United States Patent Office

3,184,346

Patented May 18, 1965

3,184,346

GRAIN ORIENTED SHEET METAL HAVING A VANADIUM NITRIDE DISPERSION

Howard C. Fiedler, Niskayuna, N.Y., assignor to General Electric Company, a corporation of New York

No Drawing. Original application Jan. 4, 1960, Ser. No. 60. Divided and this application Apr. 27, 1961, Ser. No. 105,899

1 Claim. (Cl. 148—31.55)

This invention relates to magnetizable iron and related alloys such as those used in transformers, motors, etc., and more particularly to grain oriented polycrystalline sheet-like bodies composed principally of an alloy of iron and silicon containing some vanadium and nitrogen.

This application is a division of copending application Serial No. 60, filed January 4, 1960, and assigned to the same assignee as the present invention.

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 6.0 percent and preferably about 2.5 to 3.5 percent silicon and relatively minor amounts of various impurities, such as sulfur, manganese, phosphorous, and having low carbon content as finished material.

Such alloys crystallize 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 the 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 atoms 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 edge, 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 pluarity 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 or 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 the 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 employed advantageously. 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 by adding controlled amounts of manganese and sulfur, introduced into the material as impurities. The manganese and sulfur are probably present as a dispersion of manganese sulfide. The significance of the manganese sulfide is demonstrated by the fact that strong textures cannot be developed in high purity vacuum melted silicon-iron alloys prepared from substantially pure iron and silicon and processed in the same manner as alloys containing manganese sulfide.

Before these silicon-irons may be used in certain applications, such as transformers, etc. mentioned above, it is necessary to remove substantially all of the sulfur in order to obtain optimum magnetic properties, since the presence of sulfur exerts an adverse effect upon these magnetic properties.

In actual steel mill practice, cube-on-edge materials are prepared by casting ingots from alloys containing from about 2.5 to 4.0 percent, and preferably from 2.5 to 3.5 percent by weight silicon, less than 0.035 weight percent carbon, about 0.02 to 0.03 weight percent sulfur, and less than 0.1 weight percent manganese. These ingots are conventionally hot worked into a strip or sheet-like configuration, usually less than 0.150 inch in thickness, referred to as "hot rolled band."

The hot rolled band is then cold rolled with appropriate annealing treatments to the finished sheet or strip thickness, usually involving at least a 50 percent reduction in the thickness, and given a final or texture-producing annealing treatment. As presently practiced, this final anneal is accomplished in two steps. First, a short normalizing anneal is carried out at about 800° C. for about five minutes in a wet hydrogen or wet cracked gas atmosphere. This anneal serves at least two purposes—it decarburizes the material or, stated otherwise, reduces the carbon content of the material to a value of less than 0.010 percent by weight, and additionally causes the worked metal structure to recrystallize into a fine grain microstructure. This is usually referred to as a "primary" recrystallization. Because of the relatively low temperature and short time involved in this anneal, it is possible to employ a continuous annealing technique wherein the sheet or strip of metal is fed through a controlled atmosphere furnace at a rate such that any given portion of the strip is raised to the required temperature for the necessary period of time. Such continuous annealing techniques are widely employed in the metallurgical arts and are usually more economical than batch anneals.

The decarburized strips or sheets are then cooled and coated with a refractory material and, depending upon their size and configuration, either coiled or stacked and placed in an enclosed box which is provided with an atmosphere of dry hydrogen or dry cracked gas or in a controlled atmosphere furnace and annealed therein.

During this anneal, two actions occur. First, a "secondary" recrystallization takes place wherein the small grains having the desired (100)[001] orientation grow at the expense of grains having other orientations and, secondly, the sulfur content is lowered and preferably substantially removed. As commercially practiced, it has been found necessary to anneal such material over a considerable period of time in order to accomplish the two actions previously stated and to produce acceptably strong textures. This has required the employment of a batch-type anneal, the total time required for such annealing usually extending from one to two days, since in order to acomplish the anneal in the most economical fashion, large amounts of metal are annealed in each batch.

After annealing, the sheet or strip material must then be flattened to remove warping which usually occurs during the final anneal. This is accomplished by heating the strip or sheet and applying tension thereto, according to existing stretch leveling practices.

