July 18, 1961 F. ASSMUS ET AL 2,992,952

METHOD OF MANUFACTURING MAGNETIC SHEETS

Filed Dec. 30, 1957

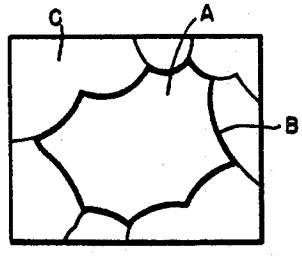


Fig. 1.

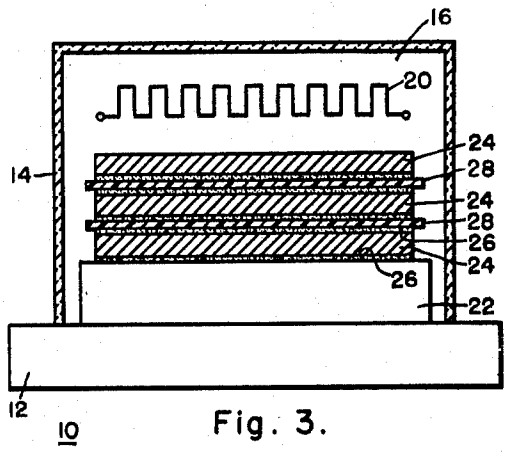


Fig. 3.

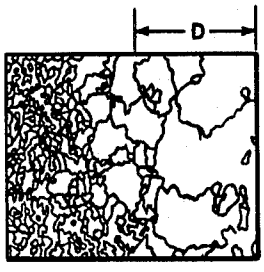


Fig. 2.

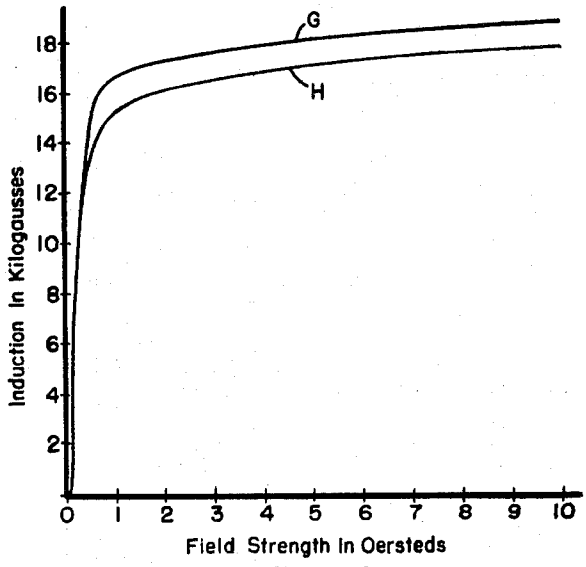


Fig. 4.

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METHOD OF MANUFACTURING MAGNETIC SHEETS

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This invention relates to the method of manufacturing magnetic sheets of silicon iron and other alloys, and the sheet magnetic products so derived.

This application is based on the following patent applications filed in Germany: V–9825–VI/18c, filed December 1, 1955; V–10655–VI/18c, filed May 17, 1956; and V–11083–VI/18c, filed August 15, 1956.

This application is a continuation-in-part of application Serial No. 623,596, filed November 21, 1956.

It is known that many soft magnetic materials, such for example as silicon iron and nickel iron alloys which crystallize in the cubic system, are characterized by the direction of easiest magnetization being along the cube edge. The permeability values of these magnetic materials are higher in the direction of the cube edge than in any other direction. The prior art manufacturing practices have produced from silicon iron alloys magnetic sheet materials in which a majority of the grains are disposed on one edge parallel to the surface of the sheet and the cube edges of a high proportion of these grains are oriented in the direction of rolling of the sheet of the magnetic alloys. In Miller indices, this is the (110) [001] orientation. Consequently, in the silicon iron alloy sheets having such a single orientation grain texture, the permeability is greatest in the rolling direction of the sheet of the alloy. However, in a direction perpendicular or crosswise to the rolling direction, the grains or crystals of the alloy are not oriented in the direction of their easiest magnetization. Consequently, substantially poorer magnetic properties are exhibited in directions crosswise to the rolling direction of the sheet.

One such well-known prior art manufacturing procedure has resulted in singly oriented magnetic sheets of silicon iron, known as the Goss texture, see U.S. Patent 1,965,559 to Goss. In the Goss texture, in the best present-day commercial material, only approximately 75% of the grains are oriented with their edges generally in the rolling direction. Further, in these grains the cube edges deviate as much as 20° with respect to the rolling direction. Consequently, any magnetic flux applied in a direction parallel to the direction of the rolling of the sheet results in substantially lower permeabilities than would be attained if a higher proportion of the grains were to be oriented, or if a more perfect alignment of the crystal axes of the grains were to be obtained. If both conditions were caused to occur, the optimum magnetic properties would be secured in the rolling direction. However, the crosswise magnetic properties of the sheets would be poorer than with present silicon iron sheets.

