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PROCESS OF RETAINING A DISPERSED SECOND PHASE UNTIL AFTER THE TEXTURE DEVELOPING ANNEAL

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This application is a continuation of copending application Serial No. 105,898, filed April 27, 1961, which is a continuation-in-part of application Serial No. 753,181, filed August 5, 1958, and copending application Serial No. 60, filed January 4, 1960 (both now abandoned), and is assigned to the same assignee.

This invention relates to iron and iron-base alloys such as used in transformers, motors, etc., to such alloys for use in the production of tapes used in manufacturing magnetic cores, and more particularly to a process for producing cube-on-edge grain oriented polycrystalline sheet-like bodies and thin tapes composed principally of iron and silicon and containing incidental impurities such as carbon, phosphorus, etc.

The sheet materials to which this invention is directed are usually referred to in the art as "electrical silicon steels" or, more properly, "silicon irons" and are conventionally composed of iron alloyed with about 1.5 to 4.0 or even 5.0 weight percent silicon. The silicon content may preferably range from about 2.5 to 3.5 percent for most applications and will contain relatively minor amounts of various impurities and/or additions such as sulfur, manganese, phosphorus, vanadium, and should preferably have a low carbon content as finished material.

These alloys crystalize in the body-centered cubic crystallographic system at room temperature. As is well known, this crystallographic arrangement refers to the symmetrical distribution or arrangement which atoms forming the individual crystals or grains assume in such materials. The body-centered cube is composed of four atoms, each arranged at the corners of the unit cube, with the remaining atom positioned at the geometric center. Each unit cell in a given grain or crystal in these materials is substantially identical in shape and orientation with every other unit cell comprising the grain.

The unit cells or body-centered unit cubes comprising these materials each have a high degree of magnetic anisotropy with respect to the crystallographic planes and directions of the unit cube and, therefore, each grain or crystal comprising a plurality of such unit cells exhibits a similar anisotropy. The silicon-iron alloys to which this invention is directed are known to have their easiest direction of magnetization parallel to the unit cube edges, their next easiest direction perpendicular to a plane passed through diagonally-opposite parallel unit cube edges, and their least easiest direction of magnetization perpendicular to a plane passed through a pair of diagonally-opposite atoms in a first unit cube face, the central atom and a single atom in the unit cube face which is parallel to the first face.

It has been found that these silicon-iron alloys may be fabricated by unidirectional rolling and heat treatment to form sheet or strip material composed of a plurality of crystals or grains, a majority of which have their atoms arranged so that their crystallographic planes have a similar or substantially identical orientation to the plane of the sheet or strip and to a single direction in said plane. This material is usually referred to as "oriented" or "grain oriented" silicon-iron sheet or strip

and is characterized by having 50 percent or more of its constituent grains oriented so that four of the cube edges of unit cells of the grains are substantially parallel to the plane of the sheet or strip and to the direction in which it was rolled and a (110) crystallographic plane substantially parallel to the plane of the sheet.

It will thus be seen that these so-oriented grains have a direction of easiest magnetization in the plane of the sheet in a rolling direction and the next easiest direction of magnetization in the plane of the sheet in the transverse-to-rolling direction. This is conventionally referred to as "cube-on-edge" orientation or the (110) [001] texture. In these polycrystalline sheet and strip materials, it is desirable to have as high a degree of grain orientation as is attainable in order that the magnetic properties in the plane of the sheet and in the rolling direction may approach the maximum attained in single crystals in the [100] direction.

Strip and sheet grain-oriented silicon-iron alloys have been previously used as transformer core materials, electric motor and generator laminations, and in other electrical and electronic applications where the high degree of electromagnetic properties in the rolling direction of the sheet or strip may be advantageously employed. For most applications, the highest degree of grain orientation or texture obtainable is desirable. Usually materials having more than about 70 percent of their crystal structures oriented in the (110) [001] texture are considered to have a strong texture.

Heretofore, the cube-on-edge texture has been produced in silicon-iron alloys principally by adding controlled amounts of manganese and sulfur which are present in the alloy as a dispersed second phase of manganese sulfide. Other materials may be used to form the dispersed second phase. For example, metals such as titanium and vanadium may replace the manganese, and nonmetals such as carbon and nitrogen may be used to replace the sulfur. Certain of these dispersed second phase materials have recently been found to be particularly useful due to the fact that they can be removed from the metal at completion of the texture-developing recrystallization anneal much more rapidly than manganese sulfide.

