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Electroless Co–P-Carbon Nanotube composite coating to enhance magnetic properties of grain-oriented electrical steel

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ABSTRACT

The effect of Co–P-CNT coating on the magnetic properties of grain oriented electrical steel was investigated. To analyse the coating, Raman spectroscopy, Superconducting QUantum Interference Device (SQUID), single strip testing, Scanning Electron Microscopy (SEM) and talysurf surface profilometry were performed. Raman spectra showed the D and G band which corroborates the presence of Multi-Walled Carbon Nanotubes (MWCNT) in the coating. The magnetic nature of the coating was confirmed by SQUID results. Power loss results show an improvement ranging 13–15% after coating with Co–P-CNT. The resistivity of the coating was measured to be 10^4 $\mu\Omega$ cm. Loss separation graphs were plotted before and after coating to study the improvement in power loss. It was found that the coating helps in reducing the hysteresis loss. The thickness of the coating was found to be 414 ± 40 nm. The surface profilometry results showed that the surface roughness improved after coating the sample.

1. Introduction

Grain-oriented electrical steel (GOES) laminations are utilized in the ferromagnetic cores of the majority of high efficiency power and distribution transformers. They are characterised by low power losses and high permeability which maximize the performance of these essential devices.

Improvements in the chemistry and process technologies for these materials have brought large improvements in their properties over the last 20 years [1]. However further optimization is likely to bring only incremental improvements. Coatings applied to these steels have the potential to provide far larger gains and are therefore the subject of significant research effort.

The main role of the steel coating is to reduce power loss which is achieved by two main mechanisms. Firstly the coatings provide an insulating layer between laminations which reduces the eddy currents circulating in the device. Secondly there is reduction in both the hysteresis [2] and anomalous loss as a result of beneficial tensile stress [3] to the substrate. A tensile stress applied on GOES helps in minimizing the losses by reducing the domains perpendicular to the direction of magnetization. The tensile stress also results in narrowing the domain wall spacing which decreases the anomalous loss due to a reduction in average wall velocity. The reverse happens when compressive stress is applied to GOES i.e. domain width increases as does the volume of perpendicular structure due to a switch to new domain configurations known as stress patterns [4]. Thus coatings which provide high levels of tension to the steel substrate or that have a high strength such that the substrate is protected from in-plane compressive stress are particularly attractive for this application.

Carbon Nanotubes (CNTs) are known for their mechanical properties such as high strength, elastic modulus, elastic strain bearing tendency [5,6], flexibility [7] and many other properties which make CNTs favourable for a number of applications. The calculation of the theoretical Young's modulus of single walled CNT of 5 GPa [8] and its bending strength of 14.2 GPa [9] make it ideal for use in a composite coating. CNTs are mostly used in composite coatings for improving the tribological properties of the material [10–14]. For example, Chen et. al. [10] showed that the addition of CNTs in the coating increases the hardness of the coating.

This work presents the use of electroless plating for depositing Co–P-CNT composite coating on the surface of grain oriented electrical steel. Cobalt was chosen as it is magnetically active and has a comparable saturation magnetization of 167 emu/g as that of iron (221 emu/g). This could offer a significant additional advantage in that it would increase the core stacking factor defined as the ratio of magnetic to non-magnetic material in the transformer core and could thus also be increased through a reduction

