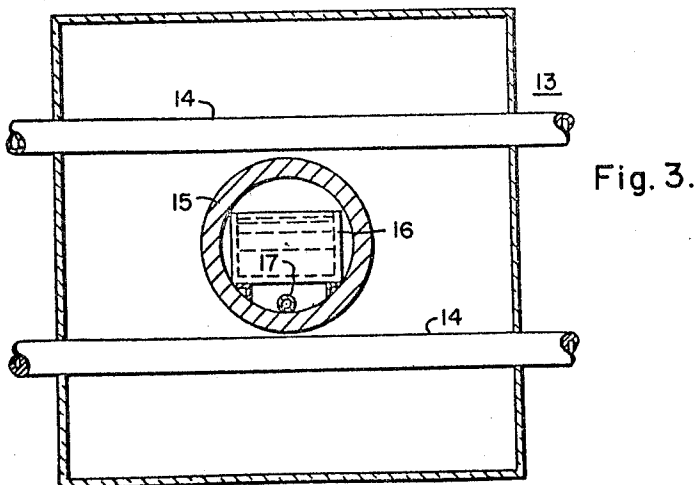
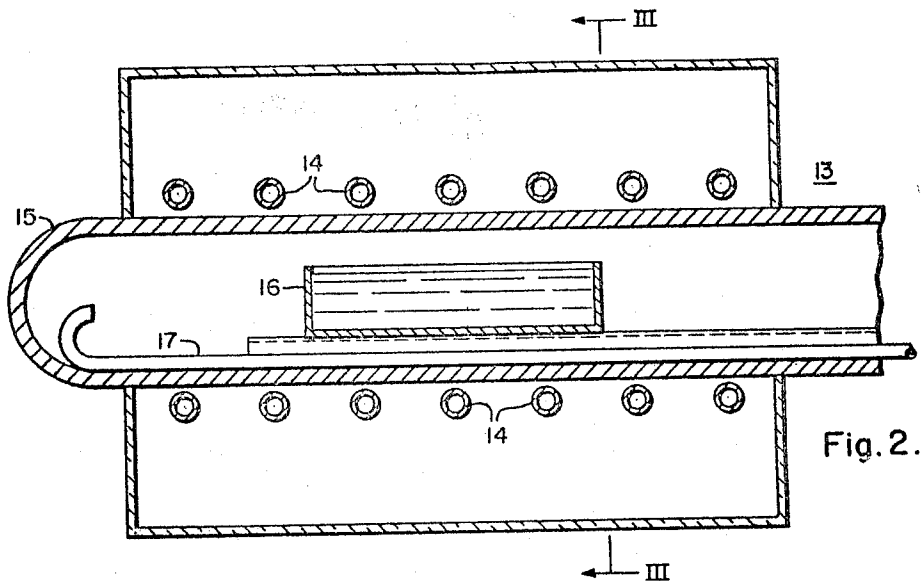
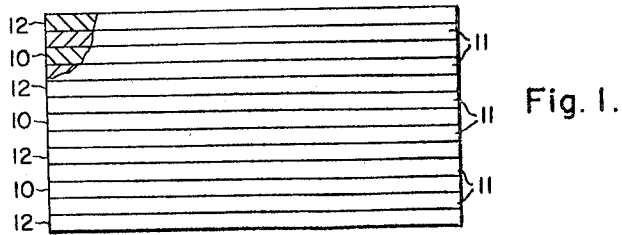


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PROCESS FOR PRODUCING DOUBLY ORIENTED CUBE-ON-FACE
MAGNETIC SHEET MATERIAL
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PROCESS FOR PRODUCING DOUBLY ORIENTED CUBE-ON-FACE MAGNETIC SHEET MATERIAL
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This application is a continuation-in-part of our application Serial No. 722,778, filed March 20, 1958 and application Serial No. 295,264, filed June 21, 1963. Both of these cases have been abandoned.

The invention relates generally to processes for producing oriented magnetic sheet and more particularly to processes for producing doubly oriented magnetic sheet having cube-on-face orientation and the product produced by such processes.

It has been known for many years that the body-centered cubic crystals of magnetic material such as iron, iron silicon, iron chromium, iron molybdenum and other iron alloys have the highest permeability in a direction parallel to the cube edge. Processes for orienting the crystals of magnetic material in one direction have been known for many years. Goss U.S. Patent 1,965,599 taught a process for producing oriented magnetic material having a crystalline structure which is known as the Goss texture. In the process taught in the Goss patent, a high percentage of the grains are oriented with the cube edge in one direction in the plane of the sheet and in the direction of rolling. In the Miller Indices this is the (110) [001] orientation. Other processes also have been disclosed and patented for orienting the grains in magnetic sheet in one direction.

When magnetic sheet is given a preferred orientation, that is, a high percentage of the grains are so aligned that the permeability in the preferred direction is much higher than when randomly oriented, it enables a great increase in the flux density at which the magnetic material may be worked when embodied in electrical apparatus. Immediately following the introduction of the orienting processes, attention was focused on taking full advantage of the magnetic sheet with preferred orientation in the manufacture of inductive apparatus such as transformers. This resulted in wound cores and specially designed laminations and core structures for three-phase transformers and other inductive apparatus. For power transformers and other inductive apparatus in which wound cores could not be used, specially designed laminations, such as employed in the well-known D-cores, were devised for taking the best possible advantage of the preferred orientation of the magnetic sheet.

The introduction of magnetic sheet with a preferred orientation in one direction was widely accepted among builders of electrical equipment. It enabled them, by taking advantage of the high permeability of the magnetic sheet in the direction of rolling, to build certain types of apparatus, of a given rating, that required a much smaller weight of both magnetic iron and copper than was possible with the magnetic sheet available theretofore. In some instances, the weight of oriented magnetic iron and copper required to build units of specified ratings was reduced to about 60% of the weight of the hot rolled non-oriented magnetic sheet and copper previously employed.

The preferred orientation of magnetic sheet in only one direction, while it is a great advance in the art, has some shortcomings. While magnetic sheet with preferred orientation had high permeability in one direction, the permeability at right angles to the preferred direction was lower than in randomly oriented material. This greatly limited its use.

Doubly oriented magnetic material comprises sheets

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in which cube faces are parallel to the plane of the sheet and two edges of the cube face are substantially parallel to the direction of rolling or the edge of the sheet, while two other edges of the cube face are perpendicular to the direction of rolling in the plane of the sheet. This is the (100) [001] orientation. Such doubly oriented sheets, or cube-on-face grain oriented sheets, provide improved magnetic sheet for the building of electrical apparatus of many types.

