United States Patent Office 3,573,112 Patented Mar. 30, 1971

3,573,112

MAGNETIC SHEETS WITH (100) [hkl] TEXTURE

Robert G. Aspden, Export, Pa., assignor to Westinghouse Electric Corporation, Pittsburgh, Pa.

No Drawing. Continuation-in-part of application Ser. No. 372,693, June 4, 1964. This application Nov. 6, 1967, Ser. No. 681,016

Int. Cl. H01f 1/16

U.S. Cl. 148—31.55 8 Claims

ABSTRACT OF THE DISCLOSURE

Iron or iron-base alloy sheet having a composition in which the gamma phase or face centered lattice structure predominates at elevated temperature while the alpha phase or body centered cubic lattice structure predominates at lower temperature levels, the sheet being composed of a high proportion of alpha phase grains exhibiting a (100) [hkl] texture.

CROSS-REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part of the copending application Ser. No. 372,693, filed June 4, 1964 now Pat. No. 3,351,501, by Robert G. Aspden and entitled "Process for Producing Magnetic Sheets With Cube-On-Face Grain Texture."

BACKGROUND OF THE INVENTION

It has long been desirable to provide magnetic sheets of ferrous base alloys in which the crystal lattices of the grains have a (100) orientation. In recent years a process has been developed for producing sheets of silicon iron having a (100) [001] texture by a series of cold rolling steps and a critical anneal, producing secondary recrystallized grains which have the cube texture. Such process is disclosed in U.S. Pat. 2,992,952. This process is limited to certain alloy compositions and calls for specific cold rolling procedures as well as requiring a critical secondary recrystallization anneal where oxygen and oxides are critically restricted to extremely low values.

For rotating electrical machines such as motors and generators, circular or sector laminations of magnetic sheets having the (100) [001] grain texture may not be as desirable as sheets with a cube-on-face grain texture with the edges randomly oriented, namely the (100) [hkl] orientation. The processes of the prior art do not provide sheets having such random cube-on-face grain texture except by extremely expensive and involved processes.

Practically all processes for producing magnetic sheets having some oriented grain texture cannot be successfully applied to ferrous alloys having a gamma to alpha phase transformation. By "gamma to alpha phase transformation" is meant that the alloy when heated to some elevated temperature, 910° C. for iron alone, but depending on the composition for alloys, the crystal structure of the alloy will transform to the gamma phase or face centered cubic lattice, and upon cooling below this temperature the alloy crystal structure will revert to an alpha or body centered cubic lattice structure. Many ferrous alloys have no gamma to alpha phase transformation, for example silicon-iron alloys having over 2% silicon and carbon below 0.01%. When sheets of an alloy having gamma to alpha phase transformation are annealed according to prior art practices in the gamma region and then cooled into the alpha region, the resulting grain texture is completely random.

As a consequence, all processes in the art directed to obtain a preferred orientation have been applied to treatment of ferrous alloys having no gamma to alpha phase transformation when heated to elevated temperatures above 900° C. as is required for satisfactory annealing or heat treatment thereof. For instance, prior art processes for producing grain oriented magnetic sheets have been restricted to iron-silicon alloys having at least 2% silicon. Again, the process of producing double oriented or cube texture sheets from ingots in which columnar grain growth is relied upon to secure (100) grain texture, can be applied only to ferrous alloy melts not having a gamma to alpha phase transformation since the occurrence of the gamma to alpha transformation causes a randomly oriented columnar structure and as a result no cube texture sheets can be produced by known processes.

When an elevated annealing temperature is applied in an atmosphere taught in the art to sheets of a ferrous alloy which have a gamma to alpha phase transformation, the sheets develop a completely random grain texture, as is taught in U.S. Pat. 3,130,091, entitled "Non-Oriented Silicon-Iron Sheet Stock and Process of Making It." At most, if an alloy having a gamma to alpha phase transformation is processed by any prior art process in order to secure or develop a preferred orientation, it can only be annealed at temperatures below the gamma region, otherwise any cube texture in the grains is lost on reaching the gamma region and cooling back to the alpha region.

SUMMARY OF THE INVENTION

This invention is directed to magnetic sheet material of iron and ferrous base alloys having a (100) [hkl] grain texture.

In accordance with this invention, magnetic sheet or strip is provided which is composed of iron or iron-base alloys characterized by a gamma to alpha phase transformation at elevated temperature, the magnetic sheet or strip having its grains derived from the gamma to alpha phase transformation, a high proportion of the said transformed grains characterized by a (100) [hkl] texture so that over 50% of the sheet area is occupied by such grains.

