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Assessment of a novel method of improving the characteristics of electrical steels by a surface diffusion technique

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A method of adding either aluminium or silicon to electrical steel sheet from a coating applied to its surfaces is described. This is done in order to improve the a.c. magnetic properties of the material through the setting up of a controlled resistivity gradient through the thickness of the material. A paste containing the chosen element in powder form mixed with sodium silicate solution is applied to the steel, which is then heated to such a temperature as permits diffusion of the element into it. Suitable control of the amount and distribution of the element can yield reductions in iron loss, magnetostriction and stress sensitivity of the material. In this paper the controlling parameters are discussed in detail; a subsequent paper will describe a series of experiments carried out on a range of materials using both silicon and aluminium pastes.

1. Introduction

Escalating energy costs have made it more important to consider ways in which iron losses in electrical machines can be reduced. Recent data [1] show that the cost of core losses in the USA is over $\$3 \times 10^9$ per annum and now there is a tendency to lower the operating flux densities in large machines in order to reduce the iron losses at the expense of increased capital cost, size and weight.

There are several approaches to the problem either by attempting to improve the core material or by using existing materials more efficiently. As far as short- or medium-term prospects are concerned it is more attractive to investigate methods of developing existing steels. To this end, much work is being carried out throughout the world on surface coatings, better control of purity, texture and grain size.

This paper discusses a novel method of reducing losses by modifying the alloy composition of a range of existing electrical steels. These range from low-grade steels used in cheap domestic motors to the high-grade alloys used in large power transformers.

A method of introducing additional alloying elements from a surface coating which could be applied during the production process is described. Depending on subsequent heat treatments these additional elements can be distributed either uniformly or in a controlled non-uniform way through the thickness of the sheet. As well as providing a source of the additional element, the residual paste can also form the basis of an insulating coating. This paper discusses the important parameters and the extent to which they can be controlled to reduce iron losses and a subsequent paper [2] will describe in detail results of a series of experiments designed to evaluate the method and assess its potential using either silicon or alternatively aluminium as the additional element.

2. Electrical steels

Electrical steels, the alloys used as the magnetic cores of electrical power devices, range from the cheapest least efficient non-oriented grades, to the more expensive, more sophisticated grain-oriented (110) [001] materials. All are iron–silicon alloys with silicon contents between zero and 3.2%. The grain-oriented grades have a tough insulating coating baked on during the production

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process. The basis of the coating is magnesia, which reacts with silicon in the steel during heat treatment to form magnesium silicate. A second layer of coating is formed by reaction of magnesia with phosphoric acid to form a hard phosphate layer which produces a tensile stress in the steel when it is baked. As well as providing electrical insulation between adjacent laminations in any core the beneficial tensile stress in the steel enhances the magnetic properties.

In addition to requiring high saturation magnetization and permeability, electrical steels for a.c. applications should have high electrical resistivity in order to minimize eddy current losses. One way of attempting to produce a material with a high resistivity is to raise the silicon content above 3%. If the silicon content is increased to 6%, the alloy not only possesses high resistivity but it also has low anisotropy and zero magnetostriction. The saturation magnetization of the alloy would drop but the other benefits would probably outweigh this disadvantage – especially in view of the anticipated greater importance of core losses in the future.

Attempts to produce 6% silicon–iron using conventional methods have only met with limited success because of the brittle nature of the alloy which makes the rolling processes more difficult. One method of overcoming the problem is to roll 3% silicon–iron to its final thickness using conventional techniques and then to diffuse silicon into it, thereby increasing the resistivity.

The next sections review previous attempts at increasing the resistivity of electrical steels by surface diffusion techniques and discuss the main relevant parameters before outlining a new method which appears to be an improvement on earlier methods.

3. Previous work

Work has been carried out on siliconizing steel for the purpose of increasing the hardness and corrosion resistance of components and a method based on such processes was used on (1 1 0) [0 0 1] oriented electrical steel by Ames *et al.* [3] who passed silicon tetrachloride gas over the material at a high temperature in order to supply the additional silicon to diffuse into the steel. The process did not appear to affect the macrostructure of the steel nor cause porosity whilst the resistivity was increased from 47 $\mu\Omega$ cm to 83 $\mu\Omega$ cm by raising the silicon content from 3.2% to 6.7%. At 1.5 T the power loss dropped from 1.22 W kg^{-1} to 0.99 W kg^{-1} after diffusion and a corresponding improvement in permeability was noted. The benefits of the process were not so significant at higher flux densities.