Certain processes for giving magnetic sheet a double orientation have limitations and shortcomings. Some processes have been applied to produce an acceptable degree of double orientation only in thin gauge material, that is, in the production of magnetic sheet the thickness of which is considerably less than 8 mils, generally in gauges not in excess of 6 mils. While thin gauge material has a wide application for some types of electrical apparatus, it is not the material that is required or used in the greatest volume in the industry for all types of electrical apparatus.

The object of the invention is to provide a process for so cold working and heat treating magnetic silicon-iron alloys both during intermediate anneal and a final anneal that secondary recrystallization of cube-on-face grains in the magnetic material when reduced to final sheet thickness of all gauges up to 25 mils or more, is promoted to the end that the magnetic material after being processed is substantially completely cube-on-face oriented and has the cube-on-face grains having the cube edges closely aligned with the direction of rolling and at right angles thereto.

It is also an object of the invention to provide, in connection with a plurality of cold rolling steps of magnetic silicon-iron alloys, an intermediate heat treatment causing coarse grain growth followed by a final heat treatment while maintaining a controlled sulfur and oxygen content in the sheet whereby there results growth of doubly oriented cube-on-face grains in magnetic sheet of a thickness of up to 25 mils and even heavier gauges.

Another object of the invention is to provide magnetic sheets of iron-silicon alloys containing one or more of nickel, molybdenum, chromium and manganese as alloying elements that respond unexpectedly well to cold working, a high temperature intermediate heat treatment resulting in coarse grain growth and a final heat treatment to produce growth of doubly oriented cube-on-face grains in magnetic sheets, which treatment when applied to the alloys is particularly effective in gauges above 8 mils.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relations of constituents which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the drawings, in which:

FIGURE 1 is a view in side elevation of a stack of sheets illustrating how they are prepared for heat treatment;

FIG. 2 is a view in section of a furnace that could be utilized for heat treating a stack of sheets such as shown in FIG. 1; and

FIG. 3 is a view in section taken along the lines III—III of FIG. 2.

The present invention comprises a method by which doubly oriented or cube-on-face magnetic sheet of 2% to 5% silicon-iron alloys which preferably may contain

certain amounts of nickel, molybdenum, chromium and manganese, and critical amounts of sulfur and oxygen, in gauges ranging from about 8 mils to 25 mils and even heavier can be produced with high permeability in the direction of rolling and also at right angles thereto. The process includes (a) subjecting the alloy to at least two stages of cold rolling with at least one intermediate anneal at temperatures of from 975° C. to 1200° C., and preferably 1050° C. to 1200° C., in dry hydrogen or vacuum for a sufficient time to produce grain growth so that the average grain diameter is at least half the thickness of the sheet, and (b) a final anneal at a temperature of at least 1100° C. which results in first producing oriented cube grain nuclei in the sheet and then causing the nuclei to grow through the heavy gauge material by a secondary recrystallization or exaggerated grain growth which produces a magnetic sheet with large grains having cube-on-face orientation and cube edges closely oriented to the direction of rolling and transverse thereto so that it exhibits a high permeability in both [100] directions which lie in the plane of the sheet, that is, parallel to and perpendicular to the rolling direction. It has been discovered that heavy gauge magnetic sheet, that is, about 8 mils to about 25 mils and heavier, can be produced in which from 80% to 100% of the grains are so oriented that they have a (100) plane lying within 10° of the plane of the sheet, while from 60% to 85% and more of the cube-on-face grains are so oriented that they have a [100] direction or edge within 15° of the rolling direction or edge of the sheet.

In order to give a clear concept of the effectiveness of the process to be described hereinafter for orienting iron-silicon alloys and iron-silicon base alloys containing from 0.1% to 1% nickel, from 0.1% to 2% molybdenum, from 0.05% to 0.4%, and preferably 0.1% to 0.2%, manganese and from 0.1% to 2.0% chromium, or any two or more thereof, a list of representative alloys that have been treated successfully by the process will now be described in detail. The processes and results obtained will be given as the description proceeds in order that the effectiveness of the process and the merits of the magnetic sheets produced thereby may be clearly understood.

In connection with the alloys to be described hereinafter, it has been found that unexpected improvement has resulted from the addition of nickel and molybdenum in varying amounts to the silicon-iron alloys. Tests reveal that quite satisfactory magnetic alloys can be produced by employing silicon from 2.5% to 4.5% by weight, nickel from about 0.1% to about 1% by weight, the remainder being iron.

An alloy comprising 2.5% to 4.5% by weight of silicon, 0.1% to 2% by weight of molybdenum, the remainder being iron, proved to have excellent magnetic properties when processed. Good ferrous magnetic sheet comprised approximately 3% silicon and 2% molybdenum. Another alloy found to be satisfactory comprised 2.5% to 4.5% by weight silicon and from traces to 1% by weight nickel and 1% to traces of molybdenum, the remainder being iron. In these latter alloys, as the nickel is increased, the molybdenum is decreased and vice versa.

In preparing magnetic alloys of silicon and nickel, which resulted in grains having double orientation in response to the processes described, it was found that the preferred range consisted of from 2.75% to 3.5% by weight silicon and from 0.2% to 0.4% by weight nickel, the remainder being iron. Other alloys containing from 2.75% to 3.5% by weight of silicon and from 0.3% to 0.5% by weight of molybdenum were highly satisfactory.

Alloys containing from 2.5% to about 4.5% by weight of silicon, 0.1% to about 2.0% by weight chromium and the remainder iron have also been given a double orientation successfully. Good magnetic sheet resulted from

ferrous alloys having 3% silicon and 2% chromium. Other alloys that have been made and having grains oriented in a cube-on-face texture comprised about 2.5% to 4.5% by weight silicon and from 0.1% to 0.2% by weight manganese, the remainder being iron. Further, it has been found that 2.5% to 4.5% by weight silicon and from 2.0% to 0.1% by weight of chromium and from 0.05% to less than 0.4% by weight of manganese and the remainder iron produce magnetic alloys that have been given a double orientation by the present processes. Another alloy which responded to the processes for producing doubly oriented magnetic sheet comprised 2.75% to 3.5% by weight silicon, traces to 0.3% chromium and the remainder iron.

The chromium and molybdenum in particular have the advantage that they can replace silicon on an equal weight basis so as to produce an alloy lower in silicon but with magnetic and electrical resistivity characteristics as good as with a higher silicon content, along with an improved grain texture and good workability.