Before the silicon-iron alloys may be used in the construction of induction apparatus such as motors, generators, cores and coils, etc., it is essential that the second phase dispersion be removed to obtain optimum magnetic properties.

While manganese sulfide has proved generally acceptable in producing magnetic bodies in the 12 to 15 mil thickness range, prior attempts to produce thin gauge magentic strip having thicknesses ranging only up to about 4 or 5 mils have required processing different from that used to produce the thicker materials. The procedures used to produce cube-on-edge oriented silicon-iron materials in the 12 to 15 mil range have not proved generally useful in producing materials of from about 0.5 to 5.0 mils in thickness. To answer the problem of producing the thinner gauge strip used in the manufacture of magnetic cores intended for use at frequencies greater than 60 cycles per second, Littmann, in Patent 2,473,156, describes a procedure whereby orientation obtained in the heavier gauge materials can be retained through subsequent rolling reductions to produce thin gauge strip. The procedure described in this patent was developed, as the specification states, to produce thin gauge oriented material which could not be produced according to the existing practices.

It has now been unexpectedly found that bodies having a high degree of cube-on-edge orientation can be developed by direct secondary recrystallization in body thick-

nesses ranging down to about 2 mils, completely eliminating the necessity for proceeding in the manner described by Littmann to obtain this orientation in thin gauge materials.

It is a principal object of this invention to provide a process for directly producing a strong (110) [001] crystalline orientation in silicon-iron bodies of thicknesses up to 15 mils.

It is another object of this invention to provide an improved process for producing cube-on-edge grain-oriented silicon-iron bodies down to about 2 mil thickness by secondary recrystallization in the material of final thickness.

It is a further object of this invention to provide a process for producing cube-on-edge grain-oriented silicon-iron bodies in which a dispersed second phase material is essentially completely retained through the texture-developing phase of the process to assure development of maximum orientation.

Another object of this invention is to provide an iron-base silicon alloy which can be processed in shorter periods of time than can existing iron-silicon alloys to produce sheet material having a preferred cube-on-edge grain orientation.

An additional object of this invention is to provide a process for treating an iron-base silicon alloy containing vanadium to precipitate a vanadium nitride phase promoting development of the preferred cube-on-edge grain orientation.

A still further object of this invention is to provide a process for treating an iron-base silicon alloy containing vanadium to precipitate a vanadium carbide phase, promoting development of the preferred cube-on-edge grain orientation.

An additional object of this invention is to provide a substantially continuous process for producing iron-base silicon alloys having a preferred cube-on-edge grain orientation.

Still another object of this invention is to provide a process for forming silicon-iron sheet material in which the material is continuously purified at comparatively lower temperatures than those used in existing processes.

Other objects and advantages of the present invention will be in part obvious and in part explained by reference to the accompanying specification.

Briefly stated, the present invention utilizes relatively small additions of metals and nonmetals to the basic silicon-iron alloy to form a dispersed second phase, assisting development of the cube-on-edge orientation by restraining normal grain growth during processing to the final gauge. The general process comprises preparing an alloy consisting of from about 1.5 to 4.0 weight percent silicon, balance substantially all iron and incidental impurities and minor additions. The minor additions comprise metals such as vanadium and manganese and nonmetals such as sulfur, carbon and nitrogen which combine with the minor metal additions to form a dispersed second phase which restricts normal grain growth. The ingot or starting body is then hot and cold rolled in a plurality of reduction stages to a final thickness of up to 15 mils, with intermediate anneals being used between successive cold rolling stages. The last cold rolling stage should effect a reduction of at least 50 percent in arriving at the final thickness.

One of the important and unexpected discoveries of this invention resides in the finding that the heat treatment after the last cold reduction must be conducted in an atmosphere which is substantially inert with respect to the nonmetallic portion of the dispersed second phase or that the body must be subjected to an oxidizing atmosphere which will form an oxide coating on the surface of the body and thereby prevent the removal of the dispersed phase during the secondary recrystallization heat treatment. Thus, when the final texture-developing anneal is carried out, essentially all of the dispersed second phase is still present, thereby insuring that optimum grain

orientation can be developed. The final anneal is, of course, carried out in an atmosphere which will not remove the second phase from the body. Following secondary recrystallization to the (110) [001] crystalline orientation, the dispersed second phase can be removed by appropriately heat treating the body in an atmosphere effective to effect such a removal, for example, dry hydrogen, i.e., dew point no higher than −40° F., or vacuum.

