Oct. 8, 1963 E. S. ANOLICK 3,106,496

PROCESS FOR COATING AND ANNEALING GRAIN ORIENTED SILICON STEELS

Filed April 28, 1961

Fig. 1.

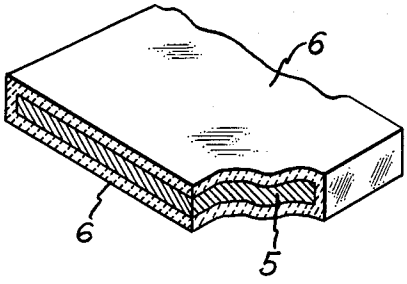


Fig. 2.

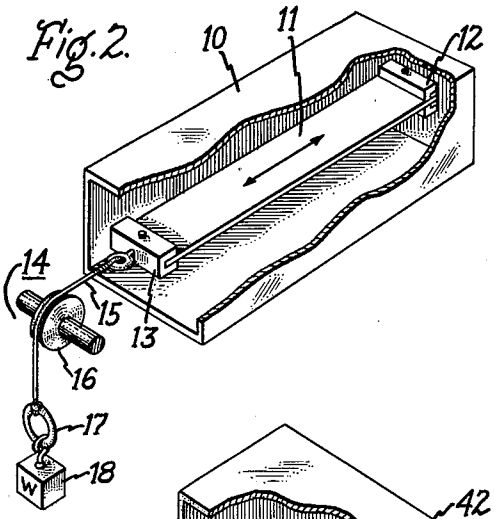


Fig. 5.

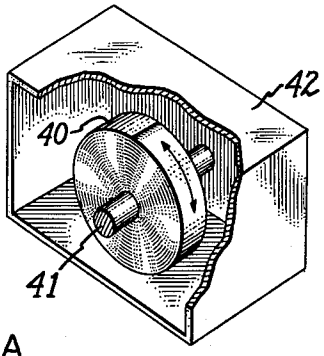


Fig. 3

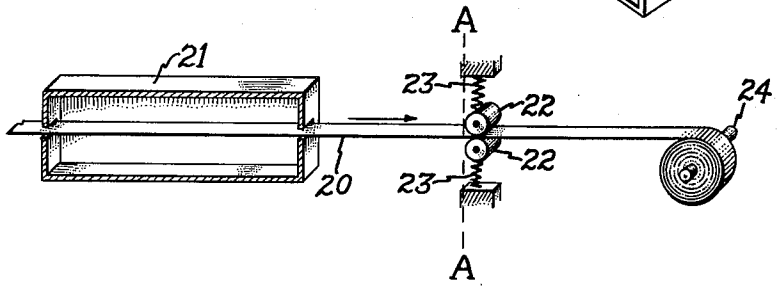
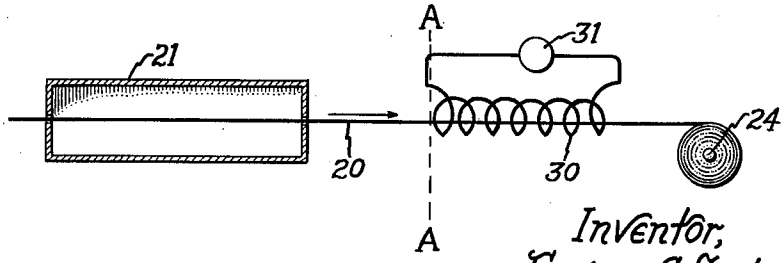


Fig. 4.



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His Attorney.

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PROCESS FOR COATING AND ANNEALING GRAIN ORIENTED SILICON STEELS

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This invention relates to an improvement in the processes for coating grain oriented silicon steels with an insulating coating of calcium orthosilicate.

