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HIGH TEMPERATURE COATING FOR SILICON STEEL

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This invention relates to the production of insulative coatings for ferrous metal stock and more particularly, to refractory coating compositions and silicon steel articles coated therewith exhibiting improved electrical properties. The invention also relates to the use of insulative coatings for the purpose of improving the electrical properties of silicon steel and for the purpose of removing impurities from silicon-bearing ferrous metal stock.

As is well known, energy losses in the cores of transformers, generators and the like are reduced by constructing the cores from thin lamination of silicon steel. The thin laminations, being insulated from each other, materially reduce core losses due to eddy currents; and the addition of silicon to the steel gives the characteristics of high permeability and low hysteresis loss, as well as lower eddy current losses due to high electrical resistance.

The core loss in watts per pound at 60 cycles and 15 kilogausses is the basis for grading silicon steel sheets. Practically all elements other than silicon, when added to iron, adversely affect the core loss of the material. Accordingly, to develop the optimum magnetic properties of iron-silicon alloys, particularly the grain oriented types, the undesirable impurities such as carbon, sulphur, nitrogen, and oxygen in the form of inclusions must be reduced to the lowest possible values. It is common practice in the art to reduce these undesirable elements at whatever stages of manufacture it is possible to do so. Iron-silicon alloys are usually melted by the basic open-hearth method, cast into ingots, slabbed, hot reduced, cold reduced, annealed, again cold reduced, decarburized, and then high-temperature annealed. As far back as the open-hearth charge, an effort is made to carefully select materials containing as low a sulphur and alloy content as possible and to minimize elements, such as aluminum, which form very stable oxides. During melting, the quantities of carbon and sulphur in particular are reduced.

A special effort is made to remove carbon by a decarburizing anneal when the strip is at gauges of 0.012 of 0.014 inch or thinner. During decarburization, the silicon sheets are open annealed at a temperature of about 1500° to 1600° F. in the presence of hydrogen and water vapor, substantially as described in U.S. Patent No. 2,385,332, issued in the name of Carpenter et al. as inventors. The water vapor effects rapid oxidation of the carbon in the silicon steel sheet while the reducing characteristics of the hydrogen prevent oxidation of the iron.

Prior to high-temperature annealing of silicon steel, which usually is in the form of thin laminations or coiled sheet having a thickness varying from about 0.001 to about 0.014 inch, a coating of refractory material must be applied to the steel. This coating is intended to serve a number of purposes not the least of which is the prevention of self-welding of the laminations or coils during the high-temperature anneal, which usually occurs at a temperature in the range of about 1850° to 2250° F. The coating is also intended to permit hydrogen, which

comprises the annealing atmosphere, to diffuse readily into the steel. This is believed to promote the removal of impurities which form compounds on the surface of the steel by combination with said hydrogen. The coating is further intended to provide electrical insulation between the laminations or coils in the final products, e.g., a transformer.

In practice, magnesia is the most commonly used refractory coating material. However, neither this material nor others disclosed in the prior art satisfactorily accomplish all of the aforementioned intended purposes. Magnesia does not provide an extraordinarily high electrical resistance. As a result certain electrical applications of silicon steel, e.g., power transformers, require an additional coating of electrically insulative material. This is true also of dolomite, which requires said additional coating where the silicon steel is intended for both distribution and power transformers.

Accordingly, a principal object of the invention is to provide a coating composition characterized by increased electrical resistance.

A second object of the invention is to provide a mixture of refractory material for use in coating silicon-bearing ferrous metal stock and for improving the electrical properties thereof.

Another object of the invention is to provide an article of manufacture exhibiting improved electrical properties comprising silicon-bearing ferrous metal having on its surface a tightly adherent insulative refractory coating.

Still another object of the invention is to provide a process for reducing the core loss of silicon steel stock by the application of a tightly adherent insulative refractory coating to the surface thereof.

Yet another object of the invention is to provide a method for removing impurities from silicon-bearing ferrous metal while applying to the surface of same a coating to prevent adhesion between laminae thereof during a high temperature anneal.

A further object of the invention is to provide a process for the production of silicon steel stock exhibiting improved electrical properties and having on its surface a tightly adherent insulative coating.

Other objects will be apparent from the following description of the invention, a preferred embodiment of which, illustrative of the best mode of practicing the invention, is set forth therein:

Preliminary investigations of many possible high-temperature coatings for silicon steel showed that mixtures of chromic oxide (Cr_2O_3) and calcium oxide (CaO) had promise, and that an addition of up to about 5% barium oxide (BaO) improved the resulting electrical properties.

A specific mixture of about 55% chromic oxide and about 45% calcium oxide was prepared in powder form and added to distilled water to form a slurry. The slurry was thoroughly agitated in a Waring Blendor and then applied to the surface of semiprocessed silicon steel. Epstein strips (see Metals Handbook, 1948 pages 588 and 589) coated thereby and control strips coated with magnesia were annealed at temperatures of 1950°, 2050° and 2150° F. for periods of 1, 5, 10 and 25 hours, in an atmosphere of dry hydrogen (below minus 20° F. dew point).

