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# Improvement of magnetic properties of electrical steels using a surface diffusion technique

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The preceding paper described the general process by which the magnetic properties of electrical steels can be improved by a surface diffusion technique. This paper describes detailed effects of adding aluminium or silicon to non-oriented and grain-oriented silicon–iron. The addition of silicon proved more difficult and surface porosity tended to increase the power loss of grain-oriented steel whereas a paste containing aluminium powder was effective on all the materials although it was found that the powder size was critical. A reduction of 10% at 1.5 T in well oriented silicon–iron was achieved using the aluminium powder and an improvement in stress sensitivity of the magnetic properties also resulted.

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## 1. Introduction

A new method has been devised for the addition of extra alloying elements to sheet silicon–iron [1]. Its purpose is to reduce eddy current losses during a.c. magnetization by an increase in resistivity. This paper describes an experimental program carried out to evaluate the potential of the process by applying a range of pastes of differing compositions to the surface of 3% silicon–iron strips which were then fired under various conditions in order to diffuse either aluminium or silicon into the bulk of the material in a controlled manner. The paste was applied using a brush which did not give good control of the coating thickness but the method was convenient since the amount of silicon and aluminium added to the steel could be controlled through alteration of the firing conditions rather than by exhausting a coating containing the required amount of the element. Prior to firing, all the pasted samples were air dried at a temperature of 150° C in order to remove most of the retained water from the sodium silicate.

## 2. Experiments using silicon paste

Tests were carried out on Epstein strips (30 cm × 3 cm) of both non-oriented and (1 1 0) [0 0 1] oriented electrical steels. The pastes which were employed contained 0.33, 0.5, 0.75, 1 or 2.5 ml of sodium silicate solution per gram of silicon. As sodium silicate had been chosen because it dries to give a glassy amorphous material it was decided to try one paste containing 0.5 g of glass powder and 0.25 ml sodium silicate solution per gram of silicon. It was thought that this might produce a more homogeneous paste upon firing without seriously interfering with the transfer of the silicon.

Because a certain instability was observed in the paste due to an exothermic reaction between the silicon powder and the silicate solution it was decided to attempt to reduce the alkalinity of the solution by the addition of a small quantity of hydrochloric acid. The resulting paste contained 2 ml sodium silicate solution and 0.2 ml of 10% HCl per gram of silicon. The full range of pastes considered is shown in Table I.

The samples were all fired at 950° C although lower power loss had been achieved during preliminary experiments at 1050° C. The lower temperature was used to eliminate buckling which occurred in most of the samples fired at the higher temperature. Power loss measurements taken on

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TABLE I Samples and pastes compositions

| Material | Sample paste number | Silicate solution (ml per g Si powder) | Firing temperature (° C), Time (h) |
|---|---|---|---|
| Non-oriented 2.8% | 1 | 0.33 | 950° C, 1 h |
| silicon–iron | 2 | 0.5 | 950° C, 1 h |
| (Transil 335) | 3 | 1.0 | 950° C, 1 h |
| | 4 | 0.25* | 950° C, 1 h |
| Non-oriented 2.9% | 5a | 2.5 | 900° C, 1 h |
| silicon–iron | 5b | 2.5 | 1000° C, 1 h |
| (Transil 300) | | | |
| Goss oriented | 6 | 2.0† | 950° C, 1 h |
| silicon–iron | 7a | 0.75 | 950° C, 1 h |
| | 7b | 0.75 | as 7a + 16 h at 850° C |
| (Hi-B grade M2H) | 8a | 2.0† | 950° C |
| | 8b | 2.0† | as 8a + 1 h at 1000° C |

*Also plus 0.2 g glass powder.
†Also plus 0.2 ml 10% HCl.

samples prepared in the manner described above are summarized in Table II.

Cross sections were cut through some of the samples, which were polished and examined using a scanning electron microscope (SEM) to obtain a view of the morphology of the samples and also to follow the variations in composition through their thickness.