Many types of electrical induction apparatus such as transformers, dynamos, and the like, have magnetic flux carrying members made from grain oriented silicon steels. Such steels are processed by several known techniques that produce an oriented grain structure having excellent magnetic properties in the direction of grain orientation. This results in minimizing watt losses, magnetizing forces and magnetostrictive strains caused by flux traveling in the direction of grain orientation.

The magnetic steels to which this invention is applicable may have up to about 6% silicon content. The steels may be produced by several well known commercial processes which usually include the following steps: A ferrous alloy containing about 2–5½% silicon and relatively minor amounts of impurities is cast into ingots; hot worked, usually by rolling as a continuous strand; and then subjected to various schedules of usually unidirectional cold rolling. The steel is then heat treated by several combinations of treating cycles which cause primary recrystallization of the grains, decarburization, secondary recrystallization of the grains, and purification by removal of sulfur and other impurities. The thickness of the fully processed steel is usually about .014". The grain orientation of the steels produced by the above type of process is often referred to as the (110) [001] type in the standard notation by Miller's indices. This designation is intended to indicate that the [001] direction of the crystals is parallel to the rolling direction and the (110) plane is parallel to the rolling plane. Considering the crystals as cubes, the designation indicates a cube on edge position of the crystal in the plane of a sheet of the steel.

When such steels are to be used in an electrical induction apparatus having flux carrying members, the steel in the form of a web of sheet material may be wound into a roll, or the web may be cut into a plurality of laminations that are arranged in stacks. The steel is usually wound into a roll or the laminations stacked before it is given the final anneal at high temperatures. During the high temperature anneal the contacting laminations or turns tend to stick together unless some means is provided for separating their surfaces. Also, when wound rolls or stacked laminations of grain oriented silicon steel are used in electrical induction apparatus, it is often necessary that the individual layers of steel be separated by an insulating coating to reduce eddy current losses.

Numerous processes for applying coating compositions that provide interlayer insulation and also separation of the adjacent layers during high temperature annealing are well known to the prior art. However, a number of the coatings employed have serious drawbacks in that they do not adhere tenaciously, they cannot be applied with uniform thicknesses, or they lack adequate insulation qualities. One coating that excels in all these properties is calcium orthocilicate (Ca_2SiO_4) which has been found to have Franklin insulation values of around .2 ampere at thicknesses ranging from about .05 to .20 mil; the coating is refractory and has excellent separating characteristics during high temperature anneals. Economical processes for applying calcium orthosilicate coatings are known to the art, so it is therefore highly desirable that such coatings be available for use on grain oriented silicon steels. Such processes usually include the steps of applying calcium hydroxide [$Ca(OH)_2$] to the surface of silicon steels and then heating to temperatures above about 900° C. for over about two hours. During the high temperature heat treatment, the water of hydration in the calcium compounds is driven off, and a chemical reaction takes place between the resulting calcium oxide (CaO) and silicon dioxide (SiO_2) on the surface of the steel to produce crystals of calcium silicate which are tenaciously bonded to the steel.

Calcium orthosilicate coatings made by heating silicon steels coated with calcium hydroxide to high temperatures have not been successfully employed in commercial electrical induction apparatus. The reason is that steels coated with calcium orthosilicate were found to have increased watt losses and magnetostrictive strains in the direction of grain orientation, when compared with the same steel that had not been coated or that had been coated with other materials, such as magnesium silicate. Consequently, it was previously believed that the only practical use for calcium orthosilicate coatings on grain oriented silicon steels was in limited areas where flux would travel in the cross-grain direction during energization of the apparatus. The reason for calcium orthosilicate coatings causing destruction of the magnetic properties of the steel in the with-grain direction was not fully understood, but it had been hypothesized that the coating prevented adequate removal of impurities during the high temperature purification anneal.

Accordingly, it is an object of this invention to provide an improved process for providing grain oriented silicon steels with an adherent coating having excellent electrical insulating and high temperature separating properties.

A further object of the invention to provide a process by which calcium orthosilicate coatings can be provided on grain oriented silicon steels without causing a reduction in the with-grain magnetic properties of the steel.