Tests were run to determine comparative core loss values and electrical resistance values. The average values obtained by preparing bundles of 24 Epstein strips

each, selecting 5 strips from each bundle and making 3 readings per strip are given in Table I.

TABLE I

Test Results of 55% Cr_2O_3–45% CaO Coating

Annealing Temp. (° F.)	Annealing Time (Hour)	Core Loss (watts/pound)		Elec. Resis. (ohms/sq. cm.)	
		MgO	55 Cr_2O_3–45 CaO	MgO	55 Cr_2O_3–45 CaO
1,950	1	0.704	0.764		
1,950	5	0.647	0.637		
1,950	10	0.655	0.673		
1,950	25	0.654	0.630		
2,050	1	0.655	0.674	9.2	[1] 100,000
2,050	5	0.707	0.658	6.0	[1] 90,000
2,050	10	0.720	0.691	6.0	[1] 500,000
2,050	25	0.638	0.641	9.2	[1] 400,000
2,150	1	0.702	0.752		
2,150	5	0.644	0.679	8.6	[1] 660,000
2,150	10	0.638	0.695	10.8	[2] 1,000,000
2,150	25	0.622	0.672		

[1] Range of a total of 30 readings.
[2] Twenty-eight out of 30 readings were infinity.

TABLE II

Test Results of 70% Cr_2O_3–30% CaO Coating Annealing Temperature of 2150° F.

Annealing Time (Hour)	Core Loss (watts/pound)		Electrical Resistance (ohms/sq. cm.)	
	MgO	70 Cr_2O_3—30 CaO	MgO	70 Cr_2O_3—30 CaO
5	0.709	0.662	7.4	20,000
10	0.689	0.665	3.0	100,000

It is evident from the Table II results that a significant improvement in electrical properties is obtained with the lower-lime mixture of 70% Cr_2O_3–30% CaO.

During the course of the present investigation chromic oxide-calcium oxide mixtures of varying proportions ranging from 100% chromic oxide to 100% calcium oxide were prepared with additions of up to 5% barium oxide. Epstein strips were coated with a number of these mixes and then annealed at temperatures of 2050° F. and 2150° F. for a period of ten hours in a dry hydrogen atmosphere. Test data for core loss and electrical resistance determinations thereof are compared with those for magnesia in Table III.

TABLE III

Test Results of Cr_2O_3–CaO-BaO Coatings

Composition (Parts by Weight)				Annealing Temp. (° F.)	Core Loss (watts/lb.)	Electrical Resistance [2] (ohms/sq. cm.)	Resistance Infinity Readings [1]
Cr^2O^3	CaO	BaO	MgO				
100	0	5		2,050	0.755	3.8	
100	0	5		2,150	0.692	5.4	
85	15	5		2,050	0.708	13.4	
85	15	5		2,150	0.668	56.1	3
70	30	5		2,050	0.747	29.6	
70	30	5		2,150	0.627		13
55	45	5		2,050	0.653	21.6	2
55	45	5		2,150	0.615	8.3	
45	55	5		2,050	0.674	20.8	7
45	55	5		2,150	0.620	22.0	6
30	70	5		2,050	0.713		13
30	70	5		2,150	0.672		13
15	85	5		2,050	0.718	96.0	3
15	85	5		2,150	0.763	20.8	
0	100	5		2,050	0.735	25.7	
0	100	5		2,150	0.679	15.4	
			100	2,050	0.684	5.5	
			100	2,150	0.641	3.6	

[1] Total of 15 readings per Epstein bundle.
[2] Average of readings other than infinity.

It will be noted from Table I that the core losses attendant the use of 55% Cr_2O_3–45% CaO coating are comparable to those attendant the use of the prior art magnesia coating for annealing temperatures of 1950° and 2050° F. However, the electrical resistance values of the 55% Cr_2O_3–45% CaO coating for the annealing temperature of 2050° F. are markedly superior. For the annealing temperature of 2150° F. electrical resistance values of the 55% Cr_2O_3–45% CaO coating are superior although core loss values are somewhat inferior.

In an effort to improve core loss values at the annealing temperature of 2150° F. the percentages of ingredients in the 55% Cr_2O_3–45% CaO mixture were varied to 70% Cr_2O_3–30% CaO on the theory that the lime fraction was too reactive at the high temperature.

In accordance with the aforementioned procedure Epstein strips coated with a mixture of 70% Cr_2O_3–30% CaO were annealed at 2150° F. for period of 5 and 10 hours and tests for core loss and electrical resistance were made, the results of which are shown in Table II.

It is significant to note that the addition of 5 parts BaO to the 55% Cr_2O_3–45% CaO and 45% Cr_2O_3–55% CaO mixtures results in improved core loss values with annealing temperatures of 2050° F. and 2150° F. This improvement is also achieved by the addition of 5 parts BaO to the 70% Cr_2O_3–30 %CaO mixture when an annealing temperature of 2150° F. is employed. In all cases Table III shows that the addition of 5% BaO to Cr_2O_3-CaO mixtures results in superior electrical resistance.