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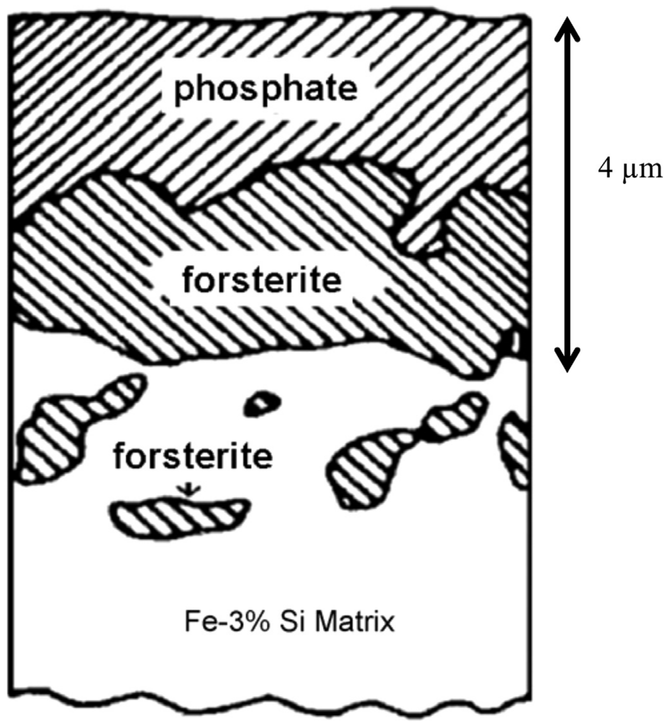

Fig. 1. Conventional coated Iron–3% Silicon showing layers of phosphate and forsterite.

in overall coating thickness. The current coating system of forsterite (Mg_2SiO_4) and aluminium orthophosphate coating, with a total thickness of 4 μm per side as shown in Fig. 1, are non-magnetic and hence reduce the stacking factor.

2. Material and method

Fully finished grain oriented (Fe–3%Si) samples (0.3 mm × 30 mm × 305 mm) were supplied by Cogent Power Ltd., Newport UK and both the coatings were removed with a solution of 7.5% sulphuric acid + 1% Hydrofluoric acid for approximately 10 min and then in 4% Nitric acid solution for approximately 7 min. The samples were then cut into 0.3 mm × 30 mm × 75 mm. Samples were coated with Co–P-CNT coating. The solution was stirred with magnetic stirrer to suspend the MWCNTs in the solution. The composition of the bath was taken from [15] and modified by adding 0.2 g/l of MWCNTs in the solution. The modified bath and operating conditions are shown in Table 1. The pH of the solution was maintained by adding ammonia hydroxide. The samples were immersed in the bath at a temperature of 50 °C and the final bath temperature recorded was 62 ± 1 °C.

The samples were coated for different time periods and optimized to get best improvement of power loss. Samples were also coated without CNTs in the plating solution to study the effect of Co–P coating on grain oriented electrical steel.

Table 1
Bath Composition and conditions.

Chemical reagent	Concentrations (g/l)
Cobalt sulphate	14
Sodium hypophosphite	25
Trisodium citrate	45
MWCNT	0.2
pH at 25 °C	9.7
Temperature	62 ± 1 °C

The MWCNTs used in coating the samples were supplied by M/s Haydale Ltd UK. The MWCNTs were used in the as received condition. The power loss testing was performed with the single strip tester (SST) [16] from a magnetic flux density of 0.1 T to 1.8 T and a frequency of 50 Hz. The results are shown at 1.5 and 1.7 T magnetic flux density and 50 Hz frequency as these are common operational parameters for distribution transformers in the UK. The resistivity of the coating was measured by a four point probe method using a glass sheet coated with Co–P-CNT. The induced voltage across two probes under controlled current excitation was measured in the coating and the resistance was calculated.

The microscopy images were obtained from a Philips XL30 Environmental Scanning Electron Microscope (ESEM) Field Emission Gun (FEG). The magnetic properties of the coating were measured at room temperature by Superconducting QUantum Interference Device (SQUID) based magnetometer from Digital Instruments. The magnetic field was applied up to ± 20,000 Oe. From −100 to +100 the rate of change in field was 0.25 Oe/s, between ±1000 and ±100 the rate of change was 1.5 Oe/s and from ±20,000 to ±1000 the rate of change was 15.15 Oe/s. The sample was manufactured from a square glass slide coated with Co–P-CNT such that the magnetic field was applied in the plane of sample.

The surface roughness of the uncoated and coated surfaces was measured by talysurf surface profilometer. The measurement was made in the direction of rolling for a distance of 40 mm for all the samples.