The work of Ames *et al.* was extended by Pegler [4] in an attempt to diffuse silicon into the steel in a similar manner but in such a way that the silicon concentration of the material would be maximum at the surface and drop in some controlled manner to a minimum at the centre of the strip. The associated resistivity gradient was hoped to nullify the effects of eddy currents, but he found in some cases the loss actually increased due to internal stresses causing an increased hysteresis component, which masked the benefits of the reduction in eddy current loss.

Another method tried by the same author [4] was to plasma spray silicon or silicon–iron mixture on to the steel and then to diffuse the constituents of the coating into the steel using a high temperature anneal. The method did not prove successful because of an apparent barrier at the interface even after spraying in an inert atmosphere to eliminate oxidation.

Several methods which involve the use of silicon powder as a pure element or as ferrosilicon have been described in patents for diffusing extra silicon into silicon–iron. One such patent [5] claims a successful method of baking a ferrosilicon–alumina mixture onto the surface of the steel at a high temperature. Another method [6] claimed to be successful is to coat the sheet with tridecyl alcohol on to which silicon powder adheres and a subsequent high-temperature anneal causes diffusion into the metal.

Electrodeposition has been attempted by various investigators. One method was to use an electroplating bath containing fine silicon powder, iron chloride and another halide which produces a layer described as a dispersion of silicon-containing particles in an iron matrix. This was claimed to reduce surface eddy currents [7].

The next most effective element to silicon for increasing the resistivity of iron is aluminium. Although the addition of this metal to iron does not produce the rolling problems associated with 6% silicon, manufacture of Fe–Si–Al steel by conventional techniques is made difficult by the oxidation of aluminium during annealing. The result of this is that alumina inclusions occur in the sheet, seriously affecting magnetic properties.

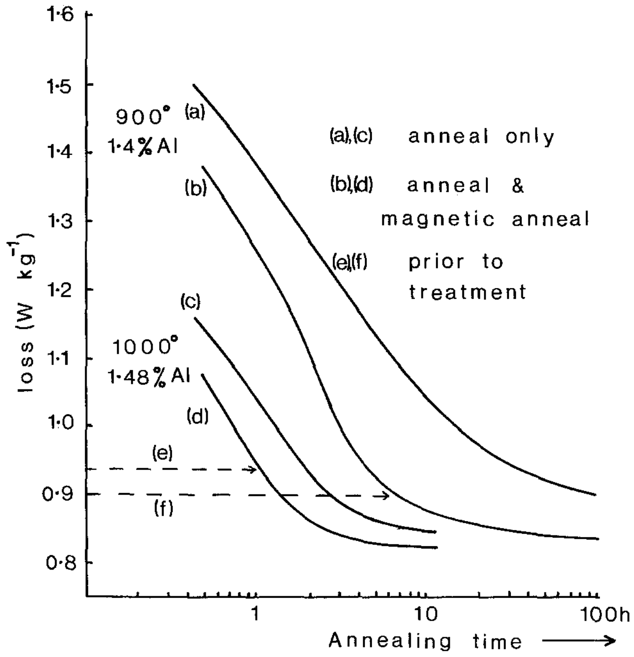

Figure 1 Variation of power loss with annealing time for aluminized samples (after Couderchon [10]).

Attempts have therefore been made to introduce aluminium to (100) [110] rolled sheet 3% silicon–iron. Brissonneau and co-workers [8, 9] and Couderchon [10] achieved this by vacuum depositing a layer of aluminium on to the surface of a sheet which was then annealed at 900 to 1100° C to cause that element to diffuse homogeneously into the steel. The best improvement was a reduction of 12% in power loss obtained after an anneal of several hours followed by magnetic annealing. Fig. 1 shows the improvement achieved. It was found that stress set up by the concentration gradient of aluminium in the early stages of diffusion produced an increase in power loss.

The same authors also added aluminium to 3% silicon–iron by a cladding method in which the weight of aluminium added is controlled by the thickness of the aluminium sheet, which was coiled with the steel during heat treatment at about 725° C [11]. It was claimed that losses of less than 0.75 W kg^{-1} at 1.5 T could be achieved in this way.