In alloys containing both molybdenum and chromium, or both molybdenum and nickel, which have corresponding functions in producing the final product, the respective alloying elements may be varied from traces to the maximum. As one is increased, the other may be decreased.

Manganese is a highly desirable constituent in any of the ternary and quaternary silicon-iron base alloys, and it is preferable that manganese be present in all the alloys.

In processing alloys comprising 2% to 5% silicon, not over 1% of nickel, not over 0.4% manganese, and not over 2% molybdenum or chromium, the remainder being iron, it was found that the annealing step between cold rolling steps could be varied within the predetermined limits as will be described. Good success was obtained when more than one step of cold rolling was employed and the intermediate annealing was carried on for from ½ hour to 5 hours and longer in a range from 975° C. to 1200° C. to effect primary recrystallization and primary grain growth, the longer times at the lower temperatures, until the average grain diameter is at least half the thickness of the sheet.

During the final anneal the sheets should have an oxygen content of 0.005% or less for sheets of about 12 mils or less, and 0.003% or less when the sheets are 15 mils in thickness or above. For cube grain growth to take place, the sulfur content of the sheets at the time the secondary recrystallization is taking place should be less than 0.001% and preferably from 0.0006 to 0.0002%, with a minimum of at least 0.00003% sulfur. The ingots of the silicon-iron alloys initially may have somewhat more than 0.001% sulfur, for example 0.010%, but during the subsequent cold rolling steps the intermediate anneals will purify the metal so as to reduce the sulfur to much lower value. Also during the initial phases of the final anneal when primary recrystallization takes place, the sheet at final gauge will evolve sulfur such that when secondary recrystallization occurs the sulfur is less than 0.001% and at least about 0.00003%. The intermediate anneal employs high temperatures, much higher than are usual in this art for such anneals, so as to help eliminate excess sulfur and also to provide that sulfur which tends to accumulate at grain boundaries as sulfides, such as manganese sulfide, is caused to dissolve throughout the grains of the iron-silicon alloy. The large grains after the intermediate anneal is one indication of such purification.

When heavy gauge silicon-iron alloy sheets are (1) cold rolled two or more times and intermediately annealed at least the final time between cold rolling steps at a temperature of about 975° C. to 1200° C. in dry hydrogen or a dew point of -30° C. or less and (2) subjected to a critical final heat treatment in excess of 1 hour, for example 2 to 16 hours, at 1100° C. to 1350° C. in an atmosphere of

dry hydrogen having a dew point of from -40°C . to -60°C . or lower or in a vacuum of at least about 10⁻³ millimeters of mercury, the cube-on-face grain growth with double orientation is very satisfactory. In making the final anneal the use of all nickel or iron-nickel alloy sheets containing over 20% by weight nickel disposed between the silicon-iron sheets or to enclose the magnetic material is helpful but not necessary.

From a large number of alloys subjected to the orienting process, the following nine examples have been selected. Some of them are disclosed herein for the first time as suitable for making oriented magnetic sheet. The compositions of the alloys are numbered so that they can be identified in the tables of test results which follow. The first five alloys have been suggested and treated by others using other processes. The alloys and their compositions, except for incidental impurities, are as follows:

Table I

- (1) 2.5% silicon, remainder iron
- (2) 3.0% silicon, remainder iron
- (3) 3.5% silicon, remainder iron
- (4) 4.0% silicon, remainder iron
- (5) 3% silicon, 0.3% manganese, remainder iron
- (6) 3% silicon, 0.2% nickel, remainder iron
- (7) 3% silicon, 0.5% molybdenum, remainder iron
- (8) 3% silicon, 0.3% nickel, 0.3% molybdenum, remainder iron
- (9) 3% silicon, 0.3% chromium, remainder iron.

The foregoing alloys were prepared from electrolytic iron which is quite pure and silicon of a commercial grade having low aluminum content. Generally, this silicon is about 98% pure. Alloys 5 to 9, inclusive, were prepared from the same kind of iron and silicon and a relatively pure grade of manganese, nickel, molybdenum and chromium as specified in each instance.

The melting of each alloy was carried on in a vacuum furnace having a magnesia crucible. After the metals to be alloyed were fed into the furnace, it was evacuated to a pressure of 0.1 micron of mercury. The charge was heated inductively in this particular instance. When the silicon began to melt, in order to prevent excessive evaporation of the metals, helium gas was admitted to the furnace and the alloying process continued. Helium was employed because it is inert. Argon and other inert gases may also be employed.

After melting was completed, each alloy was poured into a stainless steel slab mold to produce an ingot of approximately 5 pounds. This is the typical size of ingots employed for carrying on such investigations.

After each ingot was prepared in the manner described hereinbefore, a chemical analysis was made. It is not considered necessary to give an analysis of all the ingots. It is thought that it will suffice to give the analysis of a 3% silicon-iron ingot. The analysis of the number 2 silicon-iron alloy after casting, in addition to iron, was as follows:

Chemical analysis of 3% silicon-iron ingot

Si, 2.94%; C, .0022%; N, .0008%; S, .0019%; P, .005%; Al, .0037%; Mn, .002%.

The following processes were applied to the samples of all of the alloys listed in the table given hereinbefore for producing cube-on-face double orientation. The processes for treating the alloys will be identified hereinafter by the indicated letters to facilitate the making of comparisons. Processes A and B are prior art processes, while processes C and D represent the present invention.

PROCESS A

In this process the ingot of each alloy is hot rolled at a temperature of about 1000°C . to a slab about 0.100 inch in thickness. The slab is then preferably treated to remove surface oxides by any of the well-known pro-

cedures. The removal of oxides immediately after the hot reduction is not vital; however, it is desirable to remove them before the final cold reduction.

The most commonly practiced process for removing the oxides is pickling in an acid. Sulfuric and hydrochloric acids are commonly employed in pickling processes. After the slab has been pickled to remove the oxides, it is drastically cold rolled in one step to reduce it to a sheet about 12 mils in thickness.

The final heat treatment which is applied to the cold rolled sheets and is common to this process and all of the other processes to be described hereinafter will be described in detail after method D has been disclosed.

PROCESS B

In this process B the ingot is hot rolled at about 1000°C . to a slab of a thickness of about 0.100 inch. The slab is then pickled as described in process A to remove oxides.