The manufacture of oriented magnetic silicon iron alloy sheets with only one preferred magnetic orientation of the grains is carried out by drastic cold rolling of a previously hot rolled slab or plate of the alloy. Each cold rolling step reduces the thickness of the alloy at least 25% and it is followed by an intermediate annealing. When the sheet of required thickness has been produced it is usually coated with a refractory suspension and subjected to a final anneal at a temperature of 650° C. to 1300° C., usually in a hydrogen atmosphere of a dew point of from 0° C. to −20° C. The sheet enters anneal with a gray oxide film which is substantially continuous and such oxide film is not reduced, but may even be augmented during the final anneal. After the final anneal, the silicon iron sheet exhibits a cube-on-edge preferred orientation of a major proportion of the grains in the direction of rolling. This process has resulted in a lower proportion of cube-on-edge oriented grains in thin gauge sheet below about 0.30 mm. in thickness, and below 0.20 mm. the proportion of cube-on-edge grains to the total grains in the sheet falls off rapidly with decrease in thickness of the sheet. In all cases, however, this prior art process does not produce any appreciable amount of grains having cube-on-face orientation.

Since the magnetic properties of the singly oriented magnetic sheets at any other direction than in the direction of rolling are much inferior, the design of magnetic cores utilizing the singly oriented silicon iron sheets is so directed as to take advantage of the single orientation. Thus, magnetic cores are prepared by winding singly oriented material into toroidal cores and similar wound core structures. Punchings from singly oriented material, for example U-type punchings, can be produced with, for example only the legs of the U being in the preferred direction whereas the base of the U lies in a direction where the magnetization characteristics are poor. As a result, complicated structures and designs are necessary to take best advantage of the singly oriented magnetic sheet material of silicon iron.

It has been found that certain critical changes in known processes for manufacturing silicon iron alloy sheets will produce a surprising improvement in the magnetic orientation of the grains of the sheets. A high proportion of the grains will have a cube-on-face or (100) [001] orientation with the edges being substantially parallel to each other. Not only are the magnetic properties in the direction of rolling improved but, surprisingly, the orientation of the crystals in a direction at right angles to the rolling direction is so greatly improved that the magnetic properties crosswise of the sheet approach the magnetic properties in the direction of rolling. Consequently, doubly oriented silicon iron sheets having outstanding magnetic properties are obtained.

The object of the present invention is to provide a process for cold rolling and annealing silicon iron alloy under such conditions that surface oxides are removed to enable secondary recrystallization to occur with cube-on-face grain growth predominating, whereby to produce doubly oriented magnetic sheets.

A further object of the invention is to provide for the manufacture of silicon iron magnetic sheets by a cold rolling operation followed by a final anneal under specified controlled conditions of extremely low oxygen and water vapor pressure whereby there is obtained a grain texture wherein a major proportion of the grains have cube-on-face orientation in the plane of the sheet.

A still further object of the invention is to provide for an alloy of silicon and iron containing a predetermined amount of manganese, the alloy when subjected to a predetermined cold rolling and annealing process exhibiting a cube-on-face orientation.

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 FIG. 1 of the drawing wherein is shown schematically an enlarged view of a crystal structure having a cube-on-face orientation which results from the practice of the present invention;

FIG. 2 is a reproduction of a sheet of magnetic material which has been annealed partly in accordance with the invention and partly in accordance with the prior art;

FIG. 3 is a vertical cross section through an annealing furnace illustrating the practice of the invention; and

FIG. 4 is a graph of curves of the magnetic properties of sheet material in the direction parallel to and perpendicular to the rolling direction, as produced in accordance with this invention.

In accordance with the present invention, it has been discovered that silicon iron magnetic sheets may be produced with a cube-on-face grain structure whereby the sheets are doubly oriented and exhibit outstanding magnetic properties in two directions at right angles to each other.

Basically, to produce double oriented magnetic sheets, the silicon iron alloy must be drastically cold rolled and then subjected to a final anneal at a suitable temperature while in an atmosphere that (*a*) in the preliminary stages, will remove all continuous surface oxides and other films so that any cube-on-face grain nuclei in the body and on the surface will grow through the entire sheet thickness prior to the start of secondary recrystallization and (*b*) thereafter, during secondary recrystallization, these cube-on-face grains will grow laterally throughout substantially the entire sheet. No appreciable amount of surface oxides or inclusions should be present to interrupt or hinder the grain growth. Therefore, a clean surface on the sheets is indispensable. A satisfactory final annealing atmosphere generally will leave the silicon-iron sheets almost mirror bright and free from the usual gray appearance.

Briefly, we have discovered that the following conditions should be followed in producing the improved double-oriented magnetic silicon iron alloy sheets of the present invention: After drastic cold rolling, effecting a reduction of at least 50%, to reduce the silicon-iron alloy sheets to desired thickness, the final anneal is carried out in a furnace wherein the atmosphere is substantially completely free from oxygen, moisture or other oxidizing materials, such as carbon dioxide, which will react with the surface of the sheet, and, in fact, any silicon oxides are reduced or disappear during the early stages of the anneal. The reducing atmosphere during final anneal of the sheets may comprise (1) at least 50% by volume of hydrogen of a very low dew point, at any desirable pressure—either atmospheric or at a subatmospheric pressure to an absolute pressure measurable in microns, or (2) a vacuum of an absolute pressure of 10^{-3} mm. of Hg or lower. In some instances, as will be noted later, these drastic conditions may be slightly eased.

In order to favor cube-on-face grain growth, each of the following additional measures have been found to be beneficial:

(1) During final anneal there is disposed in the annealing furnace in proximity to the surfaces of the magnetic sheet a metal such as titanium which has an affinity for oxygen greater than that of silicon whereby the partial pressure of oxygen in the atmosphere at the annealing temperature is less than that resulting from silicon dioxide.