Fig. 1a shows an SEM photograph of the silicon content superimposed on the morphology of a non-oriented sample fired with paste 1. This shows the depth of penetration achieved together with the concentration gradient produced. Some evidence of surface porosity is evident but this is much more apparent in Fig. 1b where paste 3 was used. In most cases considerable amounts of porosity were observed.

## 3. Discussion of the use of silicon paste

In the non-oriented grades of material significant reductions in power loss at magnetizing frequencies of 50 and 400 Hz were obtained, although these were not as great as had been obtained during the preliminary tests carried out at higher temperatures. The most likely reason for this is that at the lower temperature the transfer of silicon from the paste to the steel is incomplete, a view reinforced by the study of the relevant SEM silicon analysis. Little difference was observed between the power loss measurements from samples with paste coatings in the range 0.33 to 1 ml sodium silicate per gram of silicon. In general the differences due to using the various paste compositions were of the same order as the variation from sample to sample coated with one paste. When the paste ratio was increased to 2.5:1 the residual coating was found to be cracked and blistered, this probably being the reason for the poorer power loss results. Considerable changes in the surface porosity were observed, however, with the 1 : 3 paste (number 1) producing the least and the 1 : 1 paste (number 3) the greatest amounts.

TABLE II Changes in power loss after treatment

| Sample paste number | Firing temperature (° C) | %change at 50 Hz and 1.0 T | %change at 400 Hz and 1.0 T |
|---|---|---|---|
| 1 | 950 | −9 | −8 |
| 2 | 950 | −5 | −9 |
| 3 | 950 | −9 | −13 |
| 4 | 950 | −1 | −3 |
| 5a | 900 | + 16 | −7 |
| 5b | 1000 | + 16 | −8 |
| 6 | 950 | + 22 | −3 |
| 7a | 950 | + 200 | + 87 |
| 7b | 950 + 850 | + 20 | 0 |
| 8a | 950 | + 33 | + 22 |
| 8b | 950 + 1000 | + 8 | + 2 |

The porosity was probably produced by vacancies generated either by stress, or the production and dissociation of intermetallic compounds. These areas had silicon contents in excess of the limit of the range being aimed for (about 8%) and were thus probably, for all practical purposes, non-magnetic. Porosity had been observed by Ihrig [2] in his original work on siliconization whilst its absence was noted by Ames *et al.* [3].

The reduction in power loss was considerably less at 400 Hz than would have been predicted from the measurements at 50 Hz, an effect which is probably due to the porous layer. At the higher frequency the flux concentration is close to the surface so the surface damage causes an increase

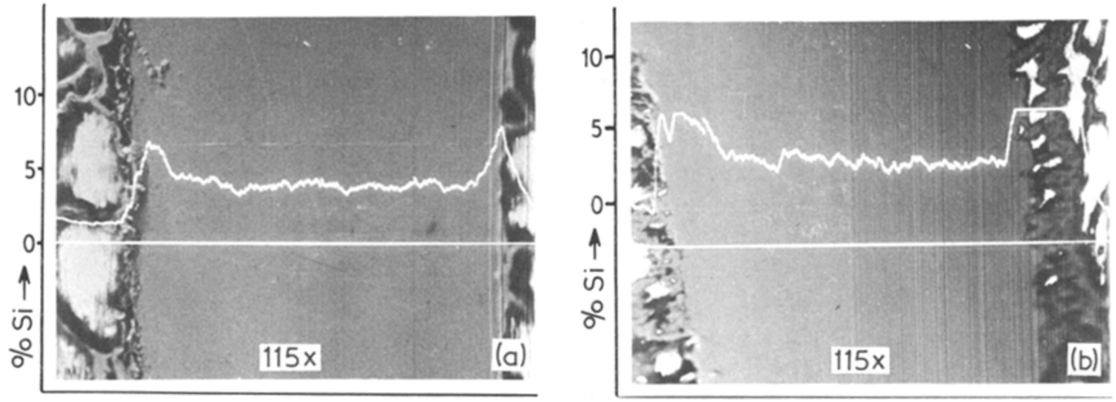

*Figure 1* (a) SEM photograph of a sample fired with silicon paste 1 at 950° C. (b) SEM photograph of a sample fired with silicon paste 3 at 950° C.

in hysteresis loss to nullify some of the reduction in eddy current loss.