The oxide-free slab is cold rolled to reduce it from a thickness of about 0.100 inch to about 0.070 inch. This is about a 30% reduction in thickness. A reduction of 30% is about the minimum that should be employed and about 80% is the maximum. After this 30% cold-rolling deformation, the slab is annealed for about 2 hours at a temperature of about 800°C . in dry hydrogen at a dew point of -30°C . After the annealing step, the slab is again cold rolled to reduce it from a thickness of about 0.070 inch to about 0.030 inch. After the second deformation, the slab is again annealed for about 2 hours at about 800°C . in dry hydrogen at a dew point of -30°C . After both of these 800°C . intermediate anneals, the grains had an average diameter far below half the sheet thickness, usually about .002 inch or less. Following the second anneal, the slab is cold rolled, reducing it from about 0.030 inch to about 0.012 inch. By this three-step cold-rolling process a sheet 12 mils in thickness is produced. This process is similar to that employed in producing single or Goss orientation of the grains in the direction of rolling. (See U.S. Goss Patent 1,965,559.) This final cold-rolled sheet is heat treated or annealed as disclosed after method D.

PROCESS C

In this process the ingot is hot rolled at about 1000°C . to produce a slab about 0.100 inch in thickness. The slab may then be pickled to remove oxides. While it is usual to remove oxides after hot rolling, it is not always required, however, the oxides should be removed before the last cold reduction.

The next step is a cold-rolling operation to reduce the slab from about 0.100 inch to about 0.070 inch which is about a 30% reduction. After this cold reduction, the slab is annealed for about 2 hours at about 1000°C . in dry hydrogen having a dew point of -30°C . Then follows another cold-rolling step reducing the slab from about 0.070 inch to about 0.030 inch, which is about a 60% reduction. The slab is again annealed for about 2 hours at about 1000°C . in dry hydrogen at a dew point of at least -30°C . While an anneal of 2 hours between cold-rolling steps is preferable, benefits may be obtained with anneals ranging from $\frac{1}{2}$ hour to 5 hours at temperatures from 975°C . to 1200°C . in an atmosphere of dry hydrogen having a dew point of at least -30°C . such that primary recrystallization and the desired grain growth occur. The grain size after this intermediate anneal averages better than 0.015 inch. A final cold-rolling step is employed to reduce the slab from about 0.030 inch to a sheet which is about 0.012 inch in thickness, which is a 60% reduction. Other percentage cold reductions may be employed depending on conditions, but the reductions should be at least 30% and not more than 80%. A final heat treatment described after method D is to be given to the 12 mil sheet.

PROCESS D

This process is a modification of process C. In practicing the process, the ingot is first hot rolled at 1000° C. to reduce it to a slab about 0.100 inch in thickness. It may be then or later pickled to remove oxides.

After or before the oxides have been removed from the slab, it is cold rolled to reduce it from about 0.100 inch to about 0.070 inch in thickness. After this cold deformation the slab is annealed for about 1 hour at about 600° C. to 800° C. in wet hydrogen having a dew point of about 25° C. followed by an anneal for 1 hour at about 975° C. to 1200° C. in dry hydrogen at a dew point of -30° C. The slab is again cold rolled, reducing it from about 0.070 inch to about 0.030 inch in thickness. The sheet is given a second anneal comprising ¼ hour to 2 hours at 600° C. to 950° C. in wet hydrogen (dew point up to 25° C.) followed by ½ hour to 5 hours at 975° C. to 1200° C. in dry hydrogen at a dew point of at least -30° C. The average grain size after this intermediate anneal is more than 0.015 inch, usually being 0.025 inch or more. After the second anneal, the slab is cold rolled to reduce it from about 0.030 inch in thickness to a sheet about 0.012 inch in thickness.

In process D the wet hydrogen portion of the intermediate anneals may be carried out at temperatures of from 600° C. to 950° C., and the wet hydrogen may have a dew point from 0° C. to 25° C. The wet hydrogen anneal may be applied for from about ¼ hour to 2 hours. It is quite important that no wet decarburization be applied after the sheet is cold rolled to final gauge, lest a thick oxide film be present which will prevent cube-on-face grain growth.

FINAL ANNEAL

Each of the processes A to D inclusive described hereinbefore requires one more step after the final cold rolling, which is a critical final heat treatment. In the final heat treatment after each method A, B, C and D, the 12 mil sheets whose surfaces are quite clean and free from continuous oxide films, are heat treated for from 2 hours to 16 hours at about 1200° C. in dry hydrogen having a dew point as low as -60° C. to effect a complete secondary cube-on-face grain growth such that the entire sheet comprises substantially cube-on-face grains. The dry hydrogen should result in the sheets being bright at the end of the anneal. A vacuum of an absolute pressure of from 10^{-3} to 10^{-6} mm. of Hg was employed with equally good results. The sheet surfaces are bright after this anneal. While the preferred temperature for the final anneal is about 1200° C., it may be varied from 1100° C. to 1350° C. The time to produce substantially complete secondary recrystallization may be an hour or somewhat less at the highest temperatures, and more than 20 hours at the lower temperatures. The hydrogen should have a dew point of at least -40° C. In each case the sulfur content of the sheets during the final anneal was in the range of from 0.00003 to 0.0006%, while the oxygen content was below 0.003%.

Prior to the final heat treatment step of each process, the alloy sheets are coated with an aluminum oxide powder to separate the sheets from each other during final anneal. The aluminum oxide should be fine and quite dry to avoid the introduction of moisture into the furnace. The aluminum oxide selected should be relatively pure. Preliminary firing of the aluminum oxide at 1200° C. is desirable. In practicing the process, a 90-mesh size powder was employed satisfactorily.

The alloy sheets 10 coated with a layer of the aluminum oxide powder 11 are then placed between nickel or nickel alloy sheets 12, as shown in FIG. 1. The size of the stack shown in FIG. 1 is only limited by the number of alloy sheets 10 that can be treated in the furnace at one time. While in the modification of the invention illustrated a nickel or nickel alloy sheet is placed between all

adjacent magnetic sheets, this is not required to practice the processes. In some cases there may be nickel or nickel alloy sheets placed around the stack of magnetic sheets.

The stacked sheets of FIG. 1 may be treated in any suitable type of furnace which is provided with the necessary equipment for controlling the atmospheric conditions. The furnace shown generally at 13 in FIGS. 2 and 3 is an electric furnace provided with resistor elements 14 disposed in spaced rows. The furnace chamber comprises a nickel alloy tube 15 which is disposed between the rows of resistor units 14.