(2) During the final anneal there is disposed adjacent the surfaces of the sheet a metal such as nickel, cobalt, or platinum or alloys thereof, which metal will promote the formation of atomic hydrogen from the hydrogen atmosphere in the furnace.

(3) The silicon iron alloy contains between 0.08% and 3% by weight, and preferably from 0.1 to 1% by weight, of manganese.

More particularly, the present invention comprises the processing of an alloy comprising from 2% to 5% by weight of silicon, and the balance being iron except for incidental impurities. From 0.08% to 3% of manganese can be present in the alloy, preferably from 0.1% to 1% of manganese. The alloy is melted and cast into an ingot following the usual metallurgical practices in the art. The ingot is then hot rolled to a slab or plate of a thickness of the order of 0.1 inch to 0.25 inch or even thicker. This hot rolled plate or slab is then subjected to a multiple cold deformation. The cold deformation comprises a series of cold rolling steps wherein the plate is reduced from 25% to 90% in thickness during each step with the last step preferably effecting a reduction of thickness from 50% to 90%. In some cases only a single cold deformation of from 50% to 90% may be adequate to reduce the hot rolled plate to a sheet of desired thickness.

Between each of the cold rolling steps the sheet is subjected to an intermediate anneal at a temperature of from 750° C. to 950° C. in a reducing atmosphere. The intermediate anneals may be in wet hydrogen though the last intermediate anneal may be carried out in a dry hydrogen atmosphere having a dew point of about −20° C., for example.

Following the final cold rolling step during which a sheet of magnetic material of desired thickness has been produced, the sheet is subjected to a critical final anneal at a temperature of above 950° C. and as high as 1425° C., and preferably between 1100° C. and 1350° C., for a period of time wherein secondary recrystallization resulting in a cube-on-face grain growth through substantially the entire sheet takes place. As short a time as five minutes at the highest temperature may be sufficient for a single sheet. A suitable period for final anneal is of the order of from 1 to 20 hours for coils and stacks of material, the longer times being required for the lower temperatures. After the last rolling, the silicon-iron sheets have the usual dull gray appearance comprising silicon dioxide and other surface oxides. The annealing should be such as to remove substantially all of the visible oxides. After anneal the sheets usually will be almost mirror bright.

During the final anneal it is necessary to correlate the temperature, the atmosphere and the time of anneal in order to produce the doubly oriented material having the cube-on-face orientation. It is critical that the atmosphere be substantially completely free from oxygen, moisture or other oxidizing material which will react with the silicon in the surface of the sheet to form silicon dioxide. In fact, the oxygen and moisture content should be so low that any silicon oxide film on the surface of the sheet shall disappear during this final anneal. It is important that the partial pressure of the oxygen and water vapor in the atmosphere at the immediate surface of the sheet be maintained so low that it will prevent oxidization of silicon and in fact will reduce silicon dioxide. It will be appreciated that the atmosphere in the main body of the annealing furnace may be low in oxygen, but at the surface of the sheet there may be oxygen present in higher proportions due to moisture or oxygen being absorbed or otherwise present in the materials employed for separating the sheets in order to prevent them from welding to each other, and care is needed to remove it. Therefore, care should be taken to fire the sheet separator refractory materials previous to use, at temperatures of, for example, 1200° C., and to keep them dry until applied to the sheets.

Accordingly, the final annealing atmosphere should comprise hydrogen of a dew point of at least about −40° C., and preferably −50° C. or lower. The treatment of the hydrogen gas with a deoxidation catalyst is desirable. Inert gases such as neon, argon or nitrogen may be present in the hydrogen. A vacuum of an absolute pressure of 10^{-3} mm. of Hg or lower may be present as the atmosphere during final anneal. The atmosphere, whether vacuum or hydrogen, will normally remove the usual gray surface film and the sheets after annealing will be mirror bright. At the lowest annealing temperatures the partial pressure of oxygen must be lower than for higher annealing temperatures.

The annealing temperature should be above 950° C., and preferably between 1100° C. and 1350° C. and be

applied for a period of time in which a primary recrystallization occurs initially wherein cube-on-face grain nuclei in the body and on the surface of the sheets grow through the thickness of the sheets. During this initial period surface oxides and films are being removed. Therefore, secondary recrystallization occurs so that the cube-on-face grains spread laterally through the sheet whereby at the end of the secondary recrystallization substantially all the crystalline structure of the sheet comprises cube-on-face grains.

In one case 3% silicon-iron sheets being annealed in dry hydrogen at 1050° C. required ten hours to develop a full cube-on-face secondary recrystallization, while the same alloy required only one half hour at 1150° C. in a similar dry hydrogen atmosphere to attain full cube-on-face secondary recrystallization.

It has been found that the application of an oxygen getter adjacent the surfaces of the magnetic sheets during this final anneal will result in an improved magnetic product. The getter materials are those that combine easily with oxygen so that they have a partial pressure of oxygen lower than that of silicon dioxide at the annealing temperature. Suitable getter materials are titanium, aluminum and base alloys thereof, such for example, as cerium-aluminum, cerium-aluminum-zirconium, and cerium-aluminum-titanium alloys. The oxygen getter materials are most effective when applied closely to or even directly on the surfaces of the magnetic sheets being annealed. Thus, a sheet of titanium may be applied over the silicon-iron sheet, preferably with a thin layer of magnesium oxide or aluminum oxide refractory powder to prevent any alloying of the two sheets. These getter materials may also be employed in granular or in powder form.

