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Investigations into sol-gel silica and silica hybrid coatings for dielectromagnetic soft magnetic composite applications

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Abstract A series of inorganic and organic–inorganic hybrid silica coatings were synthesised by a sol-gel process from tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) precursors, and used to investigate their effectiveness as insulation materials in dielectromagnetic soft magnetic composites. The coating materials and coated iron powders were analysed by FTIR, electron and atomic force microscopy. Results showed that introduction of the organic phase imparted desirable hydrophobicity and flexibility to the coating, whilst still providing effective electrical insulation at temperatures up to 500 °C. The hybrid coatings covered the iron particle surface very effectively and formed continuous coatings that could remain intact even after compaction at pressures up to 900 MPa, depending on the coating amount. Initial magnetic characterisations are also encouraging. As a result, such hybrid-coated iron powders can be considered suitable candidates as heat-treatable high-performance dielectromagnetics.

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Introduction

Dielectromagnetics are a form of soft magnetic composites which consist of soft ferromagnetic (normally iron powder) together with a small volume fraction of dielectric materials, which can be used to directly fabricate magnetic components such as motor cores and stators by net shape compaction processes. The dielectric phase is usually present as a coating on the surface of the ferromagnetic metal particles. This dielectric coating plays a key role in dielectromagnetics, fulfilling a dual function, as both the required insulating barrier to control eddy current losses in magnetic components under alternating fields, and in a mechanical role as a binder after forming and curing [1]. In addition, it is desirable if the resultant components are capable of being thermally heat treated in order to relieve internal stresses and the associated magnetic hardness arising from the compaction processes used to fabricate them.

Whilst the dielectric coating controls eddy current losses in dielectromagnetics, it also has some deleterious effects, in particular on magnetic permeability [2]. It is practically important that the dielectric addition level be as low as possible, typically less than 0.5 mass % if acceptable performance is to be achieved. This imposes a demanding set of requirements for the dielectric coating in dielectromagnetics to be able to provide electrically isolating, thin, flexible and tenacious coatings, with sufficient thermal stability to withstand heat treatment at temperatures of 500 °C or more. In addition the coating system should ideally have the minimum environmental impact and lowest possible cost.

Traditionally, the dielectric coating in dielectromagnetic soft magnetic composites has been organic resins, such as epoxy and phenolics [3]. However, such organic materials cannot withstand the thermal treatment required and in recent years there has been an increasing trend toward the development of largely inorganic thermally stable dielectric materials for dielectromagnetics. A number of dielectric systems are patented, such as phosphating [4, 5], silicon resins [6], and other inorganic compounds [7]. In this paper, we are discussing the use of a new dielectric material, organic–inorganic hybrid silica sol-gels, in attempt to exploit the feasibility as dielectromagnetic materials. The distinct advantages of using this material are that the existence of organic phase in the hybrids provides the coating with excellent flexibility, aiding the process of compaction and enabling the coatings to remain intact as the composite is subjected to high pressure compaction and additionally, the hydrophobic nature of these coatings provides an additional benefit with regard to the stability of the coated powders against surface oxidation/corrosion during long term storage. The coating system is relatively low cost and can also be applied by an aqueous process, these being important commercial benefits.

Experimental

Processing

Synthesis of the SiO_2 and SiO_2 hybrid sols

The SiO_2 and hybrid SiO_2 sols containing organic methyl group were prepared from tetraethoxysilane ($Si(OC_2H_5)_4$ or TEOS, Aldrich) or blends of TEOS and methyltrimethoxysilane ($SiCH_3(OCH_3)_3$ or MTMS, Aldrich) via a conventional sol-gel process. The quantities of precursor used for coatings were calculated on the basis of the mass of coating estimated according to the expected reactions of the TEOS and MTMS components as shown in Eqs. (1) and (2)

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \tag{1}$$

$$SiCH_3(OCH_3)_3 + 3/2H_2O \rightarrow SiCH_3O_{3/2} + 3CH_3OH \tag{2}$$

In fact both reactions (1) and (2) are normally considered two stage reactions [8] consisting of an initial hydrolysis of the alkoxy groups by nucleophilic attack of water on the silicon atom followed by polycondensation of silanol Si(OH) groups to form siloxane Si–O–Si bridges and