To determine the presence of MWCNTs in the coating the samples were analysed using a Renishaw inVia Raman microscope. The coated samples were excited with a 514 nm argon laser with the power maintained at 12.5 mW and a spot size of 5 μm. The Raman spectra spanning between 800 and 2100 cm^{-1} was obtained at five different spots.

2.1. Raman spectroscopy

The Raman spectrum of the coated samples is shown in Fig. 2. The main characteristic bands obtained were the D and G bands at around 1360 and 1590 cm^{-1}, respectively. The D band represents the disorder/distortions in the MWCNTs or the sp^3 bonds whereas the G band confirms the presence of graphite or the sp^2 bonds, both confirming a significant volume fraction of MWCNTs in the coating. All five characterised areas showed the same characteristic D and G bands which confirms that the MWCNTs were uniformly distributed in the coating whilst the uncoated sample did not show either D or G bands. The percentage, by weight, of CNTs

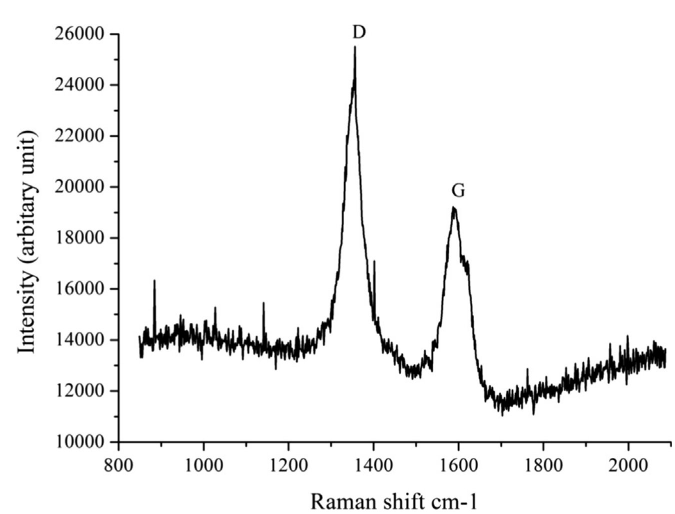

Fig. 2. Raman spectra of the Co–P-CNT coated sample showing the D and G bands.

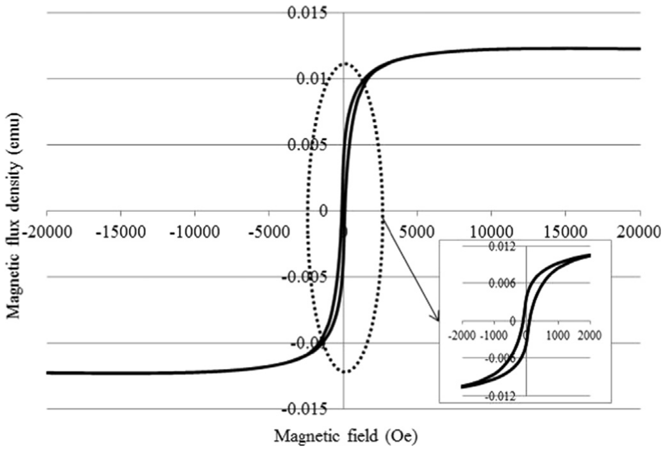

Fig. 3. Magnetic characterization of Co–P-CNT coated at pH of 9.7.

in the solution was calculated to be 0.24% by adding the weight of different components in the solution and then dividing the CNTs weight by added components.

2.2. Magnetic properties

Fig. 3 shows a hysteresis loop for Co–P-CNT coating (with a sample of volume 3 mm × 3 mm × 2 μm) at a pH of 9.7. The B–H loop measured in the SQUID confirms that the coating is ferromagnetic with coercivity 100 Oe and saturation magnetization of 683 emu/cm^3. The coercivity of cobalt varies widely depending upon the process route and alloying elements with the addition of non-magnetic elements such as phosphorus and CNT's in the coating raising the coercivity.