The magnetic alloys of this invention, as mentioned, are principally iron containing from about 1.5 to 4.0 weight percent silicon, plus some minor additions to form the dispersed second phase. More specifically, these additions will comprise from 0.50 to 2.0 weight percent vanadium and up to about 0.50 weight percent carbon if a vanadium carbide dispersion is to be used. On the other hand, additions of vanadium up to 0.15 weight percent and as little as 0.05 weight percent can be used in a melt containing as little as 0.002 weight percent nitrogen if a vanadium nitride dispersion is to be used. In either of these melts, some oxygen, sulfur and manganese will probably be present but these elements are preferably reduced to trace percentages. A greater amount of vanadium can be present in the alloy but it is not necessary to the process since any uncombined amounts will remain in solid solution. Generally, the vanadium dispersion may be formed in the metal either by placing sufficient quantities of nitrogen or carbon in the original melt or by subjecting a vanadium-containing alloy body to a nitrogen- or carbon-containing atmosphere during the final heat treatment. The carbon and nitrogen added from the gas phase will form additional particles, assisting development of the texture.

The function of the vanadium carbide or vanadium nitride particles is to prevent normal grain growth during the final anneal. Those grains with (110) [001] orientation readily grow in the fine-grain matrix which is obtained from the primary recrystallization occurring from the heat treatment immediately following the last cold rolling.

If the nitride or carbide phase is present in the ingot initially, then the final annealing atmospheres must be controlled, as by providing a partial pressure of the nonmetallic part of the dispersion in the atmosphere, to prevent premature removal of the nitrogen or carbon, particularly if only a small amount of the dispersed phase was originally present. Alternatively, the body itself may be subjected to an oxidizing atmosphere, forming an oxide coating on the exposed surface of the body to thereby prevent the premature escape of the dispersed second phase.

The procedure followed in the present invention to produce a silicon-iron body having the desired orientation is to cast the molten metal containing as little sulfur and manganese as possible into ingot or slab form. It will be appreciated that some manganese and sulfur will be present due to the impurities in the raw materials or from the refractory furnace crucible. In the event that a manganese sulfide dispersion is to be used, the heat can contain amounts of manganese and sulfur corresponding to those generally used in the industry. For example, these materials will contain about 0.02 to 0.03 weight percent sulfur and less than about 0.1 weight percent manganese. In connection with the use of manganese sulfide, if bodies of from about 12 to 15 mils thickness are to be produced, then no particular precautions need to be taken to retain the dispersion within the bodies. On the other hand, if bodies of about 10 mils thickness or less are to be produced with a high degree of orientation, then it has been found that special precautions similar to those used in connection with the vanadium nitride and carbide dispersions must also be taken. That is, the manganese sulfide dispersion will be prematurely removed from the thin gauge bodies unless atmosphere control or surface preparation of the bodies is used to prevent the escape of

the manganese sulfide particles during the final heat treatment.

Considering specific application of the invention with regard to the use of vanadium nitride dispersions, a slab or ingot is cast and upon solidification of the metal it is hot rolled to about 100 mil thickness, this particular thickness usually being referred to as the "hot rolled band." The hot rolled band is permitted to cool, then cold rolled to within the range of thicknesses of from 0.029 inch to about 0.025 inch and then given an intermediate normalizing heat treatment. The metal is then cold rolled to 12 to 14 mil thickness and if this is to be the final thickness, final annealing is done to effect secondary recrystallization, that is, to develop the (110) [001] orientation. The final anneal to develop the texture is advantageously carried out by heating the metal as rapidly as possible to a temperature between 950° C. and 1050° C. and then holding at temperature for 10 to 20 minutes to develop the texture. Texture can also be developed by heating the metal to a temperature between 1050° C. and 1150° C. at a moderate rate, such as about 7° C. per minute.

As previously mentioned, the atmosphere or environment in which the metal is given its final texture-developing anneal is important since the nitrogen already in the strip should be retained and additional nitrogen may be obtained from the atmosphere to form more particles of vanadium nitride. Lack of control of the annealing environment could result in absence of the second phase prior to development of the desired texture, thereby permitting normal grain growth and lowering of the amount of texture obtained.