In order to facilitate the loading of the stack of sheets shown in FIG. 1 into the tube in the furnace, a boat 16 is provided to hold the stack of sheets. While not necessary, it may be desirable to make the boat from a nickel alloy. While the annealing of a stack of flat sheets is shown in FIG. 1, it will be understood that a coil may be employed wherein the turns are separated by a layer of dry alumina or other non-reactive sheet separator.

The annealing furnace shown in FIG. 1 is essentially of laboratory or pilot plant type. Commercial annealing furnaces, such as bell-type furnaces, will be employed for the final annealing of large coils or stacks which latter may be flat sheets or punchings of the final cold rolled sheet.

As pointed out hereinbefore, proper heat treatment of the magnetic sheets requires careful control of atmospheric conditions. The magnetic sheet should be heat treated in an atmosphere of dry hydrogen of a dew point of at least -40° C. or a vacuum of at least 10^{-3} mm. of Hg, and relatively free from oxygen or oxidizing components so that the sheets anneal bright. In this particular furnace, the dry hydrogen is supplied through a pipe 17 having its inner end curved back on itself to direct the hydrogen delivered to the furnace over the stack of sheets carried by the boat 16. The tube 17 through which the hydrogen is delivered extends the length of the furnace so that as the hydrogen flows through the tube, it is preheated before it comes in contact with the stack of sheets.

In the heat treatment procedure, when the boat 16, loaded with the stack of magnetic sheets shown in FIG. 1, is properly positioned in the furnace, hydrogen is delivered through the pipe 17 completely flushing out the nickel alloy tube 15. After the tube 15 has been properly cleared of deleterious gases and filled with dry hydrogen, it will be sealed, though a slight flow of hydrogen is usually passed through the furnace during the entire anneal.

As set forth in the specification, the heat treatment will be carried on preferably for about 16 hours at a temperature of 1200° C., in an atmosphere of dry hydrogen of a dew point of at least -40° C. After the heat treatment is completed, the seal will be removed from the tube 15 to give access to the boat 16. In order to avoid any harmful effects from the combination of gases in the atmosphere with the hydrogen when the seal is removed, the tube is flushed with a suitable inert gas such as helium. While it is preferable to continue the heat treatment for 16 hours at 1200° C. in dry hydrogen having a dew point of at least -40° C., satisfactory results have been obtained with heat treatments of from 2 hours to 16 hours in the dry hydrogen.

When the heat treatment of the magnetic sheet is completed, the boat with its contents may be removed. The layer of aluminum oxide 11 applied to the magnetic sheets 10 in the stacking operation prevents any adhesion between the silicon-iron sheets or sticking of the nickel alloy sheets 12 to the magnetic sheets 10. The stack of fully treated magnetic sheets may be separated readily.

The final heat treatment described hereinbefore was given to sheets processed by methods A, B, C and D and brought about secondary recrystallization or an exaggerated growth of the cube-on-face grains. The final product is a doubly oriented magnetic sheet with secondary grains which have diameters that exceed twice the thickness of the sheet.

A study of the 9 sheets given in the Table I hereinbefore following the processing was made using domain pattern methods. The orientation given in the Table II which follows comprises, first, the percentage of the total sheet area or volume which is comprised of grains having (100) plane orientation within 10° of the plane of the sheet, and second, the percentage of these cube-on-face grains which have a [100] direction within 15° of the rolling direction.

In all of these examples the oxygen was of the order of 0.002% and less while the sulfur was on the order of 0.001% when the sheets were put in the furnace during the final anneal. Sulfur was evolved during the initial phases of this final anneal so that the sulfur in the sheets during secondary recrystallization was 0.001% and less. All the sheets were mirror bright at the end of the anneal.

Samples 2, 4, 5 and 8 were not processed by Process D and consequently no tests were made thereon.

Table II
ORIENTATION OF SILICON-IRON SHEETS

Alloy	Process	Grains Having (100) Planes Within 10° to Sheet Plane, Percent	Cube-On-Face Grains Having [100] Direction Within 15° to Rolling Direction, Percent
1	A	80-100	5
2	A	80-100	5
3	A	80-100	5
4	A	80-100	5
5	A	80-100	5
6	A	80-100	10
7	A	80-100	5
8	A	80-100	5
9	A	80-100	5
1	B	80-100	5
2	B	80-100	15
3	B	80-100	5
4	B	80-100	5
5	B	80-100	60
6	B	80-100	35
7	B	80-100	5
8	B	80-100	5
9	B	80-100	5
1	C	80-100	60
2	C	80-100	65
3	C	80-100	75
4	C	80-100	50
5	C	80-100	80
6	C	80-100	50
7	C	80-100	70
8	C	80-100	70
9	C	80-100	85
1	D	80-100	75
3	D	80-100	60
6	D	80-100	75
7	D	80-100	70
9	D	80-100	75

Table II shows that a high percentage of secondary cube-on-face grains grows in each specific alloy sheet following each rolling procedure or process. This is evidenced by the high percentages of grains oriented with the (100) plane in the plane of the sheet. The percentage of grains whose [100] direction is within 15° of the rolling direction resulting from processes A and B was extremely low, except for alloy 5 treated by the B process which comprises 60%. The processes C and D disclosed herein wherein there was large grain growth during the intermediate anneal, were quite effective in bringing about a high percentage of grains having the [100] direction within 15° of the rolling direction.

As evident from Table II, in the 9 alloys treated by process C and the 5 alloys by process D, there was an unexpected and highly desirable improvement in the grain edge orientation of each alloy sheet. The high percentage of grains having a [100] direction within 15° of the rolling direction is all the more important since the sheets processed were 12 mils thick. It will be noted from the Table II given hereinbefore that alloys 5 and 9 have a high percentage of grains oriented with a [100] direction in the rolling direction. This indicates that the

composition of the alloy and the intermediate annealing temperature of about 975° C. to 1200° C. with dry hydrogen employed between the successive steps of cold rolling cooperate to effect the required high degree of orientation of both cube faces and cube edges.

Further examples of the process are as follows.