It will be understood that the magnetic sheets during annealing usually will ordinarily be disposed in a stack or coil wherein successive sheets or turns of a coil are separated from each other by a porous refractory coating such as magnesium oxide, aluminum oxide, zirconium oxide or the like. The refractory oxide used must be so treated, as by previous firing at 1000° C. to 1300° C., as to be completely free from water and reactive materials and will form no reaction products with the silicon-iron sheets. Individual sheets or a continuous strip may be passed into the annealing furnace.

It has been found further that the cube-on-face orientation of the silicon iron alloys may be promoted during the final anneal by disposing in the vicinity of the sheets a substance which has a catalytic effect in dissociating molecular hydrogen into atomic hydrogen. The atomic hydrogen is more highly effective in reacting with impurities on the surface of the silicon iron sheets as compared to the reaction of molecular hydrogen with such impurities. Thus, oxides are reduced at a much faster rate, while carbon or carbides react with the atomic hydrogen very rapidly to form gaseous compounds which escape from the surface of the magnetic sheets.

The materials which promote the conversion of molecular hydrogen into atomic hydrogen are nickel, cobalt and platinum, and their alloys in which the nickel, or cobalt, or both, comprise at least 20% by weight of the alloy, while the platinum should not be employed with an excess of 30% of other elements. It will be understood that in some cases compounds of nickel, cobalt or platinum will function in a similar manner to catalyze the formation of atomic hydrogen.

A further advantage arising from the use of nickel, cobalt and platinum and their alloys during the final anneal is that the atmosphere requirements may be less stringent. Thus the dew point of a hydrogen atmosphere may be −30° C. when sheets of nickel or other catalyst metal are present. In the case of a vacuum as an annealing atmosphere, it need be only at an absolute pressure of 10^{-2} mm. of Hg when sheets of nickel are disposed near the laminations.

Only small amounts of nickel, for example, need be used in practicing this feature of the invention. Strips of nickel may be disposed between a stack of silicon iron sheets, or sheets of nickel may be wrapped around a coil, or nickel screening may be laid on the ends of a coil. Also a small amount of nickel powder may be admixed with the refractory sheet separator.

The drastic cold reduction and the annealing conditions result in the formation in the sheet in the early part of final anneal of small cube-on-face grains distributed throughout a fine grain structure comprising other orientations in the primary recrystallized metal of the sheet. The cube-on-face grains resulting from the practice of the present invention exhibit concave grain boundaries which have the characteristics, during final anneal, or growing rapidly by consuming nearby grains of other orientation.

In FIG. 1 of the drawing there is illustrated at a magnification of 200× a typical cube-on-face grain having the desired concave grain boundaries. The grain A having the cube-on-face orientation has the concave grain boundaries B which enables the grain A to consume surrounding grains C and consequently grain A will grow rapidly during the final anneal. After the final anneal the magnetic sheet will exhibit almost exclusively large cube-on-face grains, whereas previous to such anneal the sheet exhibited a great number of small grains of various orientations throughout which were distributed small grains such as A having the cube-on-face structure and showing the concave grain boundaries.

FIG. 2 illustrates the results obtained from the annealing of a sheet of 3% silicon iron wherein the right-hand half of the strip D was covered with a strip of titanium while the left-hand half of the sheet was left exposed to the annealing atmosphere without any covering other than a thin layer of powdered aluminum oxide applied to the entire sheet. As evident from FIG. 2, after annealing in dry hydrogen the right-hand half of the sheet shows large cube-on-face grains whereas the left-hand half of the sheet shows a fine grain structure which did not include many cube-on-face grains.

The process of the present invention is applicable to producing sheets or strips of silicon iron alloy having a final thickness of between 0.35 and 0.003 mm., but best magnetic properties have been obtained when the final sheet thickness did not exceed 0.1 mm. Optimum magnetic properties were obtained for sheets having a thickness of between 0.1 and 0.01 mm. thickness. The advance in the art derived by the practice of the present invention will be appreciated when it is noted that up to the present time the best magnetic properties for single oriented, or Goss texture sheet has been exhibited in sheets of thicknesses of approximately 0.3 to 0.35 mm. (12 to 14 mils) thickness. As the sheet thickness decreased from these values, the perfection of the orientation obtainable has been greatly reduced and consequently the magnetic quality has been poorer as the thickness decreased substantially below 0.3 mm.

The following examples illustrate the practice of the invention:

EXAMPLE I

An alloy was prepared by melting in vacuum relatively pure silicon and iron in the proportions of 97% of iron and 3% silicon. Ingots cast from this melt were hot rolled at approximately 1250° C. to a thickness of 0.1 inch (2.5 mm.). The hot rolled plate was pickled and subjected to six cold rolling and annealing steps as follows:

(1) Thickness reduced from 2.4 to 1.8 mm., intermediate annealing five hours at 800° C. in wet hydrogen;

(2) Thickness reduced from 1.8 to 0.8 mm., intermediate annealing five hours at 800° C. in wet hydrogen;

(3) Thickness reduced from 0.8 to 0.35 mm., intermediate annealing five hours at 900° C. in dry hydrogen;

(4) Thickness reduced from 0.35 to 0.17 mm., intermediate annealing five hours at 900° C. in dry hydrogen;

(5) Thickness reduced from 0.17 to 0.08 mm., intermediate annealing five hours at 900° C. in dry hydrogen; and

(6) Thickness reduced from 0.08 to 0.04 mm.