The addition of hydrochloric acid to raise the pH of the solution gave a slight improvement in the stability of the paste whilst the addition of glass powder gave deleterious, rather than beneficial, results.

The residual coating was generally very tenacious and could not easily be removed chemically since any effective solvent also attacked the metal underneath it.

In contrast to the results obtained using non-oriented material, the experiments on the (1 1 0) [0 0 1] steel produced increases in power loss. Oriented silicon–iron has minimum losses when it consists entirely of a bar type domain structure in which the magnetic domains extend the full thickness of the sheet. A porous surface layer of high silicon content, if present, reduces the volume of the bar domains by an amount at least as great as its depth and would create unfavourable supplementary surface domain structures. Both of these effects would produce considerable increases in the hysteresis loss. It has also been shown that considerable internal stresses are set up in the sheet during the siliconizing process. These may be relieved by suitable annealing treatments, but the porous layer cannot be reconverted to a solid structure continuous with the bulk of the sheet.

The effect of producing resistivity gradients close to the surface are thus obscured by the effects described above. In (1 1 0) [0 0 1] oriented silicon–iron low compressive stresses (less than $5\,\mathrm{MN\,m^{-2}}$) are sufficient to nullify the benefits expected from the increase in resistivity resulting from the addition of 1 or 2% silicon.

## 4. Conclusions on the use of silicon paste

The power loss of non-oriented steel can be reduced using silicon paste but attempts to improve the properties of (1 1 0) [0 0 1] material failed. In order to make progress it would appear to be essential to control the diffusion in such a way that the formation of porosity is avoided.

## 5. Experiments using aluminium paste

Because of the difficulties encountered with the formation of porosity during the firing of silicon paste, it was decided to investigate the potential use of aluminium in a similar paste form. Aluminium is the next most effective element after silicon for increasing the resistivity of iron and the iron–aluminium phase diagram closely resembles that of iron–silicon in many important respects. Aluminium has a much lower melting point (660° C) than silicon (1410° C) and would thus be expected to transfer from the paste to the steel at a far lower firing temperature. This might help eliminate the formation of porosity. Aluminium does however form intermetallic compounds with iron, these being $Fe_3Al$, FeAl, $FeAl_2$, $Fe_2Al_7$ and $FeAl_3$.

### 5.1. Experiments on aluminizing non-oriented silicon–iron

The range of aluminium pastes tested was similar to the batch containing silicon, i.e. 0.25 to 1.25 ml sodium silicate solution per gram of aluminium. It was immediately evident that pastes were more stable than their silicon counterparts, as they did not produce strong exothermic reactions. Aluminium produces a tough tenacious oxide and it is likely, that once this has been formed, the rest of the metal is protected.

Firing was carried out in the range 800 to 1000° C for one hour in a hydrogen atmosphere.

Although aluminium transferred to the steel at a low temperature, little penetration was achieved due to the slow rate of diffusion of aluminium in iron. It was thus necessary to further heat treat the samples at a higher temperature subsequent to the removal of the residual paste. The power loss of the paste made of 1.25 ml sodium silicate solution per gram of aluminium when fired at 850° C increased by 18% at 50 Hz and 10% at 400 Hz. Subsequent annealing at 950° C reduced these values to 13% and 0%, respectively. The same paste fired at 900° C yielded 13% and 28% reductions in loss however.

A paste made with 0.5 ml silicate solution per gram of aluminium showed a smaller improvement in loss after firing at 900 than at 1000° C, the latter giving a decrease of 13% at 50 Hz. Due to the drop in permeability of the material, however, measurements at 400 Hz could not be taken. SEM observations showed that aluminium had diffused into the steel, e.g. Fig. 2a. The surface compositions were 3% aluminium for a paste fired at 850° C and 6% when fired at 900° C. Penetration was approximately 75% of the thickness at 900° C. Some porosity was found, but this was very small compared to that produced after use of the silicon pastes.