In addition to producing coating compositions exhibiting improved electrical properties, the mixtures of the present invention produced smooth slurries and was unattended by the problem of thickening which normally accompanies magnesia. It was noted that application of the inventive mixtures and slurries to Epstein strips by rolling produced coatings of pronounced uniformity. Other properties such as fired uniformity, adhesion and resistance to cracking and spalling on bending were observed to be equal or superior to magnesia.

Having thus described our invention so that others

skilled in the art may be able to understood and practice the same, we state that what we desire to secure by Letters Patent is defined in what is claimed.

We claim as our invention:

1. A process for reducing the core loss of silicon steel stock having on its surface a tightly adherent insulative coating which comprises coating the surface of said stock with a slurry of ceramic material containing between about 15 to 85% chromic oxide, the balance calcium oxide, and heat treating said stock whereby said surface fuses with a portion of said ceramic material to form a glassy layer.

2. In the method of treating silicon-bearing ferrous metal stock to remove impurities while applying to the surface of the stock a coating to prevent adhesion between laminae thereof during a high temperature anneal, the steps comprising applying to the surface of the stock a coating of ceramic material containing about 15 to 85% chromic oxide, the balance calcium oxide, and subjecting the coated stock to a high temperature anneal whereby said ceramic material reacts with the impurities in the stock to form compounds on the surface thereof permitting greater diffusion of the impurities from the center of the stock to said surface while forming an insulative coating thereon.

3. In a process for the production of silicon steel stock exhibiting improved electrical properties and having on its surface a tightly adherent insulative coating the steps comprising coating the surface of said stock with a mixture of refractory material containing about 15 to 85% chromic oxide, the balance calcium oxide, and subjecting the coated stock to a high temperature anneal whereby said refractory material reacts with the impurities in the stock to form compounds on the surface thereof permitting greater diffusion of the impurities from the center of the stock to said surface while forming a glassy layer thereon.

4. An article of manufacture for use in electrical applications comprising silicon steel sheet or strip which has been subjected to a high temperature anneal after having had applied to its surface a slurry of ceramic material containing 15 to 85% chromic oxide, the balance calcium oxide.

5. An article of manufacture for use in electrical applications comprising silicon-bearing ferrous metal having on its surface a tightly adherent insulative coating obtained by applying thereto a mixture of refractory material containing 15 to 85% chromic oxide, the balance calcium oxide, and annealing.

6. An article of manufacture comprising silicon steel having on its surface a glassy layer obtained by applying thereto a mixture of refractory material containing 15 to 85% chromic oxide, the balance calcium oxide, and annealing in the range of 1850° to 2250° F.

7. An electrical coil according to claim 6.

8. A transformer coil according to claim 6,

9. A mixture of refractory material consisting essentially of 15 to 85 parts by weight chromic oxide, 85 to 15 parts by weight calcium oxide, and from an effective amount up to about 5 parts by weight barium oxide for the purpose of improving core loss in silicon steel.

10. A slurry for use in coating silicon-bearing ferrous metal stock, comprising a dispersoid consisting essentially of 15 to 85 parts by weight chromic oxide, 85 to 15 parts by weight calcium oxide and up to about 5 parts by weight barium oxide, and a liquid vehicle in sufficient amount to enable the slurry to be applied as a coating to the surface of the metal stock.

11. A coating composition for use in the prevention of self-welding of silicon-bearing ferrous metal stock, said composition consisting essentially of about 15 to 85 parts by weight chromic oxide, about 85 to 15 parts by weight calcium oxide and from an effective amount up to about 5 parts by weight barium oxide for the purpose of improving electrical resistance.

12. A coating composition according to claim 11 wherein the chromic oxide content is about 70 parts by weight.

13. A coating composition according to claim 11 wherein the chromic oxide content is about 45 to 55 parts by weight.

14. A coating composition according to claim 11 wherein the chromic oxide content is about 70 parts by weight and the calcium oxide content is about 30 parts by weight.

15. A coating composition according to claim 13 wherein the calcium oxide content is about 55 to 45 parts by weight.

16. The process of claim 1 wherein said ceramic material includes up to about 5 parts by weight barium oxide.

17. The process of claim 2 wherein said ceramic material includes up to about 5 parts by weight barium oxide.

18. The process of claim 3 wherein said ceramic material includes up to about 5 parts by weight barium oxide.

19. An article of manufacture for use in electrical applications comprising silicon-bearing ferrous metal having on its surface a tightly adherent insulative coating consisting essentially of about 15 to 85 parts by weight chromic oxide, about 85 to 15 parts by weight calcium oxide, and up to about 5 parts by weight barium oxide.

20. An article of manufacture according to claim 19 wherein the chromic oxide content is about 45 to 55 parts by weight and the calcium oxide content is about 55 to 45 parts by weight.

21. An article of manufacture according to claim 19 wherein the chromic oxide content is about 70 parts by weight and the calcium oxide content is about 30 parts by weight.

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