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D. M. KOHLER ETAL
 PRODUCTION OF ORIENTED SILICON-IRON SHEETS
 BY SECONDARY RECRYSTALLIZATION
 Filed May 14, 1959

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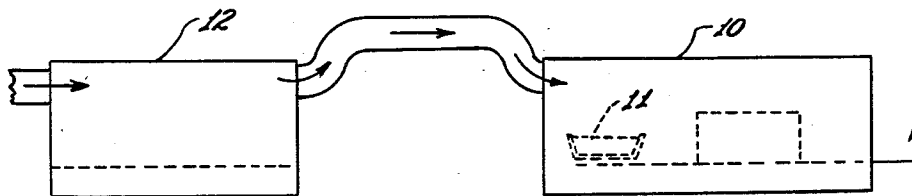


FIG. 1.

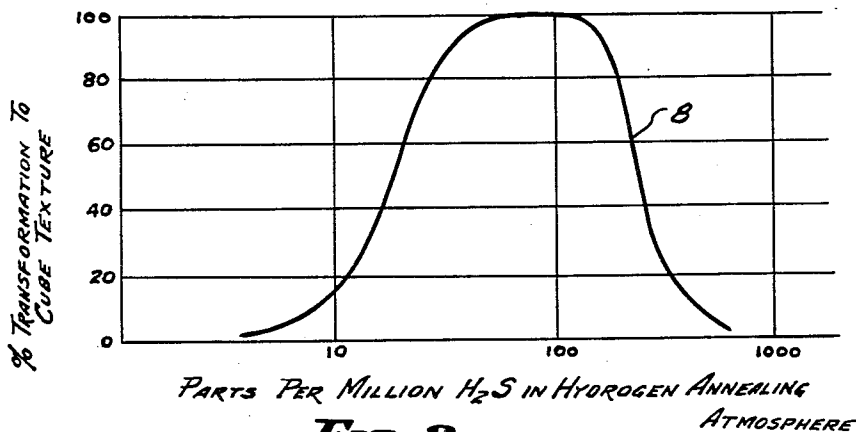


FIG. 2.

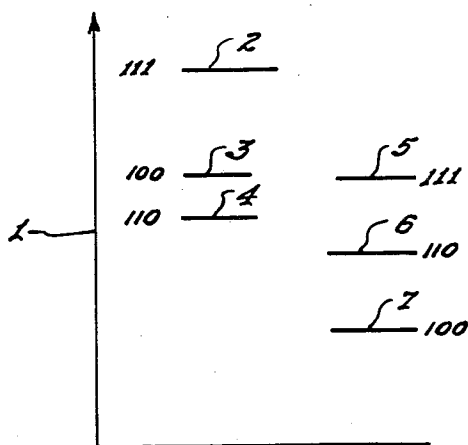


FIG. 3.

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PRODUCTION OF ORIENTED SILICON-IRON SHEETS BY SECONDARY RECRYSTALLIZATION

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7 Claims. (Cl. 148—113)

The invention has to do with the production of highly oriented silicon-iron in sheet form, and it will be described in connection with the manufacture of silicon-iron having an orientation in which a (100) plane is parallel to the sheet surface, and more particularly one which can be described as a (100) [001] orientation by Miller's indices. For convenience this orientation will hereinafter be designated as "cubic texture."

It has hitherto been understood that if a silicon-iron sheet is made having a number of the grains oriented in the cubic texture and if such a sheet is then subjected to secondary recrystallization at high temperature, under certain limiting circumstances, the grains so oriented will tend to grow at the expense of other grains in different orientations, producing ultimately a product having a high degree of cubic texture. The same thing is true for grains having a (100) plane parallel to the sheet surface, irrespective of the orientation of the [001] direction. The silicon-iron itself should have a high degree of purity and should be as free as possible from silica and other oxide inclusions.

The limiting circumstances have previously been understood as freedom of the surfaces of the stock from oxides of all kinds, the use of annealing separators of high purity, the use of metallic furnace chambers, and the use of annealing atmospheres also of high purity. European investigators have for the most part taught that the silicon-iron must be made by vacuum melting procedures, which are expensive. In both Europe and America efforts have been made, by carrying the stock through a series of successive preferred orientations of different types to arrive at an orientation which after primary recrystallization, will give a stock having as large a number as possible of nuclei having the desired cubic texture, thus making for an easier conversion of the product in a secondary recrystallization step.

Despite these efforts, difficulties have been encountered with the dependable commercial production of satisfactory stocks. The best results have been attained with very thin stocks, say sheets having a thickness of 1 to 3 mils or thereabout.