### 5.2. Experiments on aluminizing (1 1 0) [0 0 1] silicon–iron

Early experiments were carried out using 8 to 15 μm aluminium powder but upon obtaining fresh supplies from the manufacturer the size had increased to about 40 μm. This made the production of a smooth paste which did not settle out, very difficult so it was replaced by an approximate 25 μm powder from an alternative source. In order to make a usable paste, very fine ceramic powder (magnesia light) was added together, in some cases, with colloidal silica. The ceramic powder made the paste brush on more consistently and also acted as a dilutant, thereby altering the diffusion characteristics of the aluminium through the paste layer. It was hoped that this would prove beneficial since early experiments had shown that firing produced an increase in loss which required further annealing to be reversed. This suggested that the rate at which the aluminium arrived at the steel surface was too great in comparison to the rate at which it diffused through the steel.

Silicon powder was added to some of the pastes as it has been shown that its presence tends to inhibit the formation of iron–aluminium intermetallic compounds.

Experiments were carried out over a wide range of compositions and firing temperatures. The main objective was to study the effects of changing the paste composition and the firing conditions on the magnetic properties and the physical state of the steel. The outline of the process is shown in Fig. 3.

A power loss reduction of 11% at 1.0 T and 50 Hz was achieved with a paste made with 8 to 15 μm powder. (No reduction in the loss of oriented steel had been obtained using silicon paste). The stress sensitivity of both the power loss and the magnetostriction was considerably improved as shown in Figs. 4, 5 and 6, the effect being approximately double that of the coating applied to the steel commercially. The aluminium had only been added locally at the surfaces and

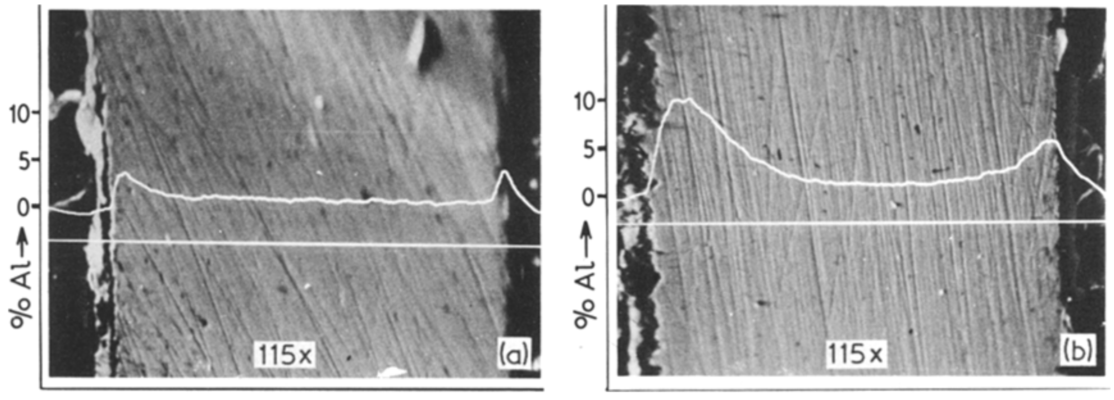

*Figure 2* (a) SEM photograph of a sample fired with aluminium paste 1 at 850° C. (b) SEM photograph of a sample fired with aluminium paste 2 at 900° C.

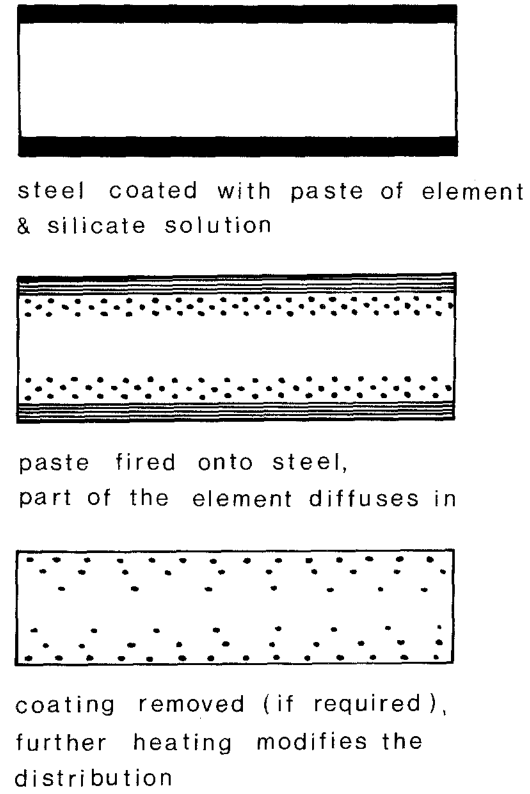

*Figure 3* Outline of paste process.