In preparation for final annealing after step 6, the silicon-iron sheets were stacked with a layer of finely powdered aluminum oxide between each of the sheets. The aluminum oxide powder was of a particle size averaging from 15 to 50 microns and it was annealed at 1350° C. before being applied to the sheets. A stack was built up by applying a layer of the aluminum oxide on a base, then a thin nickel sheet was disposed thereon, then a layer of aluminum oxide followed by a silicon-iron sheet. On the first silicon-iron sheet was then applied a layer of the aluminum oxide, a nickel sheet, more aluminum oxide and then another silicon-iron sheet, etc. The annealing was carried out for five hours in highly purified hydrogen gas free from any oxygen and of a dew point of approximately —40° C. This resulted in a sheet having a very high proportion of cube-on-face grains.

After annealing, the magnetic properties of the sheets were tested and compared with the best presently available 3% silicon-iron sheets in the industry. The optimum magnetic properties are obtained for a singly oriented silicon-iron sheet produced by known practices at a thickness of approximately 14 mils. The magnetic characteristics of a 14-mil sheet, indicated as Goss sheet, are compared with the much thinner sheet of the present invention in the following table:

Table I

[Field strength in oersteds to produce the indicated induction]

	Parallel to the rolling direction			Perpendicular to the rolling direction		
Induction	14 kg.	16 kg.	18 kg.	14 kg.	16 kg.	18 kg.
Cube-texture sheet (0.04 mm.), Oe	0.5	0.8	5.0	0.6	2.0	12
Goss sheet (14 mils), Oe	0.5	1.0	10.0	10	ca. 50	ca. 200

If the above table were to compare the best presently available 3% silicon iron alloy of a thickness of 0.04 mm., the comparison would be even more favorable to the doubly oriented sheet of the present invention.

The induction curves for the alloy of Example I are plotted in FIG. 4, wherein the upper curve G gives the induction values in the direction parallel to the rolling direction while the curve H sets forth the induction values perpendicular to the rolling direction of the sheet. These curves not only indicate much greater induction than in available sheets of 3% silicon iron alloy, but the magnetic properties in the crosswise direction are much closer to the magnetic properties in the lengthwise direction of the sheet than is exhibited by any available silicon iron alloy.

Crystallographic analysis of the sheets produced in accordance with Example I of this invention show that approximately 95% of the crystal volume has a deviation of between 0° and 5° of the cube faces with respect to the plane of the sheet, while 75% of the cube edges had a deviation of from 0° to 10° from the rolling direction. Not only is this a much greater proportion of orientation of the cube face of grains to the surface of the sheet but also a much closer uniformity of orientation of cube edges, than has been obtainable in the art heretofore.

It is believed that for a commercially desirable cube-on-face magnetic product the silicon-iron sheets should contain at least 70% of the crystal volume of grains with cube faces within 10° of the surface of the sheet. For many electrical devices the edges of the cube-on-face grains should be aligned with respect to each other so that at least 70% be within 10° of the edge of the sheet. For certain types of apparatus, it has been found that random orientation of the cube edges is not detrimental, providing over 70% of the grains have faces within 10° of the plane of the sheet surface.

In Example I, the silicon-iron sheets were stacked with sheets of nickel interposed. Otherwise, similar anneals were carried out on the silicon-iron sheets without any nickel sheets in the furnace, and excellent cube-on-face oriented sheets were produced. In this last case the atmosphere comprised, in one instance, hydrogen at a dew point of —50° C. and, in another instance, a vacuum of 10^{-4} mm. of Hg.

Referring to FIG. 3 of the drawing, there is illustrated an annealing furnace **10** suitable for carrying out the final anneal of the silicon iron alloy. The furnace **10** comprises a refractory base **12** on which is mounted a bell **14** having a good sealing contact with the base so as to prevent any oxygen from entering the furnace. It will be understood that in many instances a double bell cover is employed. Mounted within the bell **14** is a heating element **20**, for example an electrical resistance alloy element. The cover is provided with suitable means (not shown) for flushing the space **16** within the cover and to admit a desirably oxygen-free atmosphere therein. Within the bell **14** is disposed a base **22** of a suitable refractory on which is disposed a stack of the silicon-iron sheets **24** with a layer of a refractory powder **26**, such as aluminum oxide, magnesium oxide or the like, applied to the surfaces of the sheets **24**. Strips or plates **28** of an oxygen getter, such as titanium, or of a metal catalyzing the dissociation of molecular hydrogen into atomic hydrogen or both are shown disposed between each of the sheets **24** with the refractory powder **26** applied to the surfaces thereof. It should be understood strip or plates **28** need not be present.

It will be appreciated that coils of magnetic sheet may be annealed as well as stacked sheets. The turns of the coil are separated by a refractory separating layer.

EXAMPLE II

Two ingots were prepared from each of the following alloys:

(1) Silicon 2.8%, manganese 0.033% and the balance being substantially iron

(2) Silicon 2.75%, manganese, 0.13% and the balance substantially all iron.