In the process for making the oriented magnetic material described in copending application Ser. No. 372,693, strip or sheet or punchings or laminations of iron and ferrous base alloys having a gamma to alpha phase transformation generally in a thickness from less than 1 to 150 mils are heated to above the allotropic transformation temperature to develop the gamma phase therein. At this point the metal should have dissolved sulfur in the critical amount of from 0.00003% to 0.0005% at the surface. The gamma phase metal is then cooled through the transformation temperature, or transformation temperature range, to cause a phase change to the alpha phase. By so treating the particular compositions, a high volume of the metal is of cube-on-face or (100) [hkl] texture. The edges are randomly oriented from the [100] to [110] directions. Consequently, improved magnetic properties are available in the resulting members. They are suitable for use in rotating electrical equipment. The sheet or strip can be further cold rolled and annealed whereupon it produces cube texture or (100) [001] grains.

The compositions with which the present invention is concerned are binary and multi-element alloys of iron that have a gamma phase at elevated temperature and contain, as alloying constituents, one or more of the following: up to 2.0% of aluminum, up to 12% of chromium, up to 10% of germanium, up to 5% of manganese, up to 5% of molybdenum, up to 10% of nickel, up to 2% of silicon, up to 1% titanium, up to 1% of tantalum, up to 1% of vanadium, up to 6% of tungsten, up to 20 to 50% of cobalt and up to 1% of zirconium. When carbon is present, its content generally is in the range of 0.001 to

0.08%. The preferred limits for the foregoing alloying elements are: 0.001 to 0.08% of aluminum, up to 2% of chromium, up to 0.5% of germanium, up to 1% of manganese, up to 2% of molybdenum, up to 1% of nickel, up to 2% of silicon, up to 0.5% of titanium, up to 0.5% of tantalum, up to 0.5% of vanadium, up to 0.5% of tungsten, 25 to 45% of cobalt and 0.01 to 0.5% of virconium. In addition to such alloys, the invention can also be practiced with unalloyed iron.

When two or more alloying elements are present in the ferrous alloy, their total amount preferably does not exceed about 50%. Thus, ferrous alloy with over 2% silicon may be employed by incorporating substantial amounts of carbon, molybdenum, nickel, or cobalt which extend the gamma loop. Ternary, quaternary and higher alloys may be employed in practicing the invention. Illustrative examples are: (1) 1.0% silicon, 0.5% molybdenum, .01% carbon, balance iron; (2) 0.6% silicon, 0.3% manganese, 0.01% carbon, balance iron; (3) 1% chromium, 1% cobalt, 0.2% manganese, balance iron; (4) 0.5% silicon, 0.5% chromium, 0.5% nickel, 0.1% manganese, balance iron and (5) 0.8% silicon, 0.01% carbon, 0.5% molybdenum, 0.5% nickel, 0.2% chromium, balance iron. Incidental impurities such as oxygen, nitrogen and traces of various elements may be present. The alloy may be extremely pure or clean, or it may be a regular commercial product, and either will be suitable for the practice of the invention.

Oxygen has been found not to be critical in practicing the invention and relatively large amounts can be present without adverse effects.

The sulfur content and its precise form and distribution is critically important. Sulfur present as inclusions of relatively stable sulfides, such as manganese sulfide, plays no significant part in effecting the desired results of the invention. Sulfur dissolved in the ferrous phase so that it is present in critical proportions at the surface of the sheet is the indispensable constituent. At the time that the gamma to alpha transformation takes place the dissolved sulfur adjacent or at the surface must be within the range of 0.00003% to 0.0005% by weight. The sulfur content of the sheets should be so analyzed as to exclude sulfur as a relatively stable sulfide. A sheet may include a relatively high percentage, say 0.02% of sulfur, which however is nearly all in the form of manganese sulfide, and it will transform to cube-on-face during the gamma to alpha annealing because the dissolved sulfur at the surface is in the critical range.

In order to assure that there is adequate sulfur in the alloy during the gamma to alpha transformation step, particularly if the sheet is low in dissolved sulfur, the furnace atmosphere may be treated to introduce a small amount of hydrogen sulfide, for example 0.001% by volume of the hydrogen sulfide. This not only prevents evaporation of the dissolved sulfur from the metal but may even introduce enough into the metal to bring it into the desired range if the sulfur content is low.