did not amount to more than 0.5 to 1% of the bulk weight, and thus it was not surprising that the resistivity and $B/H$ loops ($B$ is the magnetic flux density and $H$ is the magnetic field strength) were not noticeably altered, compared to the as-received steel.

Many of the combinations of paste composition and firing conditions produced large increases, rather than decreases in loss. In many cases the reasons were readily apparent, such as buckling of the samples due to internal stresses, or poor adhesion of the paste to the steel with the resultant non-uniform aluminization.

One paste which gave beneficial results employed magnesia light and additional colloidal silica to retain the aluminium powder in suspension. When fired at 725° C under nitrogen and annealed for 2 h at 900° C under hydrogen, the loss when magnetized at 50 Hz dropped by 15% and by 10% at 1.0 and 1.5 T, respectively. Fig. 7 shows the variation in the change in loss with flux density for this case.

It was found that reductions in stress sensitivity occurred in cases where the loss measured at zero stress did not improve. Such a case is illustrated in Fig. 8 for a paste composition (paste 8) which produced an increase in loss of 27% at 1.5 T and 50 Hz.

Increasing the frequency of magnetization up to 400 Hz did not always give a predictable change in the loss. Table III shows a summary of the essential details of all the pastes and Table IV shows the corresponding changes in loss. An SEM photograph showing the aluminium concentration profile of a sample fired with paste 1 is shown in Fig. 9.

Experiments were carried out to study the effect of the diffusant alloy on the internal stress of the steel. This was done by coating one side only of pieces of decoated steel with the most successful silicon and aluminium pastes. Upon firing it was found that even after the removal of the residual coating the steel was bent in a concave manner when viewed from the pasted side. This was surprising because the addition of silicon

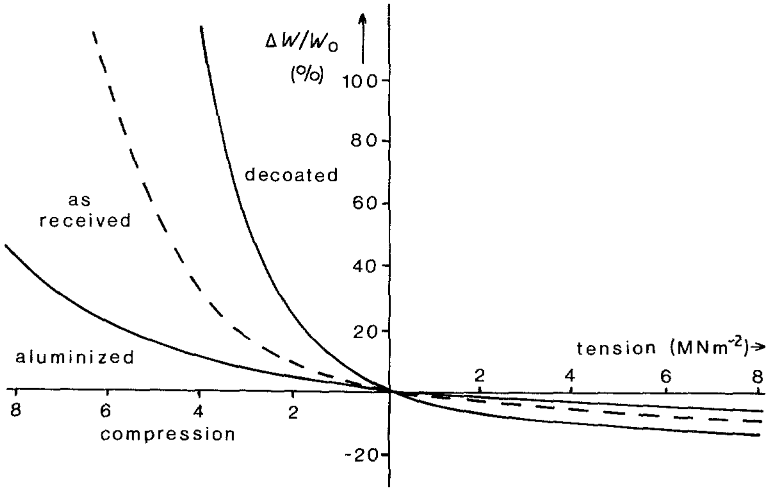

*Figure 4* Variation of power loss under applied stress for aluminized and non-aluminized samples.

