amount of sulfur, and the balance iron except for small amounts of impurities including oxygen, wherein the steps of the process comprise,

(1) Hot rolling an alloy slab to strip form,

(2) Annealing the hot rolled strip,

(3) Cold rolling the strip to sheet form,

(4) Intermediate annealing the strip between successive cold rolling steps, and

(5) Final annealing the strip to produce secondary recrystallization, the improvement comprising conducting the final anneal so as to subject the final cold rolled sheet, containing oxygen in an amount below 0.0035% by weight, to a final annealing temperature of between 1100° C. and 1400° C. in a reducing atmosphere containing sulfur and the sulfur content at the time secondary recrystallization is initiated is within the range of from 0.00003% to 0.0006%, by weight, for a period of time sufficient to enable substantially complete secondary recrystallization of the grains so that at least 70% of the volume of the sheet comprises cube grains.

6. In the process of producing a magnetic sheet having a high percentage by volume of grains having a (100) [001] orientation wherein the preliminary processing comprises,

(1) Hot rolling to a strip of a thickness of about 40 to 150 mils a slab of an alloy having small amounts of sulfur and oxygen therein comprising, by weight, from 2% to 7% silicon, less than about 0.01% nitrogen, up to 0.05% carbon, less than about 0.015% aluminum, not in excess of about 0.5% manganese and the balance iron except for small amounts of impurities,

(2) Annealing the hot rolled strip in a non-oxidizing atmosphere at a temperature of from 700° C. to 1100° C.,

(3) Removing surface oxides from the strip and cold rolling the cleaned strip to a reduction of at least 50% at least once to a sheet of a final gauge of between 5 and 20 mils, and

(4) Intermediate annealing the sheet between successive cold rolling steps at a temperature of up to 1300° C., the improvement comprising final annealing the final cold rolled sheet containing oxygen in an amount below 0.0035%, by weight, at a final annealing temperature of between 1100° C. and 1400° C. in a reducing atmosphere containing sulfur and the sulfur content of the sheet at the time secondary recrystallization is initiated is within the range of from 0.00003% to 0.0006%, by weight, for a period of time sufficient to enable substantially complete secondary recrystallization of the grains so that at least 70% of the volume of the sheet comprises cube grains.

7. In the process of producing a magnetic sheet having a high percentage by volume of grains having a (100) [001] orientation by secondary recrystallization wherein the preliminary processing comprises,

(1) Hot rolling an iron-silicon electrical steel alloy slab having a small amount of sulfur therein to strip form,

(2) Annealing the hot rolled strip,

(3) Cold rolling the strip to sheet form,

(4) Intermediate annealing the strip between successive cold rolling steps, and

(5) Cold rolling the containing at least 0.00003%, by weight, of sulfur in the final annealing furnace, the improvement comprising final annealing the coiled cold rolled sheet containing oxygen in an amount below 0.0035%, by weight, at a final annealing temperature of between 1100° C. and 1400° C. in an atmosphere capable of causing surface oxides to disappear, the sulfur content of the steel sheet at the time secondary recrystallization is initiated lying in the range of from 0.00003% to 0.0006%, by weight, and continuing the final anneal for a period of time sufficient to enable substantially complete secondary recrystallization of the grains so that at least 70% of the volume of the sheet comprises cube grains.

8. The process of claim 7 wherein at least one of the intermediate anneals includes a wet hydrogen annealing step to decarburize the strip.

9. In the process of producing magnetic sheets having a high percentage by volume of secondary recrystallized grains having a (100) [001] orientation wherein the preliminary processing comprises,

(1) Hot rolling to a strip of a thickness of about 40 to 150 mils a slab of an alloy having small amounts of sulfur and oxygen therein comprising, by weight, from 2% to 7% silicon, less than about 0.01% nitrogen, up to 0.05% carbon, less than about 0.015% aluminum, not in excess of about 0.5% manganese and the balance iron except for small amounts of impurities,

(2) Annealing the hot rolled strip in a non-oxidizing atmosphere at a temperature of from 700° C. to 1100° C.,

(3) Removing surface oxides from the strip and cold rolling the cleaned strip to a reduction of at least 50% at least once to a sheet of a final gauge of between 5 and 20 mils, and

(4) Intermediate annealing the sheet between successive cold rolling steps at a temperature of up to 1300° C.,

(5) Stacking a plurality of sheets containing at least 0.00003%, by weight, of sulfur for final annealing, the improvement comprising final annealing the stacked sheets containing oxygen in an amount below 0.0035%, by weight, at a final annealing temperature of between 1100° C. and 1400° C. in an atmosphere of hydrogen containing a dew point of —40° C. and lower which is capable of causing surface oxides to disappear, and the sulfur content of the steel sheet at the time secondary recrystallization is initiated lying in the range of from 0.00003% to 0.0006%, by weight, and continuing the final anneal for a period of time sufficient to enable substantially complete secondary recrystallization of the grains so that at least 70% of the volume of the sheet comprises cube grains.
10. The process of claim 9 wherein at least one of the intermediate anneals includes a wet hydrogen annealing step to decarburetize the sheet.

11. In the process of producing a magnetic sheet having a high percentage by volume of secondary recrystallized grains having a (100) [001] orientation wherein the preliminary processing comprises,

(1) Hot rolling to a strip of a thickness of about 40 to 150 mils a slab of an alloy having small amounts of sulfur and oxygen therein and comprising, by weight, from 2% to 7% silicon, less than about 0.01% nitrogen, up to 0.05% carbon, less than about 0.015% aluminum, not in excess of about 0.5% manganese and the balance iron except for small amounts of impurities,

(2) Annealing the hot rolled strip in a non-oxidizing atmosphere at a temperature of from 700° C. to 1100° C.,

(3) Removing surface oxides from the strip and cold rolling the cleaned strip to a reduction of at least 50% at least once to a sheet of a final gauge of between 5 and 20 mils,

(4) Intermediate annealing the sheet between successive cold rolling steps at a temperature of up to 1300° C., and

(5) Winding the sheet to coil form with an inorganic separator medium between adjacent convolutions to prevent sticking during final annealing,

the improvement comprising final annealing the coil at a temperature of from 1100 to 1400° C. first, to effect primary recrystallization of the cold rolled grain textue in an atmosphere of hydrogen having a dew point of -40° C. and a lower to reduce surface oxides and then, to effect secondary recrystallization, the oxygen content of the sheet during the final anneal being below about 0.0035% by weight, and the sulfur content in the sheet being in the range of from 0.00003% to 0.0006%, by weight, during secondary recrystallization, and continuing annealing until substantially complete secondary recrystallization occurs, whereby the secondary crystals are predominantly (100) [001] grains.

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