When the final bodies are to have a maximum thickness of only up to 5 mils, the material is rolled to a thickness at least twice that of the final desired product in order that the final cold reduction can be at least 50 percent. Thus, for a body which is to have a final thickness of 5 mils, the material from which this piece is rolled would have a minimum thickness of at least 10 mils. Once the material has arrived at thickness of not less than twice that of the final body, it is given a short recrystallization heat treatment. The atmosphere for this heat treatment is not critical but such severe oxidation of the strip as would cause difficulty in cold rolling should be avoided. After the recrystallization has been effected, the body is cold rolled to the final thickness, the cold rolling being carried out on a Sendzimir mill, for example, and then given a final texture-developing anneal which causes secondary recrystallization of the body into the preferred (110) [001] crystalline orientation.

Since it is extremely important that the dispersed second phase remain in the body during the texture-developing anneal, two different procedures can be used to insure such retention. The first of these procedures is to subject the body, after it has been cold rolled to final thickness, to an oxidizing treatment by subjecting it to atmospheres such as wet nitrogen, wet air or wet hydrogen, the first two atmospheres being preferred over the last. Sufficient moisture can be entrained in the heat treat atmosphere by bubbling the gas through water at room temperatures. The final bodies are subjected to these atmospheres at temperatures of from about 700° C. to 900° C. for several minutes, for example for 3 to 10 minutes. Following this oxidizing treatment, the bodies can be annealed in any atmosphere which is substantially inert with respect to the oxide film on the body since, obviously, the use of an atmosphere which would destroy the film would also permit the escape of the second phase.

If desired, rather than use the oxidizing treatment just described, the final anneal can be carried out in an atmosphere which contains a partial pressure of the nonmetal used as part of the second phase dispersion. Thus, in the specific illustration given previously, the atmosphere will contain some quantity of nitrogen.

Considering now specific examples of some bodies produced making use of vanadium nitride as the dispersed second phase, Table I, following, lists in weight percentages compositions of several alloys containing varying amounts of vanadium and nitrogen:

Table I

Heat No.	Ingot Analyses					
	Si	C	V	S	N	O
1	3.2	0.002	0.12	0.003	0.002	0.007
2	3.2	.003	.11	.004	.002	.009
3	3.2	.003	.12	.004	.003	.006
4	3.25	.005	.12	.004	.003	.006
5	3.25	.005	.09	.006	.003	.007
6	3.25	.005	[1].10	.004	.004	.005
7	3.25	.005	.10	.003	.003	.005
8	3.25	.005	.11	.003	.001	.005
9	3.25	.005	.10	.006	[2].004	.004
10	3.25	.005	[1].11	----------	.003	.006
11	3.25	.005	[1].07	.003	.003	.003
12	3.25	.005	.08	.004	.002	.004
13	3.25	.005	[1].10	.001	.006	.003
14	3.25	.005	.07	.002	.004	.004

[1] Nominal content based on weight added.
[2] Analysis of the strip indicated that the nitrogen content was 0.009 rather than 0.004 percent.

All of the alloys of Table I were made from a base material of electrolytic iron to which was added pure vanadium and 98 percent ferrosilicon. The amount of nitrogen in the ingot was controlled by the ratio of nitrogen to argon in the gas which was blown over the surface during melting. The ingots were made by pouring into either graphite or cast iron molds.

After casting, about one-sixteenth inch was ground off the surfaces of the ingots to remove irregularities and they were then heated to between 1000° C. and 1100° C. for rolling to 100 mil band without reheating. The hot rolled bands were pickled in a dilute hydrofluoric-hydrochloric acid solution. After a five-minute heat treatment at 900° C. in a hydrogen furnace, the bands were rolled to an intermediate gauge of 28 mils if the final gauge was to be 14 mils, and 25 mils if the final gauge was to be 12 mils. The intermediate heat treatment was also five minutes at 900° C., after which the material was rolled to final gauges.

As previously mentioned, the atmosphere or environment used during the final annealing operation is important in its effect upon the nitrogen content, and therefore the vanadium nitride content, of the body. Samples taken from Heat 9 were heated for one-half hour at 1020° C. in a dry hydrogen (−60° F. dew point or less) atmosphere. There was a pronounced tendency for nitrogen to be withdrawn from the body and this is evidenced by the fact that after the heat treating, the nitrogen content was only 0.0005 weight percent and that during the heat treatment the sample mainly underwent normal grain growth. On the other hand, samples from the same heat had complete secondary growth when annealed in a one-quarter nitrogen—three-quarter hydrogen atmosphere. After one-half hour, samples annealed in this manner had nitrogen contents of 0.008 weight percent, indicating that the atmosphere had become essentially a neutral one so that the nitrogen content of the metal remained substantially unchanged. By increasing the nitrogen content of the atmosphere to two-thirds nitrogen—one-third hydrogen, it becomes slightly nitriding, and after one-half hour at 1020° C., the nitrogen content of the sample strip was increased about 0.002 percent. The resulting greater number of vanadium nitride inclusions results in there being comparatively few large secondary grains growing in an otherwise fine-grain matrix.