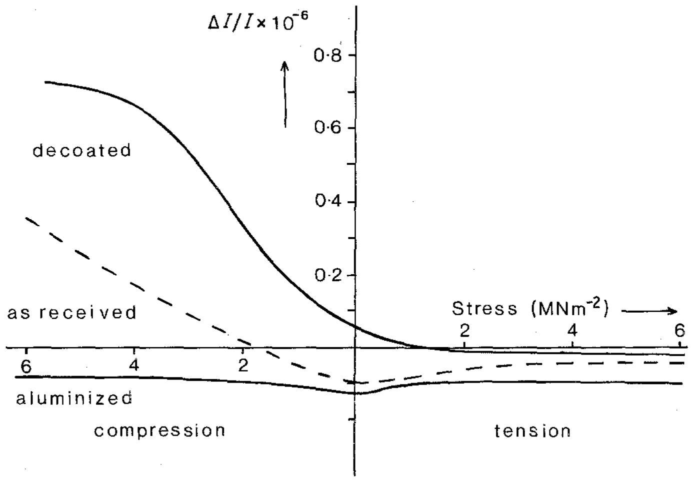

*Figure 5* Variation of magnetostriction under applied stress for aluminized and non-aluminized samples.

to iron reduces the lattice parameter, whilst additional aluminium increases it.

Calculations made from the radii of curvature, using a value of Young's modulus along the rolling direction of $1.3 \times 10^5$ MN m$^{-2}$ gave stress levels of 19 MN m$^{-2}$ and 10 MN m$^{-2}$ for aluminium and silicon, respectively.

## 6. Discussion on the use of aluminium paste

The experiments showed that, under suitable conditions, aluminium paste could be used to reduce the power loss of non-oriented silicon–iron. Far less porosity and surface damage was found after firing with aluminium paste than had been the case with silicon.

In the case of aluminium paste fired onto non-oriented silicon–iron, the improvements in loss can be attributed simply to the increase in resistivity of the material. SEM examinations showed that aluminium had diffused a considerable way into the steel with little formation of porosity.

The conditions and paste compositions which were necessary to produce maximum reductions in the power loss of grain-oriented steel were very different from those employed on the non-oriented material. Using the 8 to 15 $\mu$m powder the temperature of firing to obtain optimum results was 820° C on (1 1 0) [0 0 1] material compared with 900° C for the non-oriented steel.

Prior to annealing, considerable increases in the power loss of oriented material were observed, agreeing with the results of Couderchon's work [4] with vapour deposited aluminium. The reason for this is probably internal stress, due to the build up of aluminium at the surface with a small penetration depth. These stresses, on the evidence of the single side pasting curvature tests, are

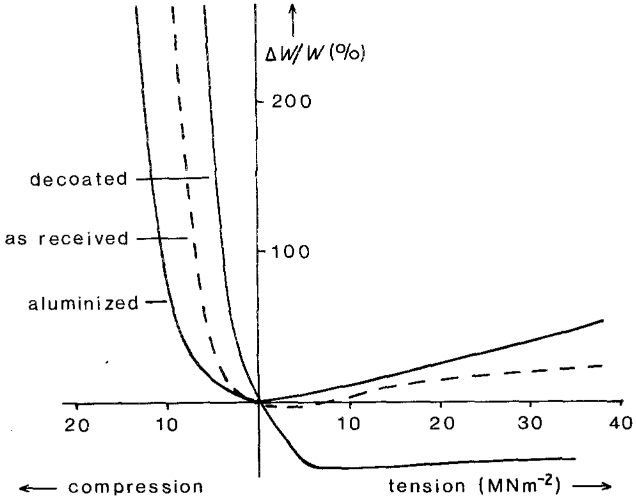

*Figure 6* Variation of power loss under higher applied stresses for aluminized and non-aluminized samples.

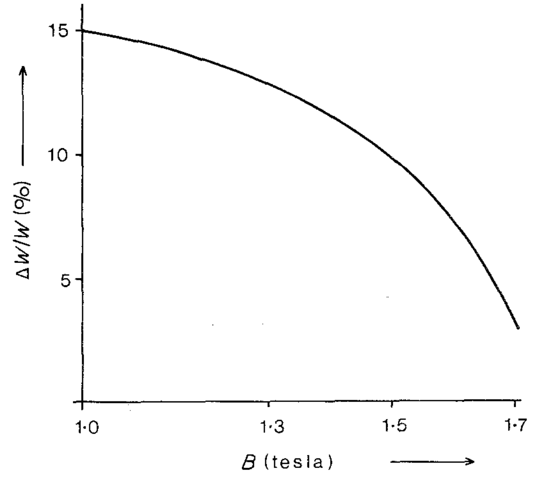

*Figure 7* Variation of reduction in power loss with flux density for aluminized and non-aluminized samples.