It is a fundamental object of this invention to provide a process of making oriented silicon-iron sheet stocks, and particularly those of cubic texture, which process is essentially free from the limiting circumstances outlined above; and it is also an object of the invention to provide a procedure for the dependable production of oriented silicon-iron sheets of substantial thickness, and for the production of oriented silicon-iron stocks from materials which have been produced by air melting, as in the conventional open hearth furnace.

These and other objects of the invention which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications are accomplished by those procedures of which certain exemplary embodiments will hereinafter be described. Reference is made to the accompanying drawings wherein:

FIG. 1 is a diagrammatic representation of an annealing furnace and an associated gas treating apparatus.

FIG. 2 is a chart showing the relationship of the concentration of an additive to the annealing atmosphere,

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to the degree of transformation of the silicon-iron sheet stock to cubic texture.

FIG. 3 is an energy diagram.

A silicon-iron sheet stock in which the (100) planes of the crystals are parallel with the sheet surfaces, the [001] direction being randomly oriented, may have permeabilities substantially equal in the straight grain and cross rolling directions, but will have a higher permeability than that of a sheet stock characterized by truly random orientation. A silicon-iron sheet stock characterized by a high degree of cubic texture is especially useful in the electrical arts because while it may have a permeability in the straight grain direction which is as high as or higher than that characteristic of any other orientation, it also has a relatively high permeability in the cross grain direction.

The present invention is based on the discovery that the presence in the annealing atmosphere, during secondary recrystallization, of minute amounts of certain highly polar compounds greatly facilitates the growth of crystals or grains having certain orientations at the expense of grains having other orientations in the silicon-iron sheet stock.

The phenomenon of differential crystal growth is due to the fact that certain orientations constitute lower energy positions as respects others, those crystals or grains which occupy lower energy positions tending to grow at the expense of those in higher energy positions. It is possible to grow crystals during secondary recrystallization which have their (111) planes, or (100) planes or (110) planes parallel to the surfaces of the sheet stock. In the preceding sentence crystals having the respective orientations have been mentioned in their normal descending order of surface energy.

It is believed that the surface energy of a crystal is dependent upon the number of unsatisfied bonds in the crystal planes which appear at the sheet surface. This in turn is dependent upon the arrangement of the atoms in the said crystal planes.

While there is no intention to be found herein by theory, it is believed that the use in the proper amounts of the highly polar compounds mentioned above changes the relative surface energies of the grains at least at the surfaces of the sheet by satisfying these bonds to a greater or lesser degree. The action is apparently a differential one, for while crystals of any orientation will have their surface energies lowered in the planes parallel to the sheet surfaces, the surface energies of those grains which have their (100) planes lying in parallelism with the sheet surfaces will be lowered to the extent that their surface energies become the lowest of all orientations.

This is illustrated in a purely diagrammatic fashion in FIG. 3 where the arrow 1 which may be regarded as indicating ascending values of surface energies, carries opposite it certain planes 2, 3 and 4 which are representative of surface energy levels for crystals respectively oriented with the (111), (100) and (110) planes parallel to the surfaces of the sheet. By the treatment hereinafter outlined the surface energy of grains having the (111) orientation may be lowered to the level 5, while the surface energy of grains having the (110) orientation may be lowered to the level 6 and the surface energy of grains having the (100) orientation lowered to the level 7, thereby reversing in part the order and making the (100) orientation the lowest of all. It will be clear that in a sheet of silicon-iron characterized by grains having these orientations the tendency of the (100) grains to grow at the expense of other grains in the sheet will be greatly enhanced by this rearrangement of the surface energies. If the amounts of the highly polar compounds present in the annealing atmosphere adjacent the surfaces of the grains are not properly adjusted, it is possible to

cause the (110) or (111) surface planes to have the lowest energy and hence to cause grains having these planes in the surface to grow at the expense of the desired (100) grains.

It is believed that the highly polar compounds of which mention has been made lower the surface energy of crystals in their planes which lie parallel to the sheet surface by being absorbed or adsorbed on or in the surfaces so as to satisfy the positive unsatisfied charges of the atoms in the surface planes.

The highly polar compounds thus far investigated include oxides of carbon, oxides of sulphur, and hydrogen sulfide. It is believed that other highly polar compounds may well be the equivalents of those just mentioned. For example, hydrogen selenide would presumably act in the same way as hydrogen sulfide. Sulfur and carbon, however, are inexpensive materials with which to work. It is not believed that carbon and its compounds are as effective as sulphur and its compounds; but there is evidence indicating that the combination of a sulphur compound and a carbon compound is more effective than a sulphur compound alone.