EXAMPLE I

A commercial heat of silicon steel of the following composition was hot rolled to 0.080 inch sheets: silicon 3.15%, manganese 0.11%, sulfur 0.019% (in hot rolled sheet), carbon about 0.015%, oxygen about 0.0015%, balance iron except for slight amounts of impurities. The hot rolled plate was annealed for one hour at 1050° C. in dry hydrogen (−55° C. dew point), and then cold rolled to 0.030 inch. The cold rolled sheet was annealed for 20 minutes in wet hydrogen (10° C. dew point) in order to decarburize the silicon steel, and then annealed for one hour at 1100° C. in dry hydrogen (−55° C. dew point). The average grain size was 0.7 millimeters. The sulfur content also was greatly reduced to about 0.002%. The annealed sheet was again cold rolled to final gauge of 0.012 inch on highly polished rolls. The surface was clean and free from oxides. The sheet was annealed for 16 hours at 1200° C. in dry hydrogen (−55° C. dew point).

The sheet was mirror bright after the final anneal and the sulfur content was below 0.001%. Analysis of the grain texture indicated over 95% of the sheet volume comprised cube-on-face secondary grains with cube faces within 5° of the plane of the sheet surface, and about 90% of the cube grains had their cube edges within 10° of the rolling direction. Magnetic tests of the sheet at 10 oersteds gave an induction (B) of 18600 gauss. The magnetic properties in both the direction of rolling and transverse thereto were substantially equal.

EXAMPLE II

An ingot of approximately 20 lb. was melted with a nominal composition of 3% silicon, 0.2% manganese, and remainder iron. Electrolytic iron and manganese and a high purity commercial silicon were used as the raw materials. The ingot was hot rolled to a slab of a thickness of 0.250 inch and pickled. The slab was then cold rolled from 0.250 inch to 0.100 inch and annealed for two hours at 800° C. in dry hydrogen. The sheet was further cold rolled from 0.100 inch to 0.040 inch and annealed for two hours at 1100° C. in dry hydrogen having a dew point of below −40° C. The average grain diameter was in excess of 0.04 inch after this anneal. The sheet was then finally cold rolled from 0.040 inch to 0.012 inch.

Strips cut from the cold rolled 0.012 inch sheet were annealed at 1200° C. in a vacuum of between 10^{−3} and 10^{−4} mm. of Hg for 16 to 20 hours. The strip oxygen content was approximately 0.002%. The strips were stacked between nickel chromium plates using alumina powder for separation. The surfaces of the strips were bright after the final anneal and had a sulfur content of less than .0006% after this final anneal. Over 90% of the volume of the strips was composed of secondary grains with a cube face within 5° of the sheet surface, and over 70% of the cube-on-face grains had their cube edges within 15° of the rolling direction.

The important function of the intermediate anneal is to enable a much closer or sharper alignment of the cube edges of the crystal lattices of the cube-on-face grains to the direction of rolling. A simple stress relief anneal which results in a fine grain texture will not result in a close orientation of the edges of the cube grains to the direction of rolling. Thus, in this last example after a simple intermediate stress relief anneal at 750° C. to 800° C. of the cold rolled sheet, followed by another cold rolling to final gauge and then a final anneal, will result in cube-on-face grain growth, but with less than 50%

of the grains having cube edges within 10° of the rolling direction.

The alloy compositions disclosed hereinbefore may be varied within the limits indicated to meet different requirements. The thickness of the magnetic sheet produced may be less than 8 mils. Cold rolling to effect substantially above 80% reductions between intermediate anneals is not desirable in practicing this invention since such extreme reductions tend to cause deviations of the cube edge directions from parallelism to the direction of rolling. The heat treatment must be carried out with great care and precision as indicated above.

It will be understood that the high temperature intermediate anneal of this invention resulting in coarse grain growth need be applied only once to the sheet between any two cold rolling steps if three or more cold rolling steps are employed. This high temperature intermediate anneal preferably precedes the final cold rolling. It may be employed for all the intermediate anneals, or the sheets may be intermediately annealed only once at the high temperatures, while the other anneals may be the usual low temperature anneals at temperatures up to 900°C . for brief periods of time, including wet hydrogen decarburization anneals.

Since certain changes in carrying out the above process, and certain modifications in the article which embodies the invention may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. In a process for producing magnetic sheet of a thickness of at least 8 mils with cube-on-face, double oriented crystal orientation, the steps comprising, hot rolling an ingot of a magnetic silicon-iron alloy containing from 2% to 5% silicon, from 0.05% to 0.4% manganese and at least one other element selected from the group consisting of from 0.1% to 2% molybdenum, from 0.1% to 2.0% chromium and from 0.1% to 1% nickel to a slab of predetermined thickness, cold rolling the slab at least to a final gauge thickness of at least 8 mils twice, each cold rolling step effecting a deformation of at least 30% and not more than 80% in thickness, intermediate annealing the sheet at least once at a temperature of from 975°C . to 1200°C . in an atmosphere of dry hydrogen for a period of time to produce primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet which recrystallized sheet will respond to further processing to become doubly oriented, and after the final cold rolling step heat treating the magnetic sheet at a temperature of from about 1100°C . to 1350°C . in an atmosphere of dry hydrogen having a dew point of at least -30°C . for a period of time sufficient to promote substantially complete secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above about 0.00003% and an oxygen content below 0.005%, whereby to produce a doubly oriented cube-on-face magnetic sheet of the final thickness.

2. In a process for producing magnetic sheet of a thickness of from 10 to 25 mils and greater with cube-on-face, double oriented orientation, the steps of, hot rolling an alloy ingot, comprising from 2% to 5% silicon, from 0.05% to 0.4% manganese and at least one other element selected from the group consisting of from 0.1% to 2% molybdenum, from 0.1% to 2.0% chromium and from 0.1% to 1% nickel, and the balance iron except for incidental impurities, to a slab of predetermined thickness, cold rolling the slab to effect at least two separate reductions in thickness to produce a sheet of final cold rolled thickness of from 10 to 25 mils and greater, each cold rolling operation effecting a deformation of at least 30% and not more than 80% in thickness, annealing the sheet at least once between cold re-

ductions first in wet hydrogen having a dew point up to 25°C . at a temperature of from 650°C . to 950°C . for a period of time ranging from $\frac{1}{4}$ hour to 2 hours, and then in dry hydrogen having a dew point of at least -30°C . for from $\frac{1}{2}$ hour to 5 hours at a temperature of from 975°C . to 1200°C . to provide for primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet so as to produce a texture in the sheet which will respond to further treatment to produce double orientation and after the final cold rolling operation heat treating the magnetic sheet for at least 1 hour at a temperature of about 1100°C . to 1350°C . in dry hydrogen having a dew point of at least -30°C . to produce secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above about 0.00003% and an oxygen content below 0.005%, whereby to produce a doubly oriented cube-on-face magnetic sheet.