probably tensile in the aluminized layer and compressive in the interior. If the surface stresses were of a suitable magnitude they could prove beneficial through stabilizing the bar domain structure and reducing the amount of supplementary domains present. What effect the internal compressive stresses could have is open to conjecture, but if the aluminized region is thin in comparison with the non-aluminized one, then these stresses would be small. The necessity of annealing the sample subsequent to firing suggests that the stress distribution attained is critical to obtaining beneficial results. As aluminium forms a substantial solid solution with iron, and aluminium is a larger atom, the stress pattern predicted would be the opposite of that suggested by the experimental evidence.

This stress arrangement is different to that induced by the commercial ceramic insulating coating which itself is in compression whilst holding the whole of the steel in tension.

In comparison with the amount of aluminium required to produce similar improvements in non-oriented iron, the percentage added to (1 1 0) [0 0 1] material is very small. This suggests that an increase in resistivity is not the major factor in bringing about the improvements in loss as it must be very slight. It would seem that the stresses induced are at least as important, if not more so, than the resistivity increase.

This view is reinforced by the improvements in magnetostriction and power loss under compressive stress, an effect which is double that produced by an insulating coating.

It would seem, therefore, that the ideal stress distribution in aluminized steel is a thin layer of moderately high (about $10\,\mathrm{MN\,m^{-2}}$) tensile stress balanced by a thicker region of lower compressive stress. In order for this to occur a critical amount of aluminium must be distributed in a precise way, thus explaining the necessity of getting the paste composition and the firing and annealing temperatures all correct. None of the aluminized samples described had the insulating coating replaced, therefore further improvement in properties could be anticipated from this stage.

The effect of adding silicon to the aluminium paste was small, and best when only small amounts were present.

## 7. Possible applications of aluminium or silicon paste

Two possible modes of usage are envisaged:

1. Treatment of the whole sheet through an

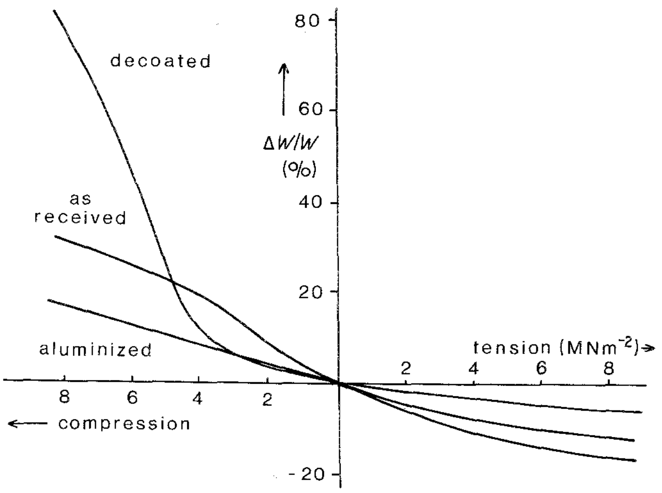

*Figure 8* Variation of the power loss stress sensitivity of a sample whose loss was not reduced at zero stress.

TABLE III Summary of aluminium paste compositions

| Paste number | Aluminium powder size (μm) | Na silicate (ml) per gram Al | Silicon | MgO | Kaolin light | $SiO_2$ | Colloidal silica |
|---|---|---|---|---|---|---|---|
| 1 | 8–15 | 0.5 | – | – | – | – | – |
| 2 | 8–15 | 0.5 | 0.2 | – | – | – | – |
| 3 | 8–15 | 2.0 | 4.0 | – | – | – | – |
| 4 | 24 | 2.5 | – | 0.6 | – | – | 0.2 |
| 5 | 24 | 1.3 | – | – | 1 | – | – |
| 6 | 40 | 0.66 | – | – | – | – | – |
| 7 | 40 | 2 | – | – | – | 2 | – |
| 8 | 24 | 1 | – | 0.3 | – | – | 0.07 |

extra stage incorporated into the production process.