The ingots were hot roller, pickled and cold rolled following substantially the procedure of Example I, differences from the procedure of Example I being present only during the final anneal. During final annealing the sheets were stacked with finely divided aluminum oxide powder between the laminations with chromium-nickel plates disposed between the successive silicon iron sheets. The stack was then annealed at 1200° C. for five hours in an atmosphere of pure dry hydrogen. After the anneal an examination revealed that alloy No. 2 having the higher manganese content exhibited a considerably more complete secondary recrystallization in the cube-on-face orientation than did alloy 1. Magnetization tests in the direction of rolling indicated that alloy 2 exhibits an induction higher than for alloy 1 by 2 kilogausses at field strengths of from 2 to 6 oersteds. This test indicates a very material improvement in the magnetic properties derived by introducing the indicated amount of manganese.

EXAMPLE III

A 3% silicon iron alloy was prepared and rolled following the procedure of Example I except for the final

anneal. The silicon iron sheets were stacked with separating layers of aluminum oxide powder. The silicon-iron sheets were formed into five separate stacks, and disposed in the aluminum oxide powder between the silicon iron sheets. Each of the stacks contained one of the following metal sheets:

(1) Pure nickel
(2) An alloy of 50% iron, 50% nickel
(3) An alloy of 18% chromium, 82% nickel
(4) An alloy of 30% chromium, 70% iron
(5) An alloy of 3% silicon, 97% iron

After the five hour anneal at 1100° C. in dry hydrogen, the magnetic sheets were all examined and were found to have an appreciable amount of cube-on-face orientation of the crystals. However, from visual examination and other tests it was found that the annealing time required to obtain a given percentage of grains having cube-on-face orientation was much less for the stacks containing the first three metals. Futhermore, the cube-on-face grain orientation was much better, more uniform, and somewhat greater in the presence of the nickel alloys as compared to the last two materials listed having no nickel.

In other tests, 5% by weight of pure nickel chips were added to the aluminum oxide powder and this mixture was applied to the surfaces of the silicon-iron sheets subjected to the final anneal. Equally favorable magnetic properties were obtained in this case as were obtained when using the nickel sheets.

In additional tests the silicon-iron sheets were covered with strips of (1) platinum, (2) an alloy of 95% platinum and 5% iridium, and (3) an alloy of 95% platinum and 5% ruthenium. In all of these cases aluminum oxide powder was interposed between the silicon iron and the sheets of platinum and platinum base alloys. After five hours annealing at 1100° C. in dry hydrogen almost complete recrystallization in the cube-on-face orientation was observed. Even with short annealing times at 1100° C. a substantial amount of cube-on-face orientation had resulted in the presence of the platinum metal. In another test, aluminum oxide powder coated with an evaporated film of platinum equal to 5% of the weight of the aluminum oxide was found to be equally effective to platinum sheets in promoting the recrystallization of the silicon iron in the cube-on-face orientation.

Cobalt can be substituted in whole or in part for the nickel for use in the practice of the present invention. The desirable catalytic effect on the hydrogen leading to improved cube-on-face orientation is obtained if the nickel or cobalt or both are present in the alloys in the amounts of at least 20%, the balance being for example iron, chromium and aluminum. With platinum the alloying content should not exceed approximately 30%.

During the final anneal the atmosphere should comprise at least 50% by volume of hydrogen. Thus, good results have been obtained with atmospheres comprising for example 97% hydrogen and 3% nitrogen.

The optimum magnetic properties in the silicon iron alloys are obtained if all of the conditions set forth herein are combined. The silicon iron alloys should contain the indicated amounts of manganese. Further, the final anneal should be carried out with both the oxygen reactive material, such as titanium, and the atomic hydrogen catalyzing material, such as nickel. With an extremely low partial pressure of oxygen adjacent the surfaces of the sheets being annealed, impurities are removed rapidly by reaction with the atomic hydrogen, and favorable conditions for growth of the crystals having cube-on-face orientation are maintained.

We claim as our invention:

1. In the process of producing a magnetic sheet characterized by a high proportion of grains having a cube-on-face orientation, the steps comprising hot rolling a member of an alloy comprising from 2% to 5% silicon and the balance being iron except for incidental additions and impurities, to produce a thick plate, subjecting the thick plate to a series of cold rolling steps to produce a sheet of the desired final thickness, each cold rolling step effecting a reduction in thickness of from 25% to 90% and the final cold rolling step effecting a reduction in thickness of from 50% to 90%, the sheet being annealed between the successive cold rolling steps at a temperature of from 750° C. to 950° C. in a reducing atmosphere, and subjecting the sheet to a final anneal after the final cold rolling step at a temperature of from 950° C. to 1425° C. for a period of time of from 5 minutes to about 20 hours until substantially complete secondary recrystallization has been effected, the atmosphere during final anneal being a dry reducing atmosphere substantially completely free from oxygen, moisture and oxidizing components which will react with the surface of the sheet and being capable of causing the reduction of silica during the final anneal, the atmosphere, annealing temperature and any materials present on the sheet surface being so correlated that during the initial period of annealing prior to secondary recrystallization any surface oxide films on the sheets will disappear and the sheet will become bright whereby cube-on-face grain growth will predominate during the ensuing secondary recrystallization.