More recently, rapidly quenched 6% silicon–iron has been produced and found to be magnetically satisfactory and mechanically ductile [12]. However, this material is a long way off commercial production for large-scale use because the finished sheet is narrow and very thin.

Most of the processes discussed in this section have been high-temperature techniques using deposition methods which would be costly to put into commercial practice. Also they are mainly aimed at producing uniform element concentration through the sheet thickness. Little information is available on the use of concentration gradients which can be put to advantage as described in the next section.

4. Possible advantages of non-uniform element distribution

Eddy currents occur to a greater extent close to the surface of a lamination than in the centre but it may be possible to set up a resistivity gradient through the thickness of the material which would modify the flux and eddy current distribution advantageously. This could be achieved by the non-uniform addition of a suitable alloying element as shown in Fig. 2.

The flux density b on a plane distance X from the centre of a lamination of thickness $2a$ at any time t can be expressed in terms of the resistivity, ρ, and permeability, μ, at that point as

$$\frac{\partial b}{\partial t}\cdot\frac{\rho}{\mu}=\frac{\partial^2 b}{\partial X^2}. \tag{1}$$

This can be modified to take into account the variation of ρ, the resistivity gradient caused by diffusion of an element into the steel and it can be shown that

$$\frac{\partial b}{\partial t}=\frac{\rho_s}{\mu}\cdot\frac{\partial^2 b}{\partial X^2}+\frac{1}{\mu}\,\frac{\partial b}{\partial X}\cdot\frac{\partial \rho}{\partial X}, \tag{2}$$

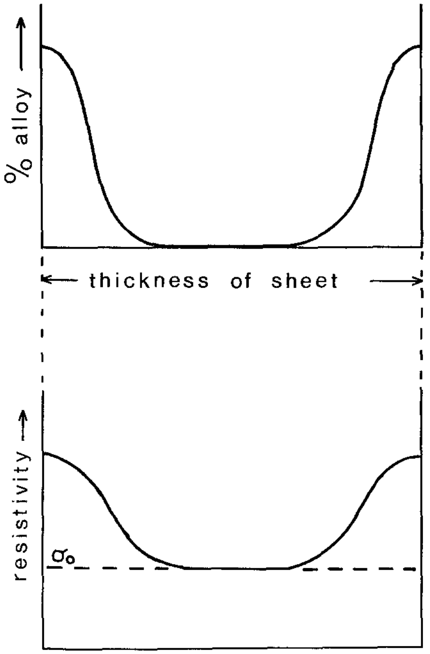

Figure 2 Possible alloy concentration and resistivity profiles through the thickness of a sheet.

where ρ_s is the surface value of resistivity. Fig. 3 shows the effect of various resistivity profiles being substituted into Equation 2 in order to estimate the effect on power loss [13]. Based on the assumption that the B–H curve is linear and domain walls are smooth with no bowing, it can be seen that theoretically a change in loss should occur. If an element is diffused into the steel in a controlled manner an optimum profile producing minimum power loss appears possible depending on the diffusion characteristics of the element in the steel and on the thickness and initial resistivity of the starting material.

5. Possible use of silicon or aluminium as diffusing elements

As silicon and aluminium are the two most effective elements to alloy with iron to increase its resistivity, they seem most suitable to consider as the diffusing element. Both reduce the saturation magnetization of the iron so it is desirable to keep their percentage as low as is consistent with low power loss values.

From available data [14, 15], it can easily be estimated that to diffuse additional silicon to the centre of a 0.33 mm thick sheet of 3% silicon–iron it would take about 6 h at 1000° C. If, as suggested by Fig. 2, complete diffusion is not necessary lower temperatures or shorter times could be employed.

The last section shows that theoretically diffusion gradients should be able to improve the losses of electrical steels. The main difficulty is to find a process which can be used to diffuse silicon or aluminium into the bulk steel using a process which is reliable, safe and economical. Since none of the methods described earlier seemed acceptable, an alternative was sought. It was felt that a paste which when applied to the sheet surface would dry to give elemental