In general, carbon is not a desirable constituent of magnetic sheets, and every effort is made to reduce the carbon content to less than 0.1%, preferably below 0.005% in the final sheet. A decarburization anneal, using wet hydrogen for example 50° F. dew point, at 800° C. to 900° C. for ¼ to 2 hours will reduce the carbon content to a low level. This treatment may precede or follow the gamma to alpha phase transformation of the invention.

The process for making the magnetic material of this invention is quite straightforward, as described in copending application Ser. No. 372,693. Sheets, either hot or cold rolled, of iron or a ferrous base alloy having a gamma to alpha phase transformation are subjected to a relatively simple annealing process passing from the gamma to alpha region to produce a random cube-on-face or (100) [*hkl*] grain texture, by suitable control of the composition as to provide a critical dissolved sulfur content therein during the gamma to alpha transformation during the anneal. The process is not only relatively simple, but is quite economical. The resulting product is commercially highly desirable.

Iron and its alloys used in making the magnetic material of this invention generally are in sheet or strip form of about 0.001 to 0.150 inch in thickness, though it has been found that the process is essentially insensitive to the thickness of the material being processed. Generally, sheet or strip material is produced by forging or hot rolling a slab directly to the desired thickness or to an intermediate thickness on the order of about 0.1 to 0.5 inch. The intermediate thickness is then reduced by cold rolling to the final thickness in one or more stages. Each stage comprises a cold rolling anneal, and pickling if necessary. At any convenient stage during the processing, the strip or sheet can be decarburized by annealing in the decarburizing atmosphere, for example wet hydrogen, that is hydrogen saturated with water vapor at about 20° to 50° C. When cold rolling is practiced, reduction at each stage on the order of 40 to 90% generally are taken.

In making the alloy sheet of the present invention use is made of the transition of iron or ferrous base alloy from the gamma phase at an elevated temperature of about 900° C. (depending on composition) to the alpha phase at a lower temperature. This allotropic transformation occurs at temperatures dependent on the specific composition being processed. For example, for ordinary iron-silicon alloys with a silicon content ranging up to about 2%, it is generally in the range of about 900° to 1000° C. In any event, a critical step in the process involves annealing the material at a temperature, for a period ranging from about 10 minutes, though it may be 30 hours or more, such temperature being in the gamma region for the material being treated. Generally, for purposes of insuring this, annealing is conducted at about 10° to 300° C. above the temperature at which the transition starts but clearly in the gamma region in all events. Thereafter the material is cooled, preferably, though not necessarily slowly cooled, through the allotropic transformation temperature, suitably to about 10° to 100° C. below it. Slow cooling at a rate below about 175° C. per hour and suitably in the range of about 4° to 12° C. per hour results in very large grain growth of the (100) [*hkl*] grains. Thereafter the treated material can be cooled as desired to room temperature and used. Also cooling the sheets rapidly to a temperature of about 10° to 200° C. below the temperature at which the transformation occurs and holding the sheets at this temperature for about 2 to 50 hours tends to convert the grain structure from one containing a substructure to one free from substructure, through selective growth of the (100) grains to a very large size and thereby further improve the magnetic properties.

Moreover, the material containing the (100) [*hkl*] texture can be further cold rolled, i.e. at about a 60 to 80% reduction, and again be given a heat treatment to produce oriented material having a cube or (100) [001] texture.

As previously mentioned, the development of the (100) [*hkl*] texture of the present invention is critically influenced by employing a selective driving force for (100) grain growth during the allotropic transformation. In this invention the driving force is provided by the presence of the critical amounts of sulfur during the gamma to alpha transformation. The sulfur can be present as an alloying constituent in the metal being treated or it can be supplied in part or entirely by an addition of a sulfur material to the atmosphere in which the process is carried out. Sulfur has also been supplied by treating material, that may be present during the annealing, with H_2S, for example an Al_2O_3 sheet separator material which evolves the sulfur by appropriate vapor pressure development. Sufficient sulfur is present for driving purposes when the alloy contains dissolved sulfur to an extent of 0.00003 to 0.0005% of the alloy or the atmosphere is provided with

a sulfur-containing compound, preferably hydrogen sulfide, in an amount to provide a partial pressure of sulfur which would produce or maintain an equilibrium condition at least at the surface of the sheet in this range.