3. In a process for producing doubly oriented cube-on-face magnetic sheet of a thickness of from 10 to 25 mils and greater, the steps of, hot rolling an ingot, comprising from about 2.75% to about 3.5% by weight silicon, from 0.2% to 0.4% by weight nickel and the remainder iron except for incidental impurities, to produce a slab of predetermined thickness, cold rolling the slab to effect at least two reductions to produce a sheet of a final cold rolled thickness of from 10 to 25 mils and greater, each cold rolling reduction effecting a deformation of at least 30% and not more than 80% in thickness, annealing the sheet at least once between the cold reductions at a temperature of from about 975°C . to about 1200°C . in an atmosphere of dry hydrogen having a dew point of at least -30°C . for from $\frac{1}{2}$ hour to 5 hours to produce primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet and after the final cold-rolling step heat treating the magnetic sheet at a temperature of from 1100°C . to 1350°C . in an atmosphere of dry hydrogen having a dew point of at least -40°C . for a period of time sufficient to promote substantially complete secondary recrystallization, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above about 0.00003% and an oxygen content below 0.005%, whereby to produce a double oriented cube-on-face magnetic sheet of the final cold rolled thickness.

4. In a process for producing doubly oriented magnetic sheet with cube-on-face crystal orientation, the steps of, hot rolling an ingot of a magnetic alloy comprising 2.5% to 4.5% by weight of silicon, 0.1% to 2.0% by weight of chromium, up to 0.4% manganese, and the remainder iron, to produce a plate of predetermined thickness, treating the plate to remove oxides, cold rolling the plate at least twice to produce a sheet of a final thickness of from about 10 mils to about 25 mils in thickness, each cold-rolling operation effecting a deformation of at least 30% and not more than 80% in thickness, annealing the sheet at least once between cold reductions at a temperature of about 975°C . to about 1200°C . in an atmosphere of dry hydrogen for from $\frac{1}{2}$ hour to 5 hours to provide for primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet so as to condition the magnetic material to respond to further processing to produce doubly oriented sheet and after the final cold-rolling operation heat treating the magnetic sheet at about 1100°C . to 1350°C . in an atmosphere of dry hydrogen of a dew point of at least -30°C . for a period of time sufficient to promote substantially complete secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above 0.00003% and an oxygen content below 0.005%, whereby the resulting sheet comprises a high proportion, of the order of 80% by volume or better, of cube-on-face grains

having their cube edges closely aligned to the direction of rolling.

5. In a process for producing doubly oriented magnetic sheet with cube-on-face crystal orientation, the steps of, hot rolling an ingot of a magnetic alloy comprising 2.75% to 3.5% by weight of silicon, 0.1% to 2% by weight molybdenum, from 0.05% to 0.4% manganese and the remainder iron, to a slab of predetermined thickness, treating the slab to remove oxides, cold rolling the slab at least twice, each cold-rolling operation effecting a deformation of at least 30% and not more than 80% in thickness to produce a sheet of a final thickness of from about 10 mils to about 25 mils in thickness, annealing the sheet at least once between cold reductions at a temperature of about 975° C. to about 1200° C. in an atmosphere of dry hydrogen having a dew point of at least -30° C. for a time to provide for primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet so as to condition the magnetic material to respond to further processing to produce doubly oriented sheet and after the final cold-rolling step heat treating the magnetic sheet at about 1100° C. to 1350° C. in an atmosphere of dry hydrogen having a dew point of at least -40° C. for a period of time sufficient to promote substantially complete secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above about 0.00003% and an oxygen content below 0.005%, whereby to produce a doubly oriented cube-on-face grain texture with a close alignment of the cube edges to the direction of rolling.

6. In the process for producing doubly oriented magnetic sheet with cube-on-face grain orientation, the steps of, hot rolling an alloy ingot comprising 2.75% to 3.5% by weight silicon, from 0.1% to 2% by weight nickel, from 0.05% to 0.4% manganese and the remainder iron, to a slab of predetermined thickness, treating the slab to remove oxides, cold rolling the slab at least twice, each cold-rolling operation effecting a deformation of at least 30% and not more than 80% in thickness to produce a sheet of a final thickness from about 8 mils to about 25 mils in thickness, annealing the sheet at least once between cold reductions at a temperature of about 975° C. to 1200° C. in an atmosphere of dry hydrogen having a dew point of at least -30° C. to provide for primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet so as to condition the magnetic material to respond to further processing to produce doubly oriented sheet, and after the final cold rolling heating treating the magnetic sheet at about 1100° C. to 1350° C. in an atmosphere of dry hydrogen having a dew point of at least -40° C. for a period of time sufficient to promote substantially complete secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above 0.00003% and an oxygen content below 0.005%, whereby to produce a doubly oriented cube-on-face grain texture with a close alignment of the cube edges to the direction of rolling.

7. In a process for producing magnetic sheets having cube-on-face orientation, the steps of, hot rolling an ingot of magnetic material comprising from 2.75% to 3.5% by weight of silicon, from 0.2% to 0.4% by weight of nickel, from 0.3% to 0.5% by weight of molybdenum, from 0.05% to 0.4% manganese and the remainder iron, to produce a slab of predetermined thickness, treating the slab to remove oxides, cold rolling the slab at least twice to reduce it to a final cold rolled thickness of from 10 to 25 mils, each cold-rolling operation reducing the slab at least 30% and not more than 80% in thickness, annealing the sheet at least once between cold reductions at a temperature of about 975° C. to 1200° C. in an atmosphere of dry hydrogen having a dew point of at least -30° C. for a period to provide for primary recrystallization and grain growth in which the average grain diam-

eter is at least half the thickness of the sheet so as to produce primary recrystallization, and after the final cold rolling heat treating the magnetic sheet at about 1100° C. to 1350° C. in an atmosphere of dry hydrogen having a dew point of at least -40° C. for a period of time to cause substantially complete secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but above 0.00003% and an oxygen content below 0.005%, so as to produce a doubly oriented cube-on-face magnetic sheet with grains having cube edges closely aligned to the sheet edge.