Although the nitrogen is lost within one-half hour at 1020° C. in a dry hydrogen (−60° F. dew point or less) atmosphere, a similar heat treatment in hydrogen with a dew point of −30° F. results in the retention of the

major portion of the nitrogen (0.006 percent, starting with an initial 0.009 percent) and complete secondary recrystallization occurs. It is believed that the nitrogen is largely retained during heat treating in a hydrogen atmosphere if the dew point is such that the atmosphere is oxidizing to the silicon at the temperature of the heat treatment. The formation of an oxide film is believed responsible for this occurrence.

Magnetic measurements were made on samples whose texture was developed either by heating at a controlled rate through the secondary grain growth temperature range or by holding for 15 minutes at a temperature within that range. In the first group, designated "A" in Table II, the samples, after coming up to 1000° C., were heated at a uniform rate, about 7° C. per minute, in a two-thirds nitrogen—one-third hydrogen mixture. The nitrogen content of the samples was then reduced to 0.0005 percent or less by holding 10 minutes with hydrogen flowing through the heating furnace. Ten minutes were used to allow time for the retort to be purged of nitrogen.

The second group of strips, designated "B" in Table II, were heated rapidly to 1040° C., held 15 minutes in a two-thirds nitrogen—one-third hydrogen atmosphere and then for an additional 5 minutes with only hydrogen flowing to allow the nitrogen to be purged. The temperature was then raised to 1100° C. and the samples held an additional 5 minutes.

The following Table II sets forth the properties obtained in the "A" and "B" group strips processed as explained above. The heat numbers correspond to the heat numbers set forth in Table I.

Table II

Schedule	Heat No.	No. of Strips	Avg. Gauge (mils)	Avg. wpp. 15,000B	Avg. percent Texture
A	4	12	12	0.64	80
	5	6	12	.65	80
	6	4	12	.62	79
	7	18	12	.68	74
B	9	3	13	.69	80
	12	1	14	.68	76
	13	1	14.7	.70	82
	14	1	14	.68	73

The texture percentages listed were obtaind by dividing the maximum torques obtained with a torque magnetometer in a field of 1000 oersteds, by the maximum torque of a single crystal.

Since it is not necessary to use a nitrogen-containing atmosphere or environment where the required amount of nitrogen is already present in the initial alloy, strips from Heats 9, 11, 12 and 13 were processed and annealed in hydrogen atmospheres of varying dew points. Other samples from the same heats were coated with magnesia and annealed in a hydrogen atmosphere having a dew point of —60° F. The strips were all heated from 900° C. to 1200° C. at 100° C. per hour in dry hydrogen and in hydrogen with a dew point of —26° F. The average percent textures obtained on these strips are shown in Table III.

Table III

	Heat 9	Heat 11	Heat 12	Heat 13
Bare Strips:				
—60° F. dp H_2	75	68	69	70
—26° F. dp H_2	86	83	79	86
MgO Coated Strips:				
—60° F. dp H_2	79	89	85	86

The macrostructure of the samples heat treated in the dry hydrogen atmosphere (—60° F. dew point) consisted of small secondary grains, plus smaller grains which grew by normal grain growth. The strips heated in the —26° F. dew point hydrogen consisted entirely of large secondary grains.

As the results in Table III indicate, the magnesia coating provides another method of keeping nitrogen within the body to perform its function. It is therefore possible, with the use of a magnesia coating, to retard the loss of nitrogen and to do conventional batch annealing, either as coils or laminations.

Strip material was also prepared from ingots of Heats 1, 2 and 3 (Table I) by heating the ingots to about 1000° C. and rolling, without reheating, 80 mil thick hot rolled band. This rolled material was then annealed at 900° C. for from 3 to 30 minutes in dry (dew point about —60° F.) hydrogen to effect complete recrystallization. This anneal may be omitted if desired and an atmosphere other than hydrogen may be used. The bands were then cold rolled to 25 mil thickness and annealed at 860° C. for two minutes in dry hydrogen, then cold rolled to 13 mil thickness. It should be noted that this intermediate annealing temperature should be maintained between about 850° C. and 950° C. for optimum results.