In annealing the metal sheets, strip or punchings or the like in stack or coiled form, the metal must contain dissolved sulfur in essentially the critical proportions of 0.00003% to 0.0005% at the time of the phase transformation. A slight excess of dissolved sulfur may be present in the metal since a small portion of the sulfur is evolved during the anneal, so that the dissolved sulfur content at the sheet surface will be in the proper range at the time the metal is in the gamma to alpha transformation temperature range whereby cube grain growth takes place. Reference should be had to copending application Ser. No. 154,803, filed Nov. 24, 1961, and particularly the drawings which show the loss of sulfur from stacks and single strips at elevated temperatures. If the sulfur content is at or slightly below the lower limit an atmosphere containing hydrogen sulfide in amounts from 2 to 30 parts per million by volume, may be flowed past the laminations in order to maintain or increase the dissolved sulfur in the ferrous metal into the critical range of from 0.00003% to 0.0005%.

When annealing a single sheet or a strip of the ferrous metal, the rate of evolution of sulfur from the surface of the metal is relatively high if the atmosphere contains no sulfur-bearing gas. Consequently, when annealing in such a relatively sulfur free atmosphere, a strip having a dissolved sulfur content above the critical range would be employed. Upon reaching the annealing temperature sulfur is removed from the surface to such an extent that after a period of time the dissolved sulfur in the surface areas of the strip is in the critical range so that cube grains will nucleate at the surface and grow inwardly during the gamma to alpha transformation. Such cube grains will extend into the interior of the strip which may still contain sulfur at a higher level, namely, above the upper critical limit, than at the surface. A strip anneal may be carried out at a rate such that the strip is at temperatures in the gamma region for about 5 to 15 minutes. Longer times may be employed but will be generally uneconomical.

Inversely, I have taken strips of pure iron which had a low dissolved sulfur content such that after annealing in pure hydrogen (—50° C. dew point) for 64 hours at 1200° C., the total sulfur was about 0.00001%. Upon cooling the strip to below 900° C., some 20% to 30% of the area comprised cube grains. However, upon adding small amounts of hydrogen sulfide to the hydrogen gas, the percentage of cube grain growth increased with the amount of hydrogen sulfide, reaching a peak of about 77% at 7 parts of hydrogen sulfide per million of hydrogen. This corresponds to a sulfur content at the surface of the sheet of 0.0001%. The optimum range of hydrogen sulfide to hydrogen is from 2 to 20 parts per million. In these examples, at the center of the strip the sulfur was below the lower limit of the critical range. When the hydrogen sulfide content reached 40 or more parts per million, cube grain growth drops to 20 to 30% of the sheet area, since the surface contained sulfur above the upper limit of the critical range.

These tests confirm the critical nature of the dissolved sulfur content at the surface of the ferrous sheets. A dynamic equilibrium of sulfur content occurs between the atmosphere, the surface of the sheet and the center of the sheet. The process therefore should be so practiced that the sulfur content at the surfaces of the sheets is in the desired range during the gamma to alpha transformation.

For stack or coil annealing of ferrous base alloys which it is anticipated will have large excesses of sulfur which would be difficult to reduce to the critical sulfur content, additions of up to 0.5% by weight of elements which have a high affinity for sulfur may be made. Such additions to the alloys of this invention which have bulk sulfur concentrations above the critical range will aid in obtaining the cube growth texture by reducing the amount of sulfur in solution by reason of the formation of very stable sulfides. Such elements, in addition to manganese, are barium, calcium, cerium, strontium and the rare earth elements such as lanthanum which forms stable sulfides.

In determining the critical range of dissolved sulfur which may be present in the alloy strip prior to annealing, various procedures and tests were employed. The limits for dissolved sulfur in the ferrous alloys was determined by the following technique. Sheets of pure iron or pure iron-silicon alloys, for instance, were equilibrated at 1200° C. for 16 hours in atmospheres containing predetermined proportions of hydrogen sulfide—ranging from zero to 200 parts per million of hydrogen sulfide. Under these conditions the surface of the sheets had a sulfur content essentially identical with the bulk sulfur content. Bulk sulfur analyses were made employing the extremely sensitive test using methylene blue as set forth in detail in application Ser. No. 154,803. No appreciable amounts of manganese or other stable sulfides were present in these test sheets.