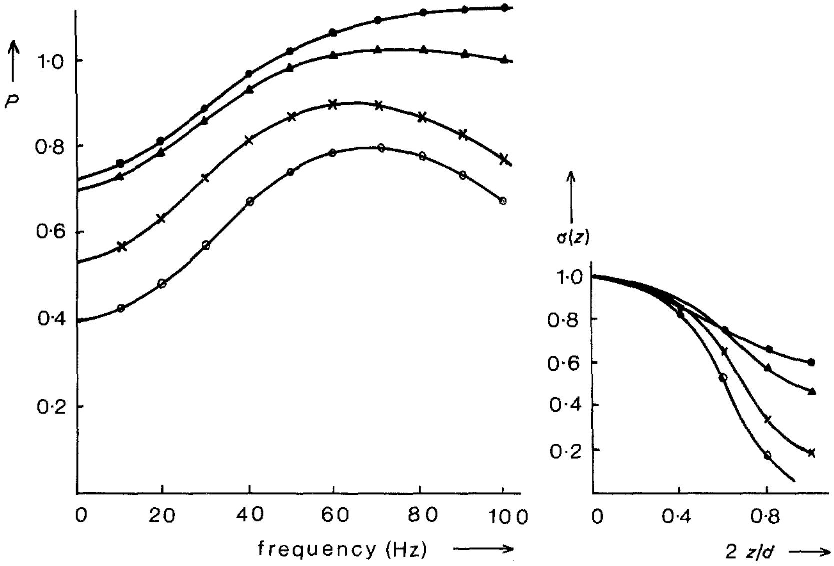

Figure 3 Relative power loss (P) shown for given resistivity profiles ($\sigma(z)$) through a sheet of thickness $2d$.

powder in a glassy matrix would provide a suitable source of the element. On heating to a suitable temperature the element should diffuse from the paste into the steel under the correct conditions. It was decided to make such a paste using as a start silicon powder and sodium silicate solution (water glass).

Sodium silicate is the name for a family of compounds whose compositions may vary over a large range. The chemical composition is usually given as $x\text{SiO}_2:\text{Na}_2\text{O}$ where x may take any non-integral values. It was thus necessary to decide which composition of sodium silicate would be the most suitable for the proposed application. In the solid form, sodium silicate forms an anhydrous glass whose structure consists of SiO_4 tetrahedra with the sodium ions randomly dispersed at the interstices. If sodium silicate is allowed to air dry the dried state can vary from tough and glassy with some elastic properties when the $\text{SiO}_2:\text{Na}_2\text{O}$ ratio is low, to a brittle, friable solid as the SiO_2 content increases. Clearly, a tough, non powdering coating is needed to achieve reliable results as the function of the paste is to allow the element to diffuse into the steel in a controllable manner. The powder must remain in suspension in the sodium silicate whilst in the liquid state without settling out. This ability depends mainly upon the size and shape of the powder particles and the viscosity and colloid content of the sodium silicate solution. Strong bonding between the liquid and solid particles hinders movement of the powder and promotes its suspension. An important effect of the sodium silicate, if the ratio $\text{SiO}_2:\text{Na}_2\text{O}$ is greater than about 2, is the presence of colloidal silica micelles which comprise polyanions which may be chemisorbed on to the surface of the powder thereby giving the powder particles strong negative surface changes making them repel each other such that settling is opposed.

The other important factor to be considered is the pH of the solution as it was found that an alkaline silicate solution tended to react strongly with the silicon powder. The pH is found to increase with the value of x.

It is thus evident that a suitable compromise had to be reached in determining the silicate used as different considerations suggested different compositions. This may be summarized as follows: the solid state toughness and alkalinity should be low whilst in order to obtain a colloid content to maintain the powder in suspension a higher value was needed. A value of $x = 2.5$ was settled upon after tests had shown it to produce a paste with good properties of application.

In order that a constant interface be maintained between the paste and the sheet, it is essential that the paste wets the metal and adheres on drying, The surface of the sheet must be clean before application of the paste to ensure this is so.

When the paste is air dried on the steel surface it consists of powder particles set in a glassy matrix. After air drying the paste will contain some water due to the water-retaining properties of sodium silicate and this is not finally removed until the paste has been heated to over 600° C when the silicate becomes close to the anhydrous state.

6. Parameters of the process

There are a wide range of variables in the diffusion process using sodium silicate as the carrier. The most obvious are listed below.

(1) Characteristics of the paste ingredients:

(a) size and shape of silicon or aluminium power;

(b) composition and strength of sodium silicate solution;

(2) Composition of the paste:

(a) ratio of sodium silicate to silicon (aluminium) powder;

(b) the amount of water added to achieve the required consistency;

(c) the amount and composition of other ingredients (e.g. HCl, silica).