2.3. Power loss and resistivity

Fig. 4 shows the average results of five uncoated and Co–P-CNT coated samples for two magnetic flux densities of 1.5 and 1.7 T. It can be seen from Fig. 4 that the coated samples show a power loss improvement ranging from 13% to 15% at 1.7 T, 50 Hz. To isolate the effect of CNTs a sample was coated with Co–P without the addition of CNTs. The coated sample did not show any improvement in power loss which confirms that the improvement was only due to the presence of CNTs in the coating.

The measured resistivity of the coating was approximately 10^4 μΩ cm due to the disorder in the lattice structure of cobalt by co-deposition of phosphorus and CNTs.

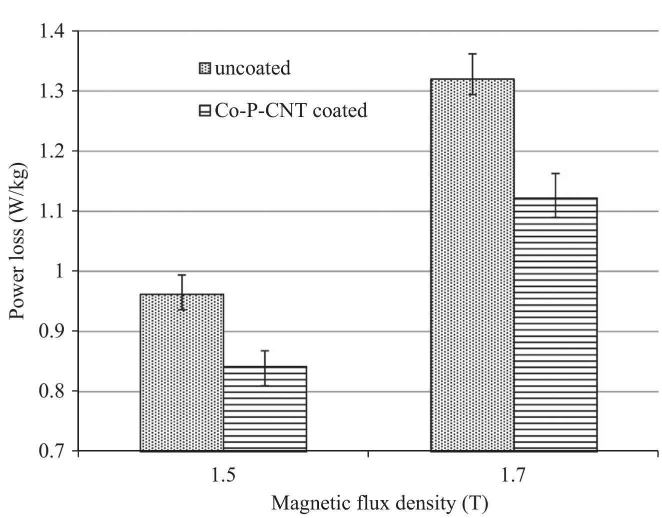

Fig. 4. Power loss of uncoated and Co–P-CNT coated sample at various flux densities and 50 Hz frequency (average of five samples).

2.4. Loss separation

The model used here for loss separation was proposed by Ionel et al. [17]. The power loss equation can be written as

$$W = k_h f B^{\alpha} + k_e f^2 B^2 + K_a f^{1.5} B^{1.5} \tag{1}$$

where W is the total loss (W/kg), f is the frequency (Hz), B is the magnetic flux density (T),

k_h, k_e, k_a are coefficients for hysteresis, eddy current and anomalous loss respectively,

$k_h f B^{\alpha}$ is the hysteresis loss, $k_e f^2 B^2$ is the eddy current, $K_a f^{1.5} B^{1.5}$ is the anomalous loss and α is a constant.

In order to extract the individual components, the total loss per cycle can be calculated from (1) as below

$$W/f = k_h B^{\alpha} + k_e f B^2 + K_a f^{0.5} B^{1.5} \tag{2}$$

$$W = a + b f^{0.5} + c f \tag{3}$$

Eq. (2) can be compared to a quadratic equation of the type $a + bx + cx^2$ as shown in (3) and the coefficients of $f^{0.5}$ can be found by plotting a fitting curve. The values were plotted over a range of frequencies from 10 Hz to 1000 Hz. The value of correlation coefficient r^2 [18] was 0.9994 and 0.9998 for the uncoated and Co–P-CNT coated sample. On plotting the loss separation graph before and after coating, the results shown in Fig. 5 were obtained. It can be clearly seen from the figure that the coated sample shows a significant reduction of 0.27 W/kg in hysteresis loss while the eddy current and anomalous loss increase was insignificant.

2.5. Scanning Electron Microscopy

Fig. 6 shows the SEM image of a 60 min coated sample. It can be seen from the image that the coating, the white area in the image, makes the surface smoother by variable deposition based on the surface contours. On visual inspection the adherence between the coating and the sample was found to be good with no gaps or cracks. The average thickness of the coating was measured to be around 414 ± 40 nm for sample coated for 60 min giving a stacking factor of 99.73% compared to 97.4% for a conventional 4 μm coating. Considering the saturation magnetization of Co–P-CNT coating (0.0123 emu) the stacking factor rises to 99.85%.