The quantities of the highly polar compounds used in the annealing gases are small, and must be confined between fairly narrow limits. Too little will not give the desired result, while, after a certain optimum is exceeded, the addition of further quantities results in a falling off of the transformation. This is illustrated in FIG. 2 which plots the results of a series of anneals at 2200° F. (in a muffle) using samples 3 cm. wide, where parts per million of hydrogen sulfide in a dry hydrogen annealing atmosphere having a dew point of -50° F. are plotted against the percentage of transformation to the cubic texture. The curve marked 8 represents a material having a thickness of 12 mils. The curve in FIG. 2 is submitted only as representative or illustrative since the percentage of transformation can be affected by various factors; and the concentration of hydrogen sulfide for optimum results will vary somewhat depending on the width of the material being annealed, the size of the charge, the rate of gas flow and the annealing temperature. In general hydrogen sulfide, present in the annealing atmosphere at the surface of the material should be confined substantially, say, to between 20 parts per million and 250 parts per million. There is generally an optimum effect in a narrower range within these limits. In large charges and using wide commercial widths it may be necessary under certain conditions to maintain a higher concentration around the outside of the charge.

The manner in which the highly polar substances are introduced into the annealing atmosphere may be varied. First, if the base silicon-iron stock itself contains sulfur, as much of this sulfur as migrates to the surface of the stock can combine with constituents of an annealing atmosphere to form a polar compound. But a high content of sulfur in silicon-iron sheet stock is undesirable for other reasons. Moreover, the transformation of the stock to cubic texture requires a high temperature secondary recrystallization varying in time with the thickness of the stock; and the proper sulfur content of the atmosphere should be maintained throughout the entire time of the transformation of the stock. It has not been found feasible to rely solely on the sulfur content of the stock itself, nor to apportion the quantity of sulfur in the stock so as to maintain the sulfur content of the atmosphere continuously in the proper range throughout the entire secondary recrystallization. The practice of the invention however, does not exclude the presence of some sulfur in the annealing atmosphere which is derived from the stock, nor is it limited to the treatment of stocks which are sulfur-free or very low in sulfur.

Second, the highly polar compounds can be formed in the annealing atmosphere from constituents in an annealing separator located between silicon-iron sheets in a stack or between the convolutions of a coil. Thus, a

quantity of calcium sulfide in an annealing separator (which otherwise may consist of calcined magnesia, alumina or other suitable substances) may react with a hydrogen annealing atmosphere to provide desired quantities of hydrogen sulfide. Calcium sulfide dissociates but slowly at the temperature of the secondary recrystallization (around 2200° F.) and can readily be apportioned in the annealing separator to maintain the desired concentration of hydrogen sulfide in the atmosphere.

It is not preferred, however, to rely on a constituent of the annealing separator alone to maintain the concentration of polar compound in the annealing gas, since in many furnaces there is no assurance that all parts of the annealing atmosphere will be equally treated. On the other hand, when stacked sheets or coiled strip are being treated under conditions where circulation or penetration of an annealing atmosphere between layers or convolutions of the metal is impeded, the use of a separator containing a small amount of a compound which dissociates or vaporizes very slowly at the temperatures involved to provide or produce a polar compound, will be of assistance in promoting uniformity of treatment across the width of the strip or sheet.

Third, the fact that an annealing separator can provide or produce a content of polar compound in the annealing atmosphere suggests that the atmosphere can be treated directly in the furnace used for the secondary recrystallization. Thus a boat or receptacle of treatment substance can be placed in the furnace in such position that the entering atmosphere will come into contact with it. Again, it will be necessary to use a substance which vaporizes, sublimates or decomposes so slowly at the temperatures of secondary recrystallization that an excess quantity of the polar compound will not be introduced into the atmosphere, while the desired quantity will be maintained throughout the treatment time. As indicated, calcium sulfide is an example of a material which may be used, as are certain other metal sulfides. In FIG. 1, a furnace for secondary recrystallization is shown at 10; and a boat containing a treatment substance has been indicated in dotted lines at 11.