Another object of this invention is to provide a process that prevents the destruction of with-grain magnetic properties of silicon steels upon the application of calcium orthosilicate coatings.

Other objects and advantages of the invention will become apparent from the specification, drawing, and claims, and the scope of the invention will be pointed out in the claims.

Briefly stated, according to one aspect of my invention, when grain oriented electrical steels having up to about 6% silicon content are coated with an adherent film of calcium orthosilicate by the process in which calcium hydroxide is applied to the surface of the steel and heated to a temperature above about 700° C., the destruction of the with-grain magnetic properties of the steel can be minimized during the cooling part of the cycle by subjecting the coated steel to a remedial anneal as it cools at temperatures below about 700° C. The expression "remedial anneal" is intended to mean subjecting the steel to a force, such as tension or a magnetic field, that causes the magnetic domains in the grains in the steel to align in the preferred direction of grain orientation.

According to another aspect of the invention, the time at which grain oriented silicon steel coated with calcium orthosilicate exists at a temperature between about 700° C. and about 300° C. during the cooling cycle should be reduced to curtail destruction of with-grain magnetic properties.

The invention will be better understood from the following description taken in conjunction with the accompanying drawings, in which:

FIGURE 1 is a perspective, partially cross sectional view of a portion of a web of grain oriented silicon steel coated with calcium orthosilicate.

FIGURE 2 is a schematic, perspective, partially broken away view of one arrangement for practicing my invention.

FIGURE 3 is a schematic, perspective side view of another arrangement for practicing my invention.

FIGURE 4 is a schematic side view for still another arrangement of practicing my invention.

FIGURE 5 is a schematic, perspective, partially broken away view for still another arrangement for practicing my invention.

It is to be understood that processes for making grain oriented silicon steels and processes for applying calcium orthosilicate coatings to such steels, in themselves, are not a part of the invention. My invention is directed to a process, or a step in a larger process, that reduces or remedies the destruction of with-grain magnetic properties in grain oriented silicon steels having calcium orthosilicate coatings. FIG. 1 shows a portion of a web of grain oriented silicon steel 5 having a refractory coating 6 of calcium orthosilicate bonded to its exterior surface.

I have discovered that the magnetic property destroying effects of calcium orthosilicate coatings on grain oriented silicon steels are caused by compression of the steel by the coating during a critical period in the cooling cycle that causes internal reorientation of the magnetic domains in an undesirable manner. When silicon steels coated with calcium hydroxide are subjected to a high temperature grain growth and purification anneal (e.g., 900 to 1250° C.), calcium orthosilicate is produced during the high temperature anneal. During the cooling cycle, the calcium orthosilicate undergoes a transformation from the alpha phase to the beta phase. This transformation occurs at around 700° C. The phase transformation causes the physical dimensions of the coating to shrink markedly. The shrinking of the coating puts the steel into compression in the direction of preferred grain orientation to a degree that causes significant internal realignment of the magnetic domains in undesirable directions. The compression continues during the cooling cycle below 700° C. and has the effect of a compression anneal that locks the improperly oriented magnetic domains in the cross-grain direction. This reduces the number of domains oriented in the preferred direction and thus increases watt losses and magnetostrictive strains from flux flowing in the with-grain or preferred deriction. The most significant damage to with-grain properties occurs between about 700° C. and about 300° C.

By subjecting the steel to a remedial anneal during the critical period when the calcium orthosilicate coating places it under compression, the damaging effects of the compression are reduced significantly. The remedial anneal can be a tension anneal in which tension is applied in the direction of preferred grain orientation. The amount of tension does not appear to be critical in that stresses of from 500 p.s.i. to 10,000 p.s.i. may be employed; the tension always must be below the elastic limit of the steel at the temperatures encountered to prevent permanent damage by plastic deformation. Satisfactory results have been obtained with tension anneals of 1,000 p.s.i. in as little as 30 seconds at temperatures below 650° C., with the tension being retained for an additional period of 3–5 minutes while the steel was cooled to 300° C. The remedial anneal can also be a magnetic anneal in which a magnetic field above about 5 oersteds is applied in the direction of preferred grain orientation for the same time and temperature cycles used for tension annealing. Fields as low as one oersted may also be employed, but the cooling time between 700° C. and 300° C. should be increased.