2.6. Surface profiling

A higher surface roughness affects the magnetization of core

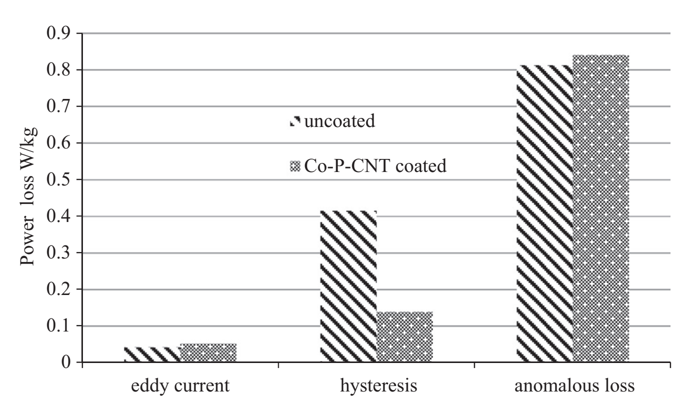

Fig. 5. Loss separation for the uncoated and Co–P-CNT coated sample at a flux density of 1.7 T and 50 Hz frequency.

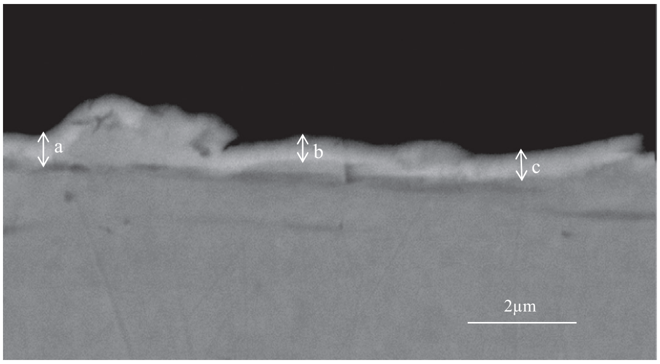

Fig. 6. SEM image of the sample coated with Co–P-CNT for 60 min showing thickness a=452 nm, b=376 nm and c=414 nm.

material by pinning the domain walls [2]. The surface roughness (Ra) of uncoated, Co–P and Co–P-CNT coated surfaces was measured to be 695 ± 10 nm, 631 ± 6 nm and 437 ± 3 nm respectively with the coated values being a combination of substrate and coating roughness.

Wang et al. [11] performed surface roughness measurements on Ni–P-CNT coated samples and found they were between 100 and 300 nm whilst Alishahi et al. [19] reported that wear properties of the surface could be enhanced by an improvement in surface roughness from a CNT coating. The surface roughness (Ra) of Ni–P and Ni–P-CNT coated sample was shown to be reduced from 192 nm to 129 nm and corrosion resistance of Ni–P coatings was improved with the incorporation of CNTs due to their high chemical stability. The improvement in surface roughness was thought to be due to the reduction in deposited particle size by addition of CNTs [20].

The surface roughness has been shown to directly affect the hysteresis loss. Wada et al. [2] showed that power losses could be reduced by 30–40% on improving the surface roughness due to a reduction in the number of free poles at the surface. These free poles pin the domain wall reducing the number of mobile walls leading to inhomogeneous domain wall motion. Freeing up these domains leads to a significant reduction in the total loss. Improving the surface roughness with a non-magnetic coating would not contribute to an improvement in magnetic properties of the material as the magnetic path on the surface would remain unchanged.

2.7. Conclusions

In general two stage non-magnetic coatings are used to impart tensile stress to grain oriented electrical steel in order to reduce power losses. In this work a novel attempt was made to improve the power loss in the range of 13–15% by enhancing the surface roughness with a magnetically active Co–P-CNT coating. The coating was shown to exhibit the desirable insulation properties with a resistivity of 10^4 μΩ cm. The loss separation data showed that hysteresis loss was reduced by the coating which was attributed mainly to a surface roughness improvement. The stacking factor was improved to 99.85% based on two factors. The thickness of Co–P-CNT coating was reduced by almost 90% to 414 nm as compared to the conventional coating of 4 μm. The high value of saturation magnetization of the coating further raised the stacking factor by replacing non-magnetic material in the core by a magnetic material.

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