While analytical procedures may be resorted to to determine the amount of dissolved sulfur in the ferrous sheet, the following practical test will enable one to determine rapidly and easily whether or not the ferrous metal contains dissolved sulfur in the critical range. At least three samples are cut off the ferrous metal strip being tested and they are heated to 1000° C. for 5 minutes in the following respective atmospheres: (a) dry hydrogen of a —50° C. dew point, (b) dry hydrogen with 5 parts per million of H_2S, and (c) dry hydrogen with 30 parts per million of H_2S. Upon furnace cooling to room temperature, the proportion of cube grains is determined for each sample. If the dissolved sulfur in the sample is at the lower limit of the critical range, the cube grain growth will be low in atmosphere (a), and high in atmosphere (b) and highest in atmosphere (c). If the dissolved sulfur is in the middle of the critical range, for instance half way between 0.00003% and 0.0005%, then cube grain growth in atmospheres (a) and (b) will be high while it will be moderate in atmosphere (c). For a sample having close to 0.0005% dissolved sulfur, the grain growth will be highest in atmospheres (a) and (b) and low in atmosphere (c). Refinements of these tests may be made, employing for instance five samples and five different hydrogen sulfide atmospheres.

Subject to this limitation regarding the necessity for critical proportions of sulfur in the surface of the sheet, the transformation can be carried out in a neutral or non-oxidizing atmosphere or in a reducing atmosphere that tends to produce a bright surface on the metal being treated at the time of transformation. Thus, the transformation can be carried out in a vacuum of at least as low as 10^{-4} mm. of Hg or in a reducing gas such as dry hydrogen, or in argon, helium, nitrogen or mixtures of gases, as for example, nitrogen and hydrogen. Where the material being treated does not develop objectional amounts of surface oxides in the presence of water vapor, the atmosphere can contain water vapor as would for example, be present in wet hydrogen (20° to 50° C. dew point) for pure iron for example and this in some cases tends to benefit the surface energy relationship that functions as a driving force. For silicon-iron alloys the atmosphere should be relatively dry, for instance of a dew point of —35° C. or lower.

Upon conclusion of this process the metal treated, whether in strip, sheet, or other form such as Epstein strips or stator punchings or the like, has a (100) [*hkl*] texture ranging from about 50% to 98% of its crystal volume or surface area. This proportion is based on counting grains whose cube faces are parallel within 12° to the surface of the sheet. Usually 40 to 50% of the grains have faces within 2° of the surface, and another

20% to 30% within 2° to 6°. The magnetic properties are outstanding.

For commercial use it is desirable that the (100) [*hkl*] texture produced in accordance with this invention be present to an extent of about 70% and preferably 80% and higher of the surface of the sheets. For those members in which such a texture is produced in at least 80% of the surface, there can be applied additional processing to produce a cube texture material. Thus when processing has achieved such a cube-on-face sheet, upon applying a further cold reduction of about 60 to 80% followed by an anneal of the material just below (i.e., 10° to 100° C.) the allotropic transformation temperature, for example at 800° C. to 900° C., there is obtained cube texture material; that is, (100) [001] orientation. By this latter orientation is meant to indicate that at least 80% of the surface area is occupied by (100) grains at least 75% of which have their [001] directions aligned within 15° of the rolling direction. The anneal below the allotropic transformation temperature secures secondary recrystallization of the (100) grains which grow to an average diameter which is many times the sheet thickness averaging well above 10 times the said thickness. This last anneal extends for about 10 to 100 hours or more and is carried out in the same conditions of atmosphere, and therefore driving force, as that indicated hereinbefore with respect to producing (100) [*hkl*] texture.

It is the object of this invention to provide magnetic sheets of iron and ferrous base alloys having a gamma to alpha phase transformation, the sheets having a random (100) [*hkl*] grain texture.

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

DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention will be described further in conjunction with the following specific examples in which the details are given by way of illustration and not by way of limitation.

Material for the following examples generally was prepared by melting, usually in a vacuum furnace, the appropriate charge contained in a magnesia crucible and then pouring the melt into a stainless steel mold. Purified iron, where its use is indicated, was obtained for this purpose by annealing electrolytic iron one hour at 760° C. in wet hydrogen followed by one hour at 1200° C. in dry hydrogen. Further, the annealing referred to in the examples, was unless otherwise stated, stack annealing using alumina as a separator and a hydrogen atmosphere of a dew point of less than −35° C.

In the following specific examples, the sulfur content values given are the total sulfur in the ferrous metal prior to annealing. A substantial or even a major proportion of the sulfur is bound as stable sulfides and plays little part in the cube grain growth process. Also some of the sulfur may be removed during annealing if the atmosphere is below the equilibrium sulfur content whereby a sulfur gradient exists between the center of each sheet and its surface. In each example where 50% or more of cube grain growth occurred, the dissolved sulfur at the surface was in the range of 0.00003% to 0.0005%.