Fourth, since treatment of the atmosphere in the secondary recrystallization furnace does not permit great flexibility of operation, and requires careful selection of the treatment substance, it has in general been found preferable (instead or in addition) to pretreat the atmosphere in a separate device and at a lower temperature. In FIG. 1 a preliminary or pretreatment furnace is indicated at 12 through which the annealing gas passes on its way to the furnace 10. Here the atmosphere may be treated to the extent desired and at a desired temperature which may differ from the temperature for secondary recrystallization. For example, the furnace 12 may contain a quantity of ferrous sulfide which will decompose sufficiently slowly at, say, 900° F., to treat the atmosphere. It will also be understood that the preheating of the atmosphere in the furnace 12 will increase the efficiency of operation of the furnace 10.

Various kinds of annealing atmospheres may be used. Argon and helium, as examples of inert gases, normally contain minute quantities of oxygen. If such gases are passed through the furnace 12 when it contains ferrous sulfide or other suitable sulfur bearing compounds slowly reactable with the oxygen at the temperatures involved, the emerging gases will contain minute quantities of sulfur oxides and will be suitable for use in the furnace 10 to obtain the desired transformation. Moreover, if the furnace 12 contains some carbon in suitable form (preferably, though not necessarily, an activated form of charcoal) the emerging gases will contain minute amounts of carbon monoxide, and the transformation of the silicon-iron will be improved. It has been found that a very slight oxidation of the silicon-iron in the furnace 10, contrary to expectations, does not interfere with the transformation. Oxygen or moisture if present in such amounts

as to form a grey film on the sheet surface should be removed from the atmosphere. The dew point, to avoid such an amount of oxidation, should generally be lower than -40°F .

As to the addition of carbon to the atmosphere, it might be supposed that an effective way of accomplishing this would be to bleed a very small quantity of methane or other carbon bearing gas into the atmosphere. No doubt this may be done; but thus far it has been found difficult as a practical matter to limit the introduction of methane sufficiently to avoid carburizing the sheet to a detectable extent, which is undesirable.

Nitrogen is generally avoided as an annealing atmosphere for the reason that it appears to promote an indiscriminate grain growth, interfering with the desired transformation.

Hydrogen, however, is entirely satisfactory and is preferred as an annealing atmosphere. It is cheaper than the inert gases; it is in itself a bright annealing medium; and it is readily freed from oxygen, water vapor and like contaminants. If hydrogen is passed through the furnace in contact with a sulfide such as ferrous sulfide, for example, it will pick up sulfur in the form of hydrogen sulfide. If the furnace also contains carbon, the hydrogen will pick up carbon in some suitable form, although it is not clear just what that form is or whether it is the same in all instances.

A high- or partial-vacuum anneal may be used and is meant to be included when annealing atmospheres are mentioned. In this case the highly polar compounds should be maintained in the furnace in such amounts that their partial pressures will be equivalent to those prevailing in the neutral or reducing atmospheres previously described, when the critical amounts of highly polarized compounds are present. For example, the partial pressure of hydrogen sulfide should be substantially within the range of 15 to 190 microns, which is the equivalent of 20 to 250 parts per million at atmospheric pressure, under the conditions prevailing for the determination of FIG. 2.

So far as can be ascertained, it is necessary that the highly polar compound shall exist in gaseous form in the annealing atmosphere prior to its sorption by the sheet surfaces. Under the conditions of annealing upon which FIG. 2 is based, sorption of a sulfur polar compound began at a temperature of about 950°F . Hydrogen containing a highly polar sulfur compound was passed through the annealing furnace and burned in air upon its emergence therefrom, a content of sulfur in the annealing gas being indicated by a blue core in the flame. As the temperature rose in the annealing furnace to about 950°F ., the blue core disappeared. When a single sheet or strip was being annealed, the blue core reappeared in the flame when the material reached a temperature of about 1050°F ., indicating that the sorption phenomenon was complete. Where stacks of sheets were being annealed, the blue core reappeared after a longer time of continued heating at rising temperature. The content of highly polar compound in the annealing atmosphere should be maintained throughout the whole time of the secondary recrystallization cycle necessary to produce the desired transformation. If this is not done, the transformation will be impeded. Circulation of hydrogen without polar compound through the annealing muffle will tend to remove polar compound which has been absorbed or adsorbed on the sheet surfaces, as can be determined by the persistence of the blue core for some time after the supply of polar compound has been cut off from the annealing gas. Where sulfur treated annealing gas is used in accordance with the example throughout the secondary recrystallization cycle, tests have indicated that there is a very slight pickup of sulfur by the sheet stock, of the order of about .001%.