Experiments have been performed which show the beneficial effect of remedial anneals on silicon steels coated with calcium orthosilicate during the critical period in the cooling cycle after the alpha to beta transformation has taken place. With-grain Epstein specimens of commercially available .014" thick, 3¼% silison steel having (110) [001] type of orientation were selected from different lots of steel and then provided with different coatings. Uncoated specimens were used as control samples. Some specimens were coated with magnesium oxide and other specimens coated with calcium hydroxide. All specimens were then given a high temperature grain growth and purification anneal at about 1175° C. for about eight hours and then slow cooled to room temperature. Some specimens were then given a with-grain tension anneal at the temperatures and stresses indicated below in Table I. Tension was applied to the specimens individually by clamping one end of a specimen in a jig and connecting known weights to the other end of the specimen. The clamping assembly without the weight was inserted in a furnace preset to the indicated temperature, and when the specimen reached that temperature, the weight was connected to the end that was not in the fixed clamp, thus producing the indicated stress on the specimen. The specimen was held under tension at the indicated temperature for 30 seconds, and then the assembly was removed to a cooling zone in the furnace and allowed to cool at a natural rate. Tension was maintained on the specimen until the temperature was less than 300° C. The tension was then removed and the specimen allowed to cool to ambient temperature. The cooling times varied for from about eight minutes at 600° C. starting temperature to about five and one-half minutes at 500° C. starting temperature. The furnace had a dry hydrogen atmosphere. The results of the test are given in Table I.

Table I

Sample Designation	Coating	Temp. (° C.)	Tension (p.s.i.)	Core Loss at 15,500 Gauss (Watts/lb.)			Magnetostriction Strain (Micro inches/inch)	
				Before Tension Anneal	After Tension Anneal	Percent Change	Before Tension Anneal	After Tension Anneal
1	None	500	0	.615	.610	−0.8	−0.9	1.2
2	do	do	1,000	.600	.579	−3.5	−0.7	−0.6
3	Calcium Ortho-silicate.	do	0	.660	.646	−2.1	2.9	1.4
4	do	do	0	.632	.633	0	−0.4	0.9
5	do	do	1,000	.670	.631	−5.8	4.1	−0.7
6	do	do	1,000	.620	.613	−1.1	−0.3	−0.6
7	Magnesuim Ortho-silicate.	do	0	.618	.620	0.3	−1.0	−1.0
8	do	do	1,000	.612	.617	0.8	−0.8	−0.9
9	None	600	0	.603	.608	0.8	−0.4	1.3
10	do	do	1,000	.600	.589	−1.8	−0.5	−0.7
11	Calcium Ortho-silicate.	do	0	.653	.647	−0.9	2.2	1.2
12	do	do	1,000	.654	.622	−4.9	3.0	−0.4
13	Magnesium Ortho-silicate.	do	0	.608	.607	0	−0.9	−0.5
14	do	do	1,000	.612	.612	0	−0.9	−0.9

Table I shows that the specimens coated with calcium orthosilicate and annealed under tension had significant reduction in watt losses and substantial improvement in magnetostriction strain when compared with similarly coated specimens that were not annealed under tension. Table I further shows that some improvement is discernible in uncoated specimens, but that specimens coated with magnesium silicate do not show noticeable improvement in either watt loss or magnetostriction strain after a tension anneal. From what is known about magnesium silicate coatings, it is believed that these coatings do not place the steel under compression at the temperatures encountered.