8. In the process for producing doubly oriented magnetic sheet with grain orientation, the steps of, hot rolling an ingot comprising about 2.5% to about 4.5% by weight of silicon, from 0.1% to 0.4% by weight of chromium, from 0.4% to 0.05% by weight of manganese and the remainder iron, to a slab of predetermined thickness, treating the slab to remove oxides, cold rolling the slab at least twice, each cold-rolling operation effecting a deformation of at least 30% and not more than 80% in thickness, to produce a sheet having a final thickness of from about 10 mils to about 25 mils in thickness, annealing the sheet at least once between cold reductions at a temperature of about 1050° C. to 1200° C. in an atmosphere of dry hydrogen having a dew point of at least -30° C. for about ½ to 2 hours to provide for primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet so as to condition the magnetic material to respond to further processing to produce doubly oriented cube-on-face magnetic sheet and after the final cold-rolling operation heat treating the magnetic sheet for about 1 to 16 hours at about 1100° C. to 1350° C. in an atmosphere of dry hydrogen having a dew point of at least -40° C. to promote substantially complete secondary grain growth, the sheet at the initiation of secondary recrystallization having less than 0.003% of oxygen and the sulfur being not less than about 0.00003% but not exceeding 0.001%, whereby a doubly oriented cube-on-face grain texture magnetic sheet results.

9. In a process for producing doubly oriented magnetic sheet with cube-on-face grain orientation, the steps of, hot rolling an ingot of magnetic material comprising from about 2.5% to about 5% by weight of silicon and from 0.1% to 2% by weight of chromium, from 0.05% to 0.4% manganese, and the remainder iron to produce a plate of predetermined thickness, treating the plate to remove oxides, cold rolling the plate at least twice, each cold-rolling operation effecting a deformation of at least 30% and not more than 80% in thickness to produce a sheet of from 12 mils to about 25 mils in final thickness, annealing the sheet at least once between cold reductions at a temperature of about 975° C. to 1200° C. in an atmosphere of dry hydrogen having a dew point of at least -30° C. for ½ to 5 hours to provide for primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet so as to condition the magnetic sheet for subsequent processing and after the final cold-rolling operation coating the sheet with pure aluminum oxide powder free of moisture and disposing nickel alloy members adjacent the sheet and heat treating the sheet at about 1100° C. to 1350° C. in a dry hydrogen atmosphere having a dew point of at least -40° C. for a time to promote substantially complete secondary grain growth, the sheet at the initiation of secondary recrystallization having less than 0.003% of oxygen and the sulfur not less than about 0.00003% but not exceeding 0.001%, so as to produce a doubly oriented cube-on-face magnetic sheet.

10. In a process for producing magnetic sheet with cube-on-face double crystal orientation, the steps comprising, hot rolling an ingot of a magnetic silicon-iron alloy containing from 2% to 5% silicon, from 0.05% to 0.4% manganese, the balance iron and incidental impur-

ities, to a slab of predetermined thickness, cold rolling the slab at least twice to a final thickness of at least 8 mils, each cold rolling step effecting a deformation of at least 30% and not more than 80% in thickness, annealing the sheet while of a thickness greatly in excess of 8 mils between each cold rolling operation, at least one intermediate anneal being carried out at a temperature of from 975° C. to 1200° C. in an atmosphere of dry hydrogen having a dew point of at least -30° C. for a period of time to produce primary recrystallization and grain growth in which the average grain diameter is at least half the thickness of the sheet which recrystallized sheet will respond to further processing to become doubly oriented, and after the final cold rolling step heat treating the magnetic sheet for from about 2 hours to 16 hours at a temperature from 1100° C. to 1350° C. in an atmosphere of dry hydrogen having a dew point of at least -40° C. to promote substantially complete secondary grain growth, the sheet at the time of secondary recrystallization having a sulfur content of below 0.001% but not less than about 0.00003% and an oxygen content below 0.005%, the atmosphere and conditions of the final anneal being sufficient to produce a bright surface on the sheets, whereby to produce a doubly oriented cube-on-face magnetic sheet.

11. The process of claim 10, wherein the final anneal atmosphere is a vacuum of at least 10^{-3} mm. of mercury.

12. In the process for producing rolled magnetic sheets of a final thickness of from 8 to 25 mils and having a high volume proportion of cube-on-face crystals having the cube edges aligned closely to the direction of rolling and in a direction transverse thereto, the sheets comprising a silicon-iron alloy having from 2% to 5% silicon, small amounts of sulfur, and the balance iron except for incidental impurities, the alloy having been hot rolled into a slab, and the slab cold rolled at least twice to effect a reduction of from 30% to 80%, with an intermediate anneal between the successive cold rollings, and a final secondary recrystallization anneal at a temperature of from about 1100° C. to 1350° C. in a reducing atmosphere capable of producing a bright surface on the sheet surfaces, the sulfur content of the sheet at the time secondary recrystallization begins being from 0.001% to 0.00003%, and oxygen less 0.005%, the improvement comprising applying at least one intermediate anneal at the temperature

of from 975° C. to 1200° C. for a period of time to cause primary recrystallization and coarse grain growth in which the average grain diameter is at least half the thickness of the sheet being annealed, whereby upon the subsequent final anneal, the secondary grains exhibit improved alignment of cube edges to the direction of rolling.

13. The process of claim 1 wherein the final anneal is carried out in a vacuum of at least 10^{-3} mm. Hg.

14. The process of claim 4 wherein the final anneal is carried out in a vacuum of at least 10^{-3} mm. Hg.

15. The process of claim 8 wherein the final anneal is carried out in a vacuum of at least 10^{-3} mm. Hg.

References Cited by the Examiner

UNITED STATES PATENTS

2,067,036	1/1937	Wimmer	148—111
2,076,383	4/1937	Pawlek et al.	148—111
2,378,321	6/1945	Pakkala	148—112
2,867,558	1/1959	May	148—111
2,867,559	1/1959	May	148—111
2,940,881	6/1960	Hollomon	148—111
2,992,951	7/1961	Aspden	148—113
2,992,952	7/1961	Assmus et al.	148—113
3,008,857	11/1961	Mobius	148—111
3,058,857	10/1962	Pavlovic et al.	148—31.55
3,089,795	5/1963	Hsun Hu	148—111
3,090,711	5/1963	Kohler	148—111
3,096,222	7/1963	Fiedler	148—31.55
3,124,491	3/1964	Foster	148—31.57
3,130,092	4/1964	Kohler et al.	148—111
3,163,564	12/1964	Taguchi et al.	148—113

References Cited by the Applicant

UNITED STATES PATENTS

2,867,559	1/1959	May.
2,940,881	6/1960	Hollomon.
2,992,951	7/1961	Aspden.
2,992,952	7/1961	Assmus et al.
3,124,491	3/1964	Foster.
3,130,092	4/1964	Kohler et al.

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