Example I

A sheet of 12 mil thick commercial ingot iron was used having the following composition by weight: 0.003% aluminum present as Al_2O_3, 0.002% N, 0.39% Mn, 0.17% Cu, 0.11% P, 0.03% C, 0.022% S and the remainder iron. The sample was annealed in dry hydrogen −35° C. dew points for one hour at about 1210° C. (about 300° C. above the gamma to alpha transition temperature) and then slowly cooled, about 110° C. per hour, to a temperature of about 860° C., which is about 50° C. below the alpha to gamma transition temperature, and then cooled to room temperature. A study was performed on the resulting sheet in which etch pits were developed by etching with a solution containing 1 part HNO_3 and 99 parts of ethyl alcohol. Domain patterns were superimposed on the resulting surface. The surface area of the specimen was found to have 54% (100) planes which were within 14° of the surface of the sheet. There was a random distribution of directions of the [001] zones in the initial rolling direction.

The evidence indicated that the dissolved sulfur was at a critical limit of the necessary sulfur range during the anneal whereby only 54% of the area comprised grains having the (100) texture. In other experiments on similar alloys, close control of the sulfur yielded material having over 80% of the area thereof composed of the (100) texture.

Example II

An iron base alloy containing about 1.11% of silicon was prepared by vacuum melting purified electrolytic iron and commercial grade silicon. This alloy was melted in a magnesia crucible and poured into a stainless steel mold. The analysis, by weight, was 0.0013% of oxygen, 0.0009% of nitrogen, 0.0015% of carbon, 0.0013% of sulfur, 1.11% of silicon and the remainder iron.

The alloy was hot rolled to sheet at a temperature in the range of 800° to 1050° C. to a thickness of 0.100 inch, pickled in a 25% sulfuric acid solution, and then cold rolled to a sheet thickness of 0.018 inch. Epstein strips ($1\frac{3}{16}$" x 12") were sheared from the sheet and annealed in a stack with dry alumina as a separator. All annealing as hereinafter indicated was done in an Inconel tube in an atmosphere of dry hydrogen (−50° C. dew point).

Stacks of the Epstein strips were annealed by heating for 4 hours at 1150° C., and then cooling at 20° C. per hour through the transformation range to 880° C. Specimens were tested for magnetic properties and found to be markedly superior to commercially available material of the same general analysis but which was not treated as just described. The 60 cycle A.C. losses at 15 kilogauss was 1.55 watts/lb., whereas commercial silicon 1.1% silicon steel had losses of 3.2 watts and higher. In the strips of this example the amount of surface area occupied by (100) grains within 12° of the rolling plane, as determined by a modified intercept method, was 88%.

Example III

A series of tests were made on iron-oxygen alloy sheets containing 0.0010 to 0.0023% sulfur and in which the oxygen was varied from 0.0010 to 0.0335%; specimens of each composition were annealed at 1050° C. for 12 to 16 hours and then cooled at 4° to 10° C. per hour to the alpha region, and other specimens were annealed for the same period but at the higher temperature of 1200° C. and then cooled at 4° to 10° C. per hour to the alpha region. It was found that changes of the oxygen concentration did not appreciably influence the amount of (001) [*hkl*] resulting. However, the annealing temperature did influence the results, with the lower (1050° C.) temperature being the better, resulting in a smaller grain size and a larger amout of (100) [*hkl*] texture which varied from 51 to 80% of the surface.

Example IV

A similar series of tests were made on iron-manganese-sulfur alloys containing about 0.093% of manganese in all instances, with the sulfur ranging from 0.0015 to 0.022%. Here again the best results were achieved in the heat treating schedule that included the anneal at 1050° C., with the amount of (100) [*hkl*] texture ranging from 83.3 to 90.2% of the surface area. It was also discovered that the presence of manganese, along with the necessary dissolved sulfur had a beneficial influence on (100) grain growth.

Example V

An alloy slab containing, by weight, 27% of cobalt, 0.1% manganese, about 0.02% sulfur and the remainder

essentially iron was hot rolled at 1000° C. to a band 100 mils thick. The hot rolled band was pickled to remove scale, and it was then cold rolled to 14 mil strip. That strip was placed in a furnace at 800° C. and heated within the furnace to 1150° C. in an atmosphere of dry hydrogen. After 16 hours the strip was furnace cooled (below 12° C. per hour) to 800° C. It is to be noted that the alpha to gamma transformation temperature for this composition is approximately 950° C.