Other tests have indicated that there is a small amount of residual compression of calcium orthosilicate-coated steels at ambient temperatures. This causes a slight reduction in with-grain magnetic properties, even after a remedial anneal, when the calcium orthosilicate-coated steel is compared with the same steel that does not have that coating. Nevertheless, the beneficial effect of a remedial anneal in accord with my teachings is sufficient to permit calcium orthosilicate coatings to be used on steels employed in commercial electrical induction apparatus in areas where flux travels in the with-grain direction during energization of the apparatus.

Turning now to the drawing, therein are illustrated several arrangements for practicing my invention. FIGURE 2 shows an annealing oven 10 in which a lamination 11 of grain oriented silicon steel, having the preferred direction of orientation in the direction of the arrow, is clamped at one end by suitable means 12 that is held in a fixed position. The other end of the lamination 11 is clamped by suitable means 13 that is free to move. The movable clamping means 13 has attached thereto, means 14 for applying tension, which may comprise a strand 15 passing over a pulley 16 and having means such as a ring 17 thereon for selective attachment of a weight 18 of known magnitude. The lamination 11 is assumed to have been coated with calcium hydroxide, as for example by dusting powdered lime on its surface. The lamination may then be given its final grain growth and purification anneal by heating for eight hours at about 1175° C. This will cause the formation of alpha calcium orthosilicate. When the lamination is subsequently cooled to about 700° C., the weight 18 should be placed in the ring 17 so that known tension will be applied to the steel during the remainder of the cooling cycle, or at least until the lamination is cooled to about 300° C. It will be apparent to those skilled in the art that a plurality of laminations such as 11 could be stacked and processed in the same manner described above for a single lamination.

FIGURE 3 shows an arrangement for tension annealing a continuous web 20 of silicon steel. The web 20 is moving in the direction of the arrow, which is also the direction of preferred grain orientation. The web is passed through a heat treating oven 21, after first having been coated with calcium hydroxide, as, for example, by dipping the web in a water slurry. In the oven, the steel is heated sufficiently to cause the final grain growth and purification anneal and also cause the formation of alpha calcium orthosilicate. When the web leaves the oven 21 it will pass into a reduced temperature zone and begin to cool. When the web passes the zone designated by the line A—A, its temperature is at about 700° C., and tension should be applied to the steel. This can be accomplished by having the web pass through pinch rollers 22 that are urged against the steel by suitable means such as springs 23. Tension may be applied only to the portion of the web that has passed through the rollers 22 by having the web pulled through the furnace 21 and rollers by rotation of a mandrel 24, upon which the web is being wound.

FIGURE 4 shows another arrangement for practicing my invention that is similar to the arrangement of FIGURE 3, in that it is applicable to continuous strand processes. The arrangement of FIGURE 4 differs from that of FIGURE 3 only in that instead of applying tension to the web 20 as it passes the line A—A where its temperature is about 700° C., and alpha to beta transformation occurs, the steel is subjected to a magnetic field traveling in the with-grain direction by having the web pass through the interior of a coil 30. The coil 30 is connected to a suitable source 31 of electric current for producing the magnetic field. The source 31 may provide either direct current or alternating current.

FIGURE 5 shows still another arrangement for practicing my invention in which a spirally wound coil 40 of calcium hydroxide-coated steel is placed on a current-conducting arbor 41 located in a heat treating furnace 42. After the steel has been given its high temperature anneal and cooled to about 700° C., current may be passed through the arbor 41. This will cause a magnetic field to permeate the coil 40 in the with-grain direction (indicated by the arrow) and thus counteract the destructive compression effects of the calcium orthosilicate coating.