Strips of this material were then heated rapidly to 1000° C. in an atmosphere consisting of two-thirds nitrogen and one-third hydrogen and subsequently heated to 1100° C. at a rate of 7° C. per minute in the same atmosphere. The secondary recrystallization was complete by the time the strip reached the 1100° C. temperature and the degree of orientation for all heats was between 75 and 90 percent.

Following this treatment, the strips were heated in dry hydrogen to a temperature of 1100° C. for about five minutes in order to remove the nitrogen. Use of slightly lower temperatures, for example, 1050° C., requires somewhat longer purification periods, e.g., up to 15 minutes.

The use of vanadium nitride inclusions has been found effective to develop cube-on-edge texture in alloys having a wide range of silicon contents. In Table IV are magentic properties measured on 28-centimeter lap-joint Epstein packs of alloys containing 2.0, 3.2 and 5.1 percent silicon. The final anneal consisted in heating from 900° C. to 1100° C. at 25° C. per hour or 100° C. per hour, in an atmosphere containing 50 to 67 percent nitrogen, remainder hydrogen. The purification treatment consisted in heating the strip at 1100° C. in hydrogen for one hour or less. It is necessary to cold roll the higher silicon content alloys, for example, 4.5 to 6.0 percent silicon, at temperatures of from 200° C. to 350° C. to avoid cracking and related rolling difficulties.

Table IV

Percent Silicon	Gauge (mils)	Wpp. at 15,000B	Induction at—		
			1H	2H	10H
2.0	10.0	.601	------	17,900	19,040
3.2	12.5	.580	16,450	17,200	18,270
5.1	14.0	.515	15,430	16,090	17,180

The advantage of the present process is that the nitride inclusions that are used to develop the texture are readily removed within five minutes at temperatures in the region of 1100° C. in dry hydrogen. The nitrogen content is decreased from about 0.005 percent to 0.0003 percent by such a heat treatment. Silicon-iron utilizing sulfide inclusions to develop the texture requires higher purifying temperatures and longer periods of time. The vanadium nitride, on the other hand, can be removed from the final product by subjecting the strip to a hydrogen atmosphere for a short period of time at a temperature as low as 1050° C.

Thin tape bodies of 2 and 4 mil thicknesses were produced as follows: Alloys containing 3.3 weight percent silicon, 0.10 percent vanadium, 0.004 percent nitrogen, 0.005 percent carbon, 0.005 percent oxygen and 0.004 percent sulfur were cast into ingots. Slices one inch

thick from the ingots were heated to 1000° C. and rolled without reheating to 80 mils. After pickling, the 80 mil bands were heated for five minutes at 900° C. in hydrogen, cold rolled to 25 mils, heat treated five minutes at 860° C. in hydrogen and cold rolled to 8 mils if the final gauge was to be 4 mils and to 4 mils if the final gauge was to be 2 mils. After heat treating for 1½ minutes at 860° C. in hydrogen, the strip was cold rolled to final gauge.

Cores weighing about 50 grams were made from 0.50 inch wide strip which had been coated with magnesia. The 4 mil cores were heated from 900° C. to 1150° C. in a 1:1 mixture of dry nitrogen and dry hydrogen to develop the grain orientation, and then for one hour in dry hydrogen to remove the nitrogen from the strip. The 2 mil core was heated in a 2:1 mixture of dry nitrogen and dry hydrogen from 950° C. to 1000° C. at 50° C. per hour, held two hours at 1000° C., and then heated to 1100° C. at 25° C. per hour. This was followed by heat treatment for one hour at 1150° C. in dry hydrogen to remove the nitrogen from the strip. When the complete anneal was done in hydrogen only, normal grain growth competed with secondary recrystallization as a consequence of the premature loss of the nitride inclusions and the magnetic properties were poor. Magnetic properties of cores in which the inclusions were retained during the secondary recrystallization anneal are shown in the following Table V:

Table V.—Core loss, watts/lb. at 400 cps.