Using an etch pit method in which etch pits are developed by etching in a solution containing 241 grams of ferric ammonium sulfate, 40 cc. of sulfuric acid and 1000 cc. of water, it was determined that 70% of the surface area of the sheet had undergone transformation to the (100) [*hkl*] texture.

Example VI

Strip of a thickness of 18 mils of cold rolled iron-molybdenum having an analysis, by weight, of 0.0112% of oxygen, 0.0027% of carbon, about 0.0005% of sulfur, 0.99% of molybdenum and the remainder iron was annealed in the gamma range and then slowly cooled through the transition in the same manner and under the conditions set forth in Example III above. The treatment including the anneal at 1050° C. was superior, and indeed resulted in one of the highest value of (100) [*hkl*] texture achieved in any of these tests, 93.5%.

In the examples given so far the critical processing step of slowly cooling through the transition temperature range was by stationary furnace cooling. Of course other procedures may be used to accomplish that step as, for example, that given in the next example.

Example VII

Single strips of the iron-molybdenum alloy analysis set forth in Example VI were inserted into a tube furnace at 1140° C. and positioned with one end of each strip in the hot zone and the other in the cold zone. The strips were held in this position for about 1 or 2 hours and then pulled at different rates into a cooling chamber. A portion of each strip that was at a temperature in the gamma temperature region was found to have developed (100) [*hkl*] texture in inverse proportion to the rate of withdrawal, and therefore the rate of cooling through the transition temperature.

Many other tests of the invention have been made using iron base alloys containing, for example, about 1% Mn or 0.25% of aluminum with equally satisfactory results. In other tests, alloy strip as described was annealed at 1000° to 1300° C., slowly cooled through the transition temperature and then further annealed below the transition temperature, i.e. at 800° C., for about 5 to 120 hours in the sulfur-containing, non-oxidizing atmosphere suitable to the growth of (100) grains. This latter procedure tends to remove substructure thereby contributing to improved magnetic qualities.

As disclosed above, material having a (100) [*hkl*] texture can be further treated, in accordance with my discoveries, to develop (100) [001] orientation. The following is an example thereof which also demonstrates the desirability of the requirement of starting with at least 80% (100) [*hkl*] texture for this particular discovery.

Example VIII

Materials of two different analyses were used. One was that set forth in Example VI and is identified hereinafter as alloy B, while the other had an analysis, by weight, of 0.0025% of sulfur, 0.0016% of carbon, 0.0002% of nitrogen, 0.0076% of oxygen and the remainder iron and is hereinafter called alloy A. These alloys were prepared by vacuum induction melting, and sheet was obtained therefrom by hot rolling at 1050° C., pickling, and then cold rolling to 0.012 inch for alloy A and cold rolling to 0.018 inch for alloy B.

Alloy A was annealed in the gamma phase by heating at 1050° C. for 8 hours followed by cooling at 8° C. per hour through the allotropic transformation temperature to 880° C. Alloy B was annealed in the gamma phase by heating at 1050° C. for 12 hours followed by cooling through the allotropic transformation temperature at 4° C. per hour to 880° C. The anneals for both alloys were conducted in dry hydrogen (below −50° C. dew point) containing traces of sulfur. A study of the grains in the resulting product showed that those in alloy A contained 51 to 71.6% of (100) grains within 12° of the rolling plane while alloy B contained 89.7 to 93.9% of its (100) grains within 12° of the rolling plane. Samples of the specimens of each alloy were then cold reduced 70%, followed by annealing for 60 hours at 880° C. in an atmosphere of the dry hydrogen indicated above. During this anneal (100) grains grew to a diameter many times the sheet thickness by secondary recrystallization. The percentage of surface area occupied by (100) grains in alloy A was 80.1% while the percentage for alloy B was 85.62%. The specific grains were then studied and it was found that alloy A had 40.7% of its (100) grains with its [001] directions within 15° of the rolling direction while 77.5% of the grains in alloy B were found to have the [001] directions within 15° of the rolling direction. The foregoing example thereby demonstrates the uniquely simple way of producing (100) [001] texture and further demonstrates the criticality of the quantity of (100) [*hkl*] texture that must be present before the final cold reduction and annealing below the allotropic transformation temperature that develops the (100) [001] orientation.