Turning now to another aspect of my invention, tests have been performed which show that with-grain magnetic properties of grain oriented silicon steels are damaged by prolonged holding of the coated steel at temperatures between 700–300° C. during the cooling cycle with no externally applied remedial force. In one test, a first group of specimens of commercially available 3¼% silicon steel having a (110) [001] type of orientation that had been coated previously with calcium orthosilicate were raised to 650° C. for one hour and then slow cooled at the rate of 100° C. per hour to about 150° C.; these specimens showed a watt loss in the with-grain direction of .685 watt per pound at 15,500 gauss. A second group of previously coated specimens from a different lot of the same type of steel were raised to 500° C. for one hour and then slow cooled at a rate of 100° C. per hour to about 150° C.; these specimens showed a watt loss of .727 watt per pound at 15,500 gauss. Then all of the specimens were raised to 750° C. and then immediately cooled rapidly to about 300° C. in about two minutes. The first group of specimens showed a watt loss of .639 after the 750° C. rapid cool treatment. The second group of specimens showed a watt loss of .665 after the 750° C. rapid cool treatment. These tests show that harmful effects occurred during prolonged cooling of the coated steel between 700° C. and 300° C. Thus another aspect of my invention is the quick cooling of steels coated with calcium orthosilicate through temperatures below the temperature where the alpha to beta transformation takes place. The quick cooling must not be carried out at a rate that causes damage to the grain structure of the steel. It is estimated that cooling rates of 200° C. to 400° C. per minute will provide satisfactory results without causing damage. This could be accomplished, for example, by blowing a stream of air at ambient temperature across the steel with fans. The rapid cooling of the steel through temperatures below the alpha to beta transformation temperature may be combined with a remedial anneal, as described previously, to minimize loss of magnetic properties.

It has thus been shown that by the practice of my invention, the desirable qualities of excellent insulation strength and adherence, and superior high temperature separation obtainable with calcium orthosilicate coatings can be provided for grain oriented silicon steels without the undesirable destruction of with-grain magnetic properties previously encountered with these coatings. In processes in which silicon steels are coated with calcium hydroxide and then given their final high temperature grain growth and purification anneal, my invention can be economically practiced as the last step in the process, since the steel must pass through the critical temperature range below the alpha to beta transformation temperature while being cooled to ambient temperatures. Thus the practice of my invention does not require the expenditure of energy for

heating the steel or for maintaining the steel for prolonged periods at high temperatures. When a tension anneal is employed as the remedial anneal, the stresses found effective do not cause plastic deformation in the temperature range of the anneal. Also, my invention is suitable for use with either continuous strand or batch type processes.

It will be understood, of course, that while the forms of the invention herein shown and described constitute preferred embodiments of the invention, it is not intended herein to illustrate all of the equivalent forms or ramifications thereof. It will also be understood that the words used are words of description rather than of limitation, and that various changes may be made without departing from the spirit or scope of the invention herein disclosed, and it is aimed in the appended claims to cover all such changes as fall 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. In the process of coating grain oriented electrical steels of up to about 6% silicon content with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, in which process steel coated with calcium orthosilicate is heated to a temperature above 700° C. for providing predetermined grain orientation in the steel and then cooled to ambient temperatures, the improvement whereby destruction of with-grain magnetic properties during cooling is reduced comprising subjecting said coated steel as it cools between the temperatures of about 700° C. and 300° C. to a force in the direction of said grain orientation sufficient to substantially counteract the re-orientation effects of the calcium orthosilicate coating.

2. In the process of coating grain oriented electrical steels of up to about 6% silicon content with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, in which process the steel coated with calcium orthosilicate is heated to a temperature above 700° C. for providing predetermined grain orientation in the steel and then cooled to ambient temperatures, the improvement whereby destruction of with-grain magnetic properties during cooling is reduced comprising cooling the calcium orthosilicate-coated steel at a rate of about 200–400° C. per minute from about 700° C. to about 300° C. and simultaneously subjecting the steel as it cools between about 700° C. and 300° C. to a force in the direction of said grain orientation sufficient to substantially counteract the re-orientation effects of the calcium orthosilicate coating.