(3) Application of the paste:

(a) thickness of paste layer;

(b) time of air drying of the paste.

(4) Firing conditions:

(a) the soak temperature;

(b) the time at the soak temperature;

(c) rate of rise and fall of temperature;

(d) the atmosphere during firing.

7. Use of the paste

There are two fundamental ways of controlling the quantity of element which diffuses into the steel from the paste. One is to limit the amount of silicon or aluminium available by controlling the composition and thickness of the paste so that after suitable firing time and temperature all the available element is transferred to the

TABLE I Change in power loss produced by diffusing silicon into 2.9% non-oriented silicon-iron

	Loss (W kg^{-1})			
	50 Hz		400 Hz	
	1.0 T	1.25 T	1.0 T	1.25 T
As-received	1.38	2.05	22	37.6
After firing	1.20	1.80	18.8	34.8
Percentage improvement	13%	12%	15%	7%

steel. The other is to provide more element in the paste than required and control the amount entering the steel by altering the time and temperature of the firing – then the residual coating must be removed.

The concentration profile may be modified once the requisite amount of silicon or aluminium has been introduced to the steel by further annealing. This increases the penetration depth of the element. If the finite source method is used the firing and subsequent annealing can be combined but when excess element is available during firing the excess coating must be removed before annealing.

8. Preliminary results

In order to determine the possibilities and feasibilities of the process a series of experiments were carried out. Some of the preliminary results are reported here.

Silicon powder, 99% pure, granular and of size approximately 45 μm was mixed with sodium silicate solution of strength 1.57 g l^{-1}. This provided a workable paste and was used for all the preliminary experiments.

A paste was prepared and brushed onto 0.35 mm thick strips of 2.9% non-oriented steel and air dried for 12 h. The samples were fired at 1100° C for 1 h in a tube furnace with a hydrogen atmosphere. The heating and cooling rate was 200° C h^{-1}.

The residual coating was removed with emery paper after firing.

The resistivity of the material was found to increase from 47 $\mu\Omega$cm to 60 $\mu\Omega$cm suggesting that the silicon content of the strips had risen to 4% (not accounting for the non-uniform distribution of the silicon through their thickness).

Power loss was measured using a standard single strip loss tester incorporating an electronic wattmeter whose inputs were signals proportional to H, the field in the sample, and dB/dt, the rate of change of flux density in the sample. Table I shows the average improvement in loss measured at frequencies of 50 and 400 Hz.

Further experiments were carried out using the same procedure and composition, but with the firing temperature reduced to 900° C. At this temperature no perceivable reaction between the paste and steel occurred, as expected from diffusion data.

Samples were prepared for analysis on a scanning electron microscope and Fig. 4 shows a typical silicon profile measured through the thickness of the steel after firing at 1100° C. The silicon gradient is easily seen but also of significance is the large amount of surface porosity which would tend to increase the hysteresis loss of the steel. It is interesting to note that separating the losses into classical eddy current and hysteresis components indicate that both components drop by approximately equal amounts after diffusion whereas the simple theory suggests that eddy current losses should be reduced whilst the porosity should increase the hysteresis loss.

9. Conclusions

The preliminary results show that diffusion of

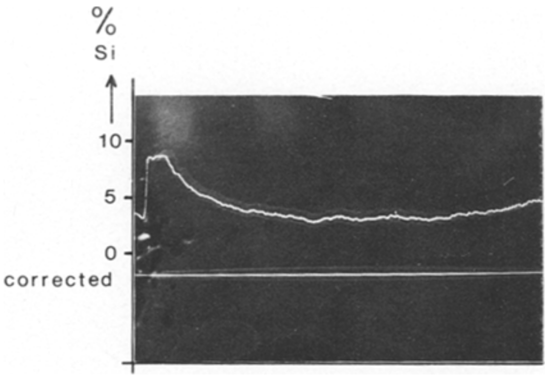

Figure 4 Scanning electron micrograph showing the variation of silicon content through the thickness of a sample after firing at 1100° C (× 210).

silicon from a surface paste into silicon–iron is possible using a simple technique and a reduction in iron loss can be achieved. A high firing temperature was required but a diffusion gradient could be set up although surface porosity was bad. Because of the preliminary success it was decided to carry out a comprehensive series of tests using different pastes on various materials in order to attempt to optimize conditions and these are reported in a subsequent paper.

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