In further tests of the type described in Example VIII, it has been determined that where the (100) [*hkl*] orientation is to be developed, it is possible to cool at higher rates from the gamma phase to the alpha phase and the slow cooling limitation associated in the other examples with development of a substantial percentage of (100) [*hkl*] texture need not be followed. In still further tests of the embodiments of the invention in which the (100) [*hkl*] texture or (100) [001] orientation are developed, it has been found that magnetic annealing, that is cooling the strip or other shape while it is subject to a magnetic field in a field of at least 10 oersteds, brings about further improvement in the quality of domain orientation obtained. Where such magnetic annealing is practiced, it can be used while cooling to a temperature as low as about 300° C.

Unless otherwise noted or apparent, the annealing indicated in the foregoing examples was conducted in dry hydrogen (−50° C. dew point). In other tests, the procedure was changed to substitute +20° C. dew point hydrogen. For those alloys that were insensitive to water vapor, e.g. iron-molybdenum and the like, the desired (100) [*hkl*] texture was still achieved. However, for alloys that thereby developed a heavy oxide surface film, e.g. iron-silicon alloys, a low value of the desired texture resulted thereby indicating the need to anneal at conditions that result in a bright surface during the phase change.

Numerous samples of strip, sheet, Epstein punchings and the like prepared in accordance with the invention as described have been tested for their desired characteristics. As expected, materially lower A.C. losses, compared to analogous commercially available material, were found in all instances. Percentages and parts given herein are by weight unless otherwise indicated or apparent.

From the foregoing discussion and description it is evident that the present invention has provided iron and iron base alloys having a unique texture and therefore improved magnetic properties. While the invention has been described in detail with reference to particular alloys, it should be understood that changes, substitutions and the like can be made without departing from the scope and clear teachings of the invention. Using the principles set

forth herein, numerous variations thereof will be apparent to those skilled in the art.

I claim as my invention:

1. A heat treated sheet of metal selected from the group consisting of iron and ferrous-base alloy characterized by a stable alpha phase at room temperature and which transforms to the gamma phase at selected elevated temperature, the sheet having over 50% of its surface area containing grains having a (100) [*hkl*] orientation.

2. The heat treated sheet of claim 1 wherein the metal is commercial ingot iron, and at least 80% of the alpha phase grains have the (100) [*hkl*] orientation.

3. The heat treated sheet of claim 1 wherein the metal is a ferrous-base alloy containing up to 2% by weight of silicon, balance iron except for small amounts of incidental impurities, at least 80% of the alpha phase grains having the (100) [*hkl*] orientation.

4. The heat treated sheet of claim 1 wherein the metal is a ferrous-base alloy containing from 25% to 45% by weight of cobalt, balance essentially iron except for small amounts of incidental impurities.

5. The heat treated sheet of claim 1 wherein the metal is a ferrous-base alloy containing up to 2% by weight of molybdenum, balance essentially iron except for small amounts of incidental impurities, at least 80% of the alpha phase grains having the (100) [*hkl*] orientation.

6. The heat treated sheet of claim 1 wherein the metal is a ferrous-base alloy containing about 1% by weight of manganese, balance essentially iron except for small amounts of incidental impurities.

7. The heat treated sheet of claim 1 wherein the metal is a ferrous-base alloy containing about 0.25% by weight of aluminum, balance essentially iron except for small amounts of incidental impurities.

8. A sheet of a metal having a gamma to alpha phase transformation, the metal being a ferrous-base alloy containing, by weight, at least one element selected from the group consisting of up to 2% of aluminum, up to 12% of chromium, up to 10% of germanium, up to 5% of manganese, up to 5% of molybdenum, up to 10% of nickel, up to 2% of silicon, up to 1% of titanium, up to 1% of tantalum, up to 1% of vanadium, up to 6% of tungsten, up to from 20% to 50% of cobalt, up to 1% of zirconium and from 0.001 to 0.08% of carbon, the total amount of such elements not exceeding 50%, by weight, of the alloy when more than one of said elements is present, the sheet having over 50% of its area comprised of grains derived from the gamma to alpha phase transformation, said grains having a (100) [*hkl*] orientation.

References Cited

UNITED STATES PATENTS

3,008,857	11/1961	Möbius	148—111
3,061,486	10/1962	Jackson	148—111
3,089,795	5/1963	Hu	148—112X
3,130,090	4/1964	Jackson	148—111X
3,218,202	11/1965	Ganz	148—111X
3,240,638	3/1966	Weiner	148—111X
3,287,184	11/1966	Koh	148—113

L. DEWAYNE RUTLEDGE, Primary Examiner

G. K. WHITE, Assistant Examiner

U.S. Cl. X.R.

148—111, 112