The principal difficulty encountered in the use of sulfur is that of removing it from the alloy. At present, the alloy must be heat treated at moderately high temperatures, e.g., 1175° C. for about one hour. Obviously, the extreme length of the heating period materially increases the cost of producing the final sheet, both through the cost of the operation itself and by resulting in a batch process.

It is a principal object of this invention to provide iron-base silicon alloy strip which can be processed in shorter periods of time and at lower temperatures than can existing iron-silicon alloys to produce sheet or strip material having a preferred cube-on-edge grain orientation.

Another 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.

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 vanadium in silicon-iron electrical steels for precipitation as vanadium nitride both in the ingot and when the metal is subjected to an annealing treatment within a nitriding atmosphere. The vanadium nitrides are effective in controlling the secondary recrystallization to develop a preferred grain orientation and are also readily removed from the finished material after the preferred orientation has been developed.

More specifically, it has been found that small additions of vanadium up to 0.15 weight percent, and as little as 0.05 weight percent, to the melt will provide a sufficient amount of vanadium nitride to enable subsequent development of a strong preferred orientation when the solidified melt, after processing to strip form, is given a final texture-developing anneal. A greater amount of vanadium can be present in the alloy but it is not necessary to the process. As little as 0.002 weight percent nitrogen will generally form enough nitride to be effective. The nitrogen present in the ingot is believed to be largely present as vanadium nitride, the uncombined vanadium remaining in solid solution. Generally, the vanadium nitride dispersion may be formed in the metal either by placing sufficient quantities of vanadium and nitrogen in the original melt or by subjecting a vanadium-containing alloy body to a nitrogen-containing atmosphere during the final heat treatment. This nitrogen combines with the solid solution vanadium and forms additional vanadium nitride, which assists development of the texture. The function of the vanadium nitride particles is to prevent normal grain growth. Those grains with (110)[001] orientation readily grow in the fine grain matrix, and result in the development of a strong texture. Of course, if the nitride phase is present in the ingot initially, then the final annealing atmosphere must be controlled to prevent premature removal of the nitrogen, particularly if only a small amount of vanadium nitride was originally present.

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 traces of sulfur and manganese will probably be found in the alloy due to the impurities in the raw materials or from the refractory furnace crucible.

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 and 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 final annealing done to effect secondary recrystallization, that is, to bring on 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 or by heating it to a temperature between 1050° C. and 1150° C. at a moderate rate, such as about 7° C. per minute.

According to the present invention, the atmosphere or environment in which the metal is given its final texture-developing anneal is important since, in some instances, the nitrogen already in the strip should be retained, while in other instances, some additional nitrogen should be added to form more particles of vanadium nitride. The particles formed by combination of the vanadium remaining in solution and the nitrogen from the atmosphere are particularly effective in preventing normal grain growth. 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.

To more clearly illustrate the present invention, several alloys were cast and subjected to varying conditions to develop the cube-on-edge orientation.

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 casing, 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-quarters 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 five minutes with only hydrogen atmosphere and then for an additional five 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 five minutes.

The following Table II sets forth the properties obtained in the "A" and "B" group strips processed as ex-

plained 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 obtained 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 magnetic 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.

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 claim 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:

A polycrystalline sheet-like body having a majority of the constituent grains oriented in the (110)[001] direction consisting essentially of from 2 to 6 weight percent silicon, from about 0.05 to 0.15 weight percent vanadium, at least 0.002 weight percent nitrogen combined with said vanadium to form a vanadium nitride dispersion promoting said (110)[001] grain orientation direction within said sheet-like body, and the remainder substantially all iron.

References Cited by the Examiner

UNITED STATES PATENTS

2,209,686 7/40 Crafts ---------------- 148—111
2,867,559 1/59 May ------------------ 148—111

OTHER REFERENCES

The Iron Age, vol. 171, No. 6, February 5, 1953, pages 147–152 and 186 (pages 148–149 relied on).

Metals and Alloys, vol. 10, January-June 1939, pages 26–31 relied upon.

DAVID L. RECK, *Primary Examiner.*

MARCUS U. LYONS, *Examiner.*