Sample	Thickness in mils	Induction in kilogausses				
		14	15	16	17	18
1	4	5.70	6.70	7.70	9.00	10.5
2	4	5.60	6.55	7.60	9.00	10.6
3	2	6.20	7.20	8.50	10.1	11.9

Additional thin tape samples were produced which contained manganese and sulfur to determine whether or not thin gauge material could be produced making use of the manganese sulfide inclusions. In this case, material about 100 mils thick containing 3.17 percent silicon, 0.020 percent sulfur, 0.062 percent manganese and 0.024 carbon was used. The as-received material was pickled and cold rolled to 30 mils. At this thickness, it was decarburized to 0.004 percent carbon by three treatments of 10 minutes each in wet nitrogen at 800° C. with pickling after each treatment The material was then cold rolled to 8 mils, heat treated for two minutes at 900° C. in hydrogen to effect primary recrystallization, and cold rolled to 4 mils, the final gauge.

After slitting into one-half inch widths, some of the strips were given a surface oxidizing treatment, five minutes at 800° C. in either wet nitrogen or wet hydrogen, before coating with magnesia or alumina. Other strips were coated with magnesia or alumina with the surfaces in the as-rolled and degreased condition. All of the coated strips were wound into cores weighing about 50 grams and having a mean diameter of about 4.2 centimeters. The cores were then heated in argon or hydrogen with the temperature being raised from 900° C. to 1100° C. at 50° C. per hour and then for two hours at 1150° C. in hydrogen to remove the manganese sulfide dispersion.

Since both hydrogen and magnesia are desulfurizing agents, the strips which had not been surface oxidized had appreciable secondary recrystallization only in those instances where alumina had been used as the coating material and argon constituted the final annealing atmosphere. While the situation was improved only slightly by first oxidizing the strip in wet hydrogen, very marked improvement was obtained when a more severe oxidizing treatment in wet nitrogen was used. When a severe oxidizing treatment was given, nearly complete secondary recrystallization into the (110) [001] crystalline orientation was obtained regardless of whether magnesia or alumina was used as the coating material if the initial portion of the final heat treatment was done in argon. This clearly points out that the use of hydrogen as the final annealing atmosphere results in breakdown of the oxide film with subsequent removal of the sulfur from the body so that only a small amount of secondary recrystallization can occur.

Magnetic properties of cores first oxidized in wet nitrogen then heated in argon to develop texture and finally in hydrogen to remove the sulfur are shown in Table VI:

Table VI.—Core loss, watts/lb., 400 cps.

Sample	Induction—B in kilogausses						
	10	12	14	15	16	17	18
M-d	2.72	4.05	6.00	7.30	9.00	11.0	13.5
M-g	2.74	4.20	6.30	7.70	9.50	11.8	14.4
M-i	2.74	4.20	6.20	7.60	9.30	11.4	14.0

Considering now the use of vanadium carbide as the dispersed second phase, a number of heats of different alloys were made, of which the following listed compositions are representative:

Table VII

Heat	Si	C	V	S	O	N
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	3.28	.04	1.7	.005	.004	.003
2	3.20	.03	.7	.004	.004	.002
3	3.22	.05	.7	.004	.005	.003

Strip material was prepared from the preceding alloys by heating the ingots to about 1000° C. and rolling without reheating to strip or hot rolled band 80 mils thick. This rolled material was then annealed at 900° C. for one-half hour in dry (dew point about −60° F.) hydrogen to effect complete recrystallization. However, this anneal may be omitted if desired, and an atmosphere other than hydrogen may be used. The annealed bands were then cold rolled to 25 mil thickness and annealed at 860° C. for two minutes in dry hydrogen, then cold rolled to 13 mil thickness. It should be noted that this intermediate annealing temperature is not critical but should be maintained between about 850° C. and 950° C. for optimum results.

Specimens of this cold rolled strip or sheet material were then subjected to a texture-developing anneal comprising heating for between two and four hours at about 950° C. in vacuum. The annealing time and percent cube-on-edge texture in each of these samples is indicated in the following Table VIII, percent texture being calculated from torque values observed when the samples were suspended in the field of a magnetometer:

Table VIII

Heat	Annealing Time (hrs.)	Percent Texture
1	4	77
2	2	88
3	2	92

Table IX shows the percent texture developed in samples treated in pure hydrogen and in various methane-hydrogen atmospheres at 1000° C. for 20 to 30 minute periods of time:

Table IX

Heat	Percent Texture—Atmosphere			
	H_2	H_2:CH_4/200:1	H_2:CH_4/100:1	H_2:CH_4/50:1
1	66	76	81	----
2	----	----	----	65
3	----	----	----	80

It can be seen that pure hydrogen alone does not develop the same degree of texture as the hydrogen-methane mixtures, probably due to partial decarburizing of the alloy. As a consequence, normal grain growth competes with secondary recrystallization and the full texture is never developed. By adding enough methane so that the atmosphere is neutral or even slightly carburizing, normal grain growth is completely prevented and secondary recrystallization goes to completion.