3. In the process of coating grain oriented electrical steels of up to about 6% silicon content with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, in which process steel coated with calcium orthosilicate is heated to a temperature above 700° C. and then cooled to ambient temperatures, the improvement whereby destruction of with-grain magnetic properties during cooling is reduced comprising cooling the calcium orthosilicate-coated steel at a rate of about 200–400° C. per minute at temperatures below about 700° C.

4. In the process of coating grain oriented electrical steels of up to about 6% silicon content with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, in which process calcium hydroxide is applied to the surface of said steel and said steel is heated to a temperature above about 900° C. for over about 2 hours for providing predetermined grain orientation in the steel and then cooled to ambient temperatures, the improvement whereby destruction of with-grain magnetic properties during cooling is reduced comprising subjecting the calcium orthosilicate-coated steel as it cools between the temperatures of about 700° C. and 300° C. to a force in the direction of said grain orientation sufficient to substantially counteract the re-orientation effects of the calcium orthosilicate coating.

5. In the process of coating grain oriented electrical steels of up to about 6% silicon content with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, in which process the steel coated with calcium orthosilicate is heated to a temperature above 700° C. for providing predetermined grain orientation in the steel and then cooled to ambient temperatures, the improvement whereby destruction of with-grain magnetic properties during cooling is reduced comprising subjecting the calcium orthosilicate-coated steel to tension in the with-grain direction as it cools between the temperatures of about 700° C. and 300° C., said tension being first applied at about 700° C. and being sufficient to substantially counteract the re-orientation effects of the calcium orthosilicate coating.

6. The process defined in claim 5 in which the tension is from about 500 to 10,000 p.s.i. and always below the elastic limit of the steel.

7. In the process of coating grain oriented electrical steels of up to about 6% silicon content with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, in which process the steel coated with calcium orthosilicate is heated to a temperature above 700° C. for providing predetermined grain orientation in the steel and then cooled to ambient temperatures, the improvement where destruction of with-grain magnetic properties during cooling is reduced comprising subjecting the calcium orthosilicate-coated steel to a magnetic field in the with-grain direction as it cools between the temperatures of about 700° C. and 300° C., said magnetic field being first applied at about 700° C. and being sufficient to substantially counteract the re-orientation effects of the calcium orthosilicate coating.

8. The process for coating a continuous web of (110) [001] grain oriented 2–5½% silicon steel with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, comprising in sequence applying calcium hydroxide to the surface of said web, passing said web through a high temperature zone and there annealing above about 900° C., passing said web through a reduced temperature zone and there cooling to about 700° C., and then applying tension in the with-grain direction sufficient to counteract the re-orientation effects of said coating to the portion of web cooled below about 700° C. as the steel cools to about 300° C., whereby destruction of with-grain magnetic properties during cooling is reduced.

9. The process for coating a continuous web of (110) [001] grain oriented 2–5½% silicon steel with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, comprising in sequence applying calcium hydroxide to the surface of said steel, passing said web through a high temperature zone and there annealing above about 900° C., passing said web through a reduced temperature zone and there cooling to about 700° C., and then applying a magnetic field in the with-grain direction sufficient to counteract the re-orientation effects of said coating to the portion of the web cooled below about 700° C. as the steel cools to about 300° C., whereby destruction of with-grain magnetic properties during cooling is reduced.

10. The process for coating a web of (110) [001] grain oriented 2–5½% silicon steel with an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties, comprising in sequence applying calcium hydroxide to the surface of said steel, winding said web into a spiral coil, passing an electrical conductor axially through the center of said coil, annealing above about 900° C. for over about 2 hours, cooling to about 700° C., passing current through

said conductor to produce a magnetic field in the with-grain direction sufficient to counteract the re-orientation effects of said coating as the steel cools between the temperatures of about 700° C. and 300° C., whereby destruction of with-grain magnetic properties during cooling is reduced.

11. A grain oriented electrical steel of up to about 6% silicon content having an adherent calcium orthosilicate coating having good electrical insulating and high temperature separating properties produced by the process defined in claim 1.

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