By "silicon-iron" in the application is meant a ferrous metal containing substantially 2.5 to 4.0% silicon. The metal should have a high degree of purity, by which is

meant freedom from carbon, nitrogen, oxygen, inclusions and the like. If the metal is open hearth metal, it will be decarburized in some suitable way. A decarburization in wet hydrogen as known in the art may be practiced, but if this is done, precautions should be taken to remove iron oxide and silica from the surfaces of the sheet stock. It is preferred to decarburize in a non-oxidizing atmosphere, e.g., dry hydrogen at a relatively high temperature of 1900° to 2200°F . as known in the art.

By way of example but without limitation, a silicon-iron may be used containing from about 2.90 to 3.30% silicon, .007% or less carbon, from about .06 to .12% manganese, the remainder being substantially all iron with a total oxide content of .01% or less. Although some sulfur may be tolerated, it is preferred to have the metal low in sulfur.

The metal may be treated in various ways to provide a sheet product characterized by a sufficient number of nuclei or grains having the cubic texture. In one way, as set forth in a copending application of Kohler and Littmann, Serial No. 816,889, filed May 29, 1959, and entitled Oriented Silicon-Iron and Process of Making It, the starting material may be the highly oriented commercial silicon-iron characterized by a (110)[001] orientation, having a high permeability in the straight grain direction and a relatively low cross grain permeability. Such material, after a heat treatment in hydrogen at about 2200°F ., is subjected to a cold rolling treatment producing a reduction of about 55 to 90%. It is then again annealed at a temperature of about 1150° to 2200°F . and subjected to a second cold rolling treatment producing a reduction of about 50 to 80%. During the course of these treatments, it has passed through a series of orientations which need not be outlined here. At the conclusion of the second cold rolling, it will be in a condition such that primary recrystallization will provide a relatively large number of grains oriented in the cubic texture.

In another procedure as set forth in the copending application of Kohler and Littmann entitled The Manufacture of Silicon-Iron Having Cubic Texture, Serial No. 819,589, filed June 11, 1959, now abandoned in favor of continuation-in-part application Serial No. 145,540, filed October 13, 1961, now Patent No. 3,130,094, issued April 21, 1964, slabs or thin bars of the silicon-iron are box annealed for about 24 hours at temperatures of about 1400° to 1800°F . and are then cold rolled with a reduction of about 55% to 80%. The cold rolled material is annealed in hydrogen at a temperature of about 2200° to 2350°F ., after which it is cold rolled with a reduction of about 75 to 90%. Such a material is also in a condition to provide a substantial number of grains having the cubic orientation upon primary recrystallization.

As an example of an anneal of such material in accordance with the teachings of this invention, 3 cm. wide strips 30.5 cm. long were coated with alumina to prevent sticking together, and were heated to 2200°F . in a 2 inch inside diameter Inconel tube. Throughout the entire heating-up period, an 8 hour soak at 2200°F ., and the subsequent cool-down period, an atmosphere of dry hydrogen containing a small, controlled amount of hydrogen sulfide, was maintained. The hydrogen flow was maintained at 5 cubic feet per hour, and a hydrogen sulfide content of approximately 35 parts per million was obtained by passing the hydrogen first through a small furnace (furnace 12 of FIG. 1) in which it comes into contact with a quantity of iron sulfide heated to 870°F .

After this anneal the strips were found to have about 95% of their area transformed to cubic texture, and the magnetic permeability measured parallel to the rolling direction of the strip was 1836 at an induction of 10 kilogausses.

As another example of an anneal of such material made in accordance with the teachings of this invention,

similar strips of the same starting material were annealed in exactly the same manner except that the atmosphere was treated to contain a mixture of CO and SO₂ in an atmosphere of helium. Since the commercial helium contained a minute quantity of oxygen, something of the order of .00002%, the polar compounds were formed in a controlled concentration by first passing the helium through a small furnace (furnace 12 of FIG. 1) held at 1800° F., which contained iron sulfide and carbon. Here the oxygen in the helium reacted substantially completely to form the desired CO and SO₂. After the anneal the strips were found to have about 95% of their area transformed to cubic texture and the magnetic permeability measured 1822.

The primary recrystallization may be carried on as a separate step, but can be and preferably is combined with the secondary recrystallization, since the primary recrystallization occurs quite rapidly during the heating-up of the material in the final furnace. The presence of the polar compound in the annealing atmosphere does not interfere with the primary recrystallization.