2. The process of claim 1, wherein the alloy further comprises from 0.08% to 3% by weight of manganese.

3. In the process of producing a magnetic sheet characterized by a high proportion of grains having a cube-on-face orientation, the steps comprising hot rolling a member of an alloy comprising from 2% to 5% silicon and the balance being iron except for incidental additions and impurities, to produce a thick plate, subjecting the thick plate to a series of cold rolling steps to produce a sheet of the desired final thickness, each cold rolling step effecting a reduction in thickness of from 25% to 90% and the final cold rolling step effecting a reduction in thickness of from 50% to 90%, the sheet being annealed between the successive cold rolling steps at a temperature of from 750° C. to 950° C. in a reducing atmosphere, and subjecting the sheet to a final anneal after the final cold rolling step at a temperature of from 950° C. to 1425° C. for a period of time of from 5 minutes to about 20 hours until substantially complete secondary recrystallization has been effected, and disposing closely to the surface of the sheet during the final anneal a metal from at least one of the group consisting of nickel, cobalt and platinum and alloys thereof containing at least one of these metals in amounts of at least 20% by weight of nickel, 20% by weight of cobalt and 70% by weight of platinum, the atmosphere during final anneal being a reducing atmosphere substantially free from oxygen, moisture and oxidizing components, and the atmosphere comprising one of the group consisting of hydrogen of a dew point of at least −30° C. and a vacuum at an absolute pressure of not in excess of 10^{-2} mm. of mercury, the atmosphere during final anneal being a reducing atmosphere substantially completely free from oxygen, moisture and oxidizing components which will react with the surface of the sheet and capable of causing the reduction of silica during the final anneal.

4. The process of claim 3, wherein the alloy further comprises from 0.08% to 3% by weight of manganese.

5. In the process of producing a magnetic sheet characterized by a high proportion of grains having a cube-on-face orientation, the steps comprising hot rolling a member of an alloy comprising from 2% to 5% silicon and the balance being iron except for incidental additions and impurities, to produce a thick plate, subjecting the thick plate to a series of cold rolling steps to produce a sheet of the desired final thickness, each cold rolling step effecting a reduction in thickness of from 25% to 90% and the final cold rolling step effecting a reduction

in thickness of from 50% to 90%, the sheet being annealed between the successive cold rolling steps at a temperature of from 750° C. to 950° C. in a reducing atmosphere, placing the sheet in an assembly with surfaces closely adjacent to each other with an inert dry refractory separator between adjacent surfaces, and subjecting the sheet assembly to a final anneal after the final cold rolling step at a temperature of from 1100° C. to 1350° C. for a period of time of from 1 hour to about 20 hours until substantially complete secondary recrystallization has been effected, the atmosphere during final anneal being a dry reducing atmosphere substantially completely free from oxygen, moisture and oxidizing components which will react with the surface of the sheet and capable of causing the reduction of silica during the final anneal, and the atmosphere comprising one of the group consisting of hydrogen of a dew point of at least −40° C. and a vacuum at an absolute pressure of 10^{-3} mm. of mercury, the atmosphere, annealing temperature, and applied refractory separator being so correlated that during the initial period of annealing prior to secondary recrystallization any surface oxide films on the sheets will disappear whereby cube-on-face grain growth will predominate during the ensuing secondary recrystallization.

6. The process of claim 1 wherein an oxygen getter metal selected from the group consisting of titanium and aluminum and base alloys thereof is disposed adjacent the surface of the silicon iron alloy sheets during final anneal in order to reduce the partial pressure of oxygen in the annealing atmosphere.

7. In the process of producing a magnetic sheet having a high proportion of grains having a cube-on-face orientation, the steps comprising hot rolling a member of an alloy comprising from 2% to 5% by weight of silicon, and the balance being iron except for incidental small additions and impurities, to produce a plate of a thickness of the order of from 0.1 inch to 0.25 inch, subjecting the hot rolled plate to a series of cold rolling steps to produce a sheet of a final desired thickness, each cold rolling step effecting a reduction in thickness of from 25% to 90%, and the final cold rolling step effecting a reduction in thickness of from 50% to 90%, the sheet having a thickness of from 0.01 to 0.35 mm. after the final cold rolling step, the sheet being given intermediate anneals between successive cold rolling steps at a temperature of from 750° C. to 950° C. in a reducing atmosphere, wet hydrogen being employed for the first intermediate annealing atmosphere and dry hydrogen of a dew point of −20° C. and lower for the last intermediate annealing atmosphere, the cold rolled sheet being given a final anneal after the final cold rolling step for at least 5 minutes at a temperature of from 950° C. to 1425° C. until substantially complete secondary recrystallization has been effected, the atmosphere during the final anneal being a reducing atmosphere free from oxygen and oxidizing components and moisture, said last reducing atmosphere comprising hydrogen of a dew point of at least −50° C., and capable of effecting the reduction of silicon dioxide at annealing temperature, the atmosphere, annealing temperature and any materials present on the sheet surface being so correlated that during the initial period of annealing prior to secondary recrystallization any surface oxide films on the sheets will disappear and the sheet will become bright whereby cube-on-face grain growth will predominate during the ensuing secondary recrystallization.