Three strips 0.0125 to 0.013 inch thick were made from Heat 3 of Table VII in the same manner as previously set forth, except that the purifying was carried out at 1100° C. for one-half hour. The electrical losses were found to be 0.63 watt per pound, which compares favorably with ordinary mill-made material.

While specific examples of the invention have been recited in the foregoing specification, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the invention, and it is intended to cover in the appended claims all such changes and modifications that come within the true spirit and scope of the invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A process for producing a polycrystalline sheet-like body having a majority of the constituent grains oriented in the (110) [001] crystalline direction comprising producing a starting body consisting essentially of from about 1.5 to 4.0 weight percent silicon, balance substantially all iron and incidental impurities, and including a dispersed second phase selected from the group consisting of nitrides and carbides of vanadium and manganese sulfide, reducing the thickness of the starting body in a plurality of hot and cold rolling stages to a final thickness of from about 2 to 15 mils when the second phase is one of said nitrides and carbides and to a final thickness of from about 2 to 10 mils when the second phase is manganese sulfide, and heating the body in an atmosphere which will not reduce the dispersed second phase at the heating temperature, said heating effecting secondary recrystallization of a majority of the grains into the (110) [001] crystalline direction.

2. A process as defined in claim **1** wherein the atmosphere present during the secondary recrystallization heating contains a partial pressure of a non-metal of the group consisting of carbon, nitrogen and sulfur.

3. A process as defined in claim **1** wherein said sheet-like body of final thickness is subjected to an atmosphere forming an oxide coating on the exposed surfaces thereof.

4. A method for producing a polycrystalline sheet-like body having a majority of the constituent grains oriented in the (110) [001] direction comprising, preparing an alloy consisting essentially of from 1.5 to 4.0 weight percent silicon, trace percentages of nitrogen, and the balance substantially all iron, adding up to 0.15 weight percent vanadium to said alloy to combine with said trace nitrogen and form a vanadium nitride second phase dispersion, casting said vanadium-containing alloy and hot reducing said casting to form an elongated sheet-like body less than 150 mils in thickness, cold rolling said body to effect at least a 40 percent reduction in thickness, annealing said cold worked body in an atmosphere non-reducing with respect to vanadium nitride and annealing said body to decompose the vanadium nitride phase and effect removal of the nitrogen from the metal body.

5. A method for producing a polycrystalline sheet-like body having a majority of the constituent grains oriented in the (110) [001] direction comprising, preparing an alloy consisting essentially of from 1.5 to 4.0 weight percent silicon, trace percentages of nitrogen, and the balance substantially all iron, adding up to 0.15 weight percent vanadium to said alloy to combine with said trace nitrogen and form a vanadium nitride second phase dispersion, casting said vanadium-containing alloy and hot reducing said casting to form an elongated sheet-like body less than 150 mils in thickness, cold rolling said body to effect at least a 40 percent reduction in thickness, annealing said cold worked body at a temperature not lower than about 950° C. in an atmosphere non-reducing with respect to vanadium nitride to develop the desired orientation, and annealing said body to decompose the vanadium nitride phase and effect removal of the nitrogen from the sheet-like body.

6. The method as recited in claim **5** wherein said strip is heated to about 1100° C. at a rate of about 7° C. per minute to develop the desired grain orientation.

7. A method for producing a polycrystalline sheet-like body having a majority of the constituent grains oriented in the (110) [001] direction comprising, preparing an alloy consisting essentially of from 1.5 to 4.0 weight percent silicon, trace amounts of nitrogen, and the balance substantially all iron, adding from about 0.05 to 0.15 weight percent vanadium to said alloy to form a vandium nitride second phase dispersion therein, casting said vanadium-containing alloy and hot reducing said casting to form an elongated sheet-like body less than 150 mils in thickness, cold rolling said body to effect at least a 40 percent reduction in thickness, annealing said cold worked body in an atmosphere preventing removal of nitrogen from said body to introduce additional nitrogen into said alloy to combine with any remaining uncombined vanadium and form additional vanadium nitride particles, and annealing said body at a temperature not lower than about 1050° C. to decompose the vanadium nitride phase and effect removal of the nitrogen from the metal body.

No references cited.

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