2. Treatment of selected parts of a cut lamination for the increase in resistivity of critical areas.

In the first case the cost and reliability of the process would be the important factors with aluminium the most likely diffusant. The extra cost involved would almost certainly mean that only highly oriented material would be worth treating in this way. One problem would be the residual paste which would have to be either removed or incorporated into the insulating layer. If it was necessary to remove the residual coating prior to the application of an insulating layer, the process would probably be uneconomical. The treatment is most effective at lower flux densities which are in line with present trends in transformer operation. The reduction in stress sensitivity of the steel could also be important in such applications, as compressive stress is believed to be one of the major reasons why material in a transformer exhibits far higher power loss than it does in its unstacked form [5].

In the second case, the treatment would only be applicable to non-oriented steel prior to the application of the insulating coating. This would be carried out by the machine manufacturer, rather than the steelmaker as would be the case in the first method. Aluminium would also be favoured in this case due to the lack of problems with porosity, though silicon could be used if this could be overcome.

There would appear to be considerable scope for future work due to the large number of variables present at each stage of the process. Paste composition could be varied almost indefinitely with the use of other, less alkaline, sodium silicate solutions, and could be particularly worth investigating. Powder size and shape has also been seen to be critical and requires further study.

## 8. General conclusions

Aluminium and silicon can be diffused into steel from a paste made from the appropriate element and sodium silicate solution. Reductions in the power loss of non-oriented 3% silicon–iron have been achieved using either element, these improvements being ascribed to straightforward increases in the resistivity of the steel. Surface porosity was observed following the firing of silicon paste and this must be eliminated if the full potential of its application is to be fulfilled.

When applied to (1 1 0) [0 0 1] oriented silicon–

TABLE IV Summary of power loss results after firing and annealing

| Paste number | Firing temperature (°C) | 50 Hz | | | 400 Hz |
|---|---|---|---|---|---|
| | | 1.0 T | 1.5 T | 1.7 T | 1.0 T |
| 1 | 850 | + 16% | – | – | + 12.7% |
| 1b | 820 | – 11% | – | – | – 13% |
| 2 | 820 | – 17% | – | – | – 3.6% |
| 3 | 850 | – 6% | – | – | + 13% |
| 3b | 850(×2) | – 1.6% | – | – | – 5% |
| 4 | 725 | – 14.3% | – 11% | – 0.8% | – 16.6% |
| 5 | 725 | + 12% | + 5% | – | – 3% |
| 6 | 750 | + 26% | + 27% | – | + 32% |
| 7 | 725 | + 14.2% | + 12% | – | + 14% |
| 8 | 750 | + 26% | + 27% | – | + 33% |

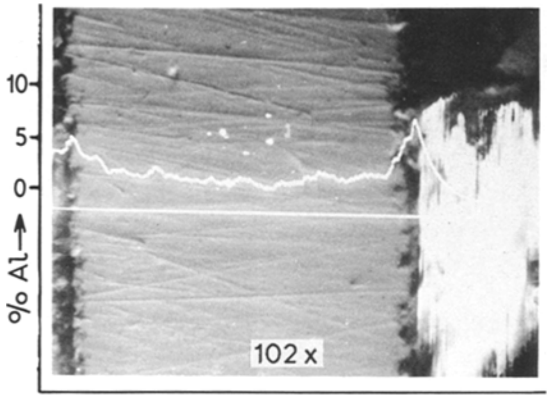

*Figure 9* SEM photograph of a sample fired with aluminium paste 1 at 820° C followed by annealing.

iron, power loss reductions were obtained using aluminium but not with silicon. The best results obtained were loss reductions of 10% at 1.5 T when quite small amounts of aluminium had been added. Considerable stresses seemed to have been set up in the steel during processing, which are tensile at the surface. These were believed to be the main factors responsible for the improvements in power loss under zero and applied compressive stress.

It was found that paste composition, viscosity and powder particle size were all very critical in obtaining beneficial results together with the heat treatment times and temperatures.

## Acknowledgements

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