8. In the process of producing a magnetic sheet having a high proportion of grains having a cube-on-face orientation, the steps comprising hot rolling a member of an alloy comprising from 2% to 5% by weight of silicon, and the balance being iron except for incidental small additions and impurities, to produce a plate of a thickness of the order of from 0.1 inch to 0.25 inch, subjecting the hot rolled plate to a series of cold rolling steps to produce a sheet of a final desired thickness, each cold rolling step effecting a reduction in thickness of from 25% to 90%, and the final cold rolling step effecting a reduction in thickness of from 50% to 90%, the sheet having a thickness of from 0.01 to 0.35 mm. after the final cold rolling step, the sheet being given intermediate anneal between successive cold rolling steps at a temperature of from 750° C. to 950° C. in a reducing atmosphere, wet hydrogen being employed for the first intermediate annealing atmosphere and dry hydrogen of a dew point of −20° C. and lower for the last intermediate annealing atmosphere, the cold rolled sheet being given a final anneal after the final cold rolling step for at least 5 minutes at a temperature of from 950° C. to 1425° C. until substantially complete secondary recrystallization has been effected, the atmosphere during the final anneal being a reducing atmosphere free from oxygen and oxidizing components and moisture, there being disposed close to the surface of the cold rolled sheets during final anneal a metal of the group consisting of nickel, cobalt and platinum and alloys thereof containing at least one of these metals in amounts of 20% by weight nickel, 20% by weight cobalt and 70% by weight of platinum, and the atmosphere during final anneal comprising one of the groups consisting of hydrogen of a dew point of at least −30° C. and a vacuum at an absolute pressure of not in excess of 10^{-2} mm. of Hg, the sheets after the final anneal being bright.

9. The process of claim 7, in which the alloy comprises from 0.08 to 1% by weight of manganese.

10. In the process of producing a magnetic sheet characterized by a high proportion of grains having a cube-on-face orientation, the steps comprising cold rolling a hot rolled plate of silicon iron alloy composed of from 2% to 5% silicon, and the balance being iron except for incidental impurities to effect at least a final reduction of from 50% to 90%, and subjecting the cold rolled sheet to a final anneal at a temperature of from 950° C. to 1425° C. for a period of time to effect substantially complete secondary recrystallization of the sheet, the atmosphere during final anneal being substantially completely free of oxygen, water vapor and capable of reducing silicon dioxide, there being disposed close to the surface of the cold rolled sheets during final anneal a metal of the group consisting of nickel, cobalt and platinum and alloys thereof containing at least one of these metals in amounts of 20% by weight nickel, 20% by weight cobalt and 70% by weight of platinum, and the atmosphere during final anneal comprising one of the group consisting of hydrogen of a dew point of at least −30° C. and a vacuum at an absolute pressure of not in excess of 10^{-3} mm. of Hg, the sheets after the final anneal being bright.

11. In the process of producing a magnetic sheet having a high proportion of grains having a cube-on-face orientation, the steps comprising hot rolling an alloy comprising from 2% to 5% by weight of silicon, and the balance being iron except for incidental small additions and impurities, to produce a plate of a thickness of the order of from 0.25 inch, subjecting the hot rolled plate to a series of cold rolling steps to produce a sheet of a final desired thickness, each cold rolling step effecting a reduction in thickness of from 25% to 90%, and the final cold rolling step effecting a reduction in thickness of from 50% to 90%, the sheet having a thickness of from 0.01 to 0.35 mm. after the final cold rolling step, the sheet being given intermediate anneals between successive cold rolling steps at a temperature of from 750° C. to 950° C. in a reducing atmosphere, wet hydrogen being employed for the first intermediate annealing atmosphere and dry hydrogen of a dew point of −20° C. and lower for the last intermediate annealing atmosphere, the cold rolled sheet being given a final anneal after the final cold rolling step for at least 5 minutes at a temperature of from 950° C. to 1425° C. until substantially complete secondary recrystallization

has been effected, the atmosphere during the final anneal being a reducing atmosphere free from oxygen and oxidizing components and moisture, said last reducing atmosphere comprising a vacuum at so low an absolute pressure not exceeding 10^{-2} mm. Hg that silicon dioxide will be reduced at the annealing temperatures, the atmosphere, annealing temperature and any materials present on the sheet surface being so correlated that during the initial period of annealing prior to secondary recrystallization any surface oxide films on the sheets will disappear and the sheet will became bright whereby cube-on-face grain growth will predominate during the ensuing secondary recrystallization.

12. In the process of producing magnetic sheets of iron-silicon alloy with a high proportion of cube-on-face grain texture, the alloy comprising from 2% to 5% silicon, up to 3% manganese, the balance being iron and small amounts of incidental impurities, the steps comprising cold rolling the sheet to effect a reduction of at least 50% and a final thickness of from about 0.003 mm. to 0.35 mm., the cold rolled sheet having properties such that on being annealed to effect primary recrystallization thereof the sheet will contain a fine grained structure of various grain orientations having distributed therein small cube-on-face grain nuclei, subjecting the cold rolled sheet of the alloy to a secondary recrystallization anneal, the secondary recrystallization anneal of the sheet

being at a temperature of from 1050° C. to 1350° C. in an atmosphere comprising one of the group consisting of hydrogen of a dew point of at least −30° C. and a vacuum at an absolute pressure of not in excess of 10^{-2} mm. of mercury, the atmosphere being so free of oxidizing components that it is capable at the annealing temperatures of removing silica from the surface of the sheet, the anneal being applied for a period of up to 20 hours, the atmosphere, annealing temperature and any materials present on the sheet surface being so correlated that during the initial period of annealing prior to secondary recrystallization occurring, any surface oxide films on the sheets will disappear and the sheet will become bright, whereby substantially complete secondary recrystallization of the sheet occurs and the cube-on-face grain nuclei grow and the cube-on-face grain texture predominates in the sheet volume.

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