The phenomenon of secondary recrystallization starts to occur at temperatures around 1900° F. and higher and requires a length of time sufficient to permit the desired grain growth. The nuclei or crystals characterized by cubic texture either originally extend through the thickness of the sheet stock as a result of the primary recrystallization, or they rapidly grow during secondary recrystallization so as to extend through the thickness of the sheet. Then they begin to grow laterally at the expense of adjacent grains or crystals having other and higher energy orientations.

There is no way of indicating precisely the number of grains having the (100)[001] orientation required for the transformation since in some instances it is possible to produce a sheet material consisting essentially of a single crystal. In normal operations, at least about 5 to 10% of the nuclei preferably have the cubic texture orientation. The greater the number of grains so oriented in the stock after primary recrystallization, the smaller will be the grain size in the finished product. A relatively small grain size is generally preferred for the minimizing of core loss.

As indicated, the annealing atmosphere during the secondary recrystallization should be controlled so that it does not permit a harmful degree of carburization, nitriding, or oxidation; but it should contain a gaseous polar compound capable of lowering the surface energy of the crystals as hereinabove explained. Expedients such as electropolishing the stock, rolling it on polished rolls and the like may be practiced if desired but are not ordinarily necessary. The sheet stock may be formed from vacuum melted material if desired; but it is an advantage of the invention that excellent silicon-iron sheet stock characterized by cubic orientation can be made from air melted metal such as produced in the open hearth or electric furnace. By "nuclei or grains having the cubic texture orientation" is meant not only grains precisely oriented in the (100)[001] position by Miller's indices, but also grains departing from that orientation by no more than about 5 degrees. The presence of the highly polar compound in the annealing gas so greatly facilitates the transformation that in many instances satisfactory material may be made in a final heat treatment or secondary recrystallization step which is an open or continuous anneal as distinguished from a box anneal. Materials may be made, of course, with different degrees of perfection of the cubic texture orientation; but for purposes of this application a sheet stock characterized by cubic texture orientation may be taken as one in which at least the majority of the surface area is composed of grains having a (100)[001] orientation by Miller's indices.

While the invention has been described primarily in connection with cubic orientation, it will be equally effective

in promoting secondary crystal growth of any crystal having a (100) cube face essentially parallel to the surface of the sheet, regardless of its orientation otherwise.

Where carbon in gaseous form is employed along with some other highly polar compound such as hydrogen sulfide, it is used in amounts generally less than the amounts of the other polar compound present, and may be used in such amounts as to be in equilibrium with a carbon content of about .005% in the silicon-iron.

Modifications may be made in the invention without departing from the spirit of it. The invention having been described in certain exemplary embodiments, what is claimed as new and desired to be secured by Letters Patent is:

1. In a process of making silicon-iron sheets having a high proportion of cube-on-face grains, the steps comprising annealing cold rolled sheets of silicon-iron at a temperature of at least about 1900° F. in an atmosphere of dry hydrogen, said atmosphere containing a vapor of a sulfur containing compound which will dissociate at the annealing temperature to produce elemental sulfur, the partial pressure of said vapor being in the range of from 15 to 190 microns of mercury, and continuing the annealing until substantially complete cube-on-face grain growth by secondary recrystallization takes place.

2. In a process of making silicon-iron sheet stock, the steps of providing a sheet stock which, after primary recrystallization, will be characterized by a plurality of crystals having (100)[001] orientation, and heat treating the said stock in a furnace in which its temperature is raised through the temperature of primary recrystallization to a temperature of at least about 1900° F. for secondary recrystallization, while passing through said furnace an atmosphere of hydrogen containing from about 20 to about 250 parts per million of hydrogen sulfide.

3. A process of making silicon-iron sheet stock characterized by cubic texture orientation which comprises providing a silicon-iron sheet stock characterized by a number of grains having a (100)[001] orientation, subjecting said stock to secondary recrystallization at an elevated temperature in an enclosure containing a highly polar substance comprising a compound of sulfur entrained in an annealing atmosphere in a concentration at the sheet surface of substantially 20 to 250 parts per million at atmospheric pressure when said enclosure is filled with said atmosphere, said annealing atmosphere other than said sulfur compound being chosen from the class consisting of argon, helium, and hydrogen at a pressure substantially no greater than atmospheric.

4. The process claimed in claim 3 wherein said sulfur compound is mixed with said annealing atmosphere prior to its introduction into said enclosure.

5. The process claimed in claim 3 wherein said sulfur compound is derived in part at least from a material present in said enclosure.

6. The process claimed in claim 5 wherein said sulfur compound is derived in part at least from an annealing separator.

7. The process claimed in claim 5 wherein said sulfur compound is derived in part at least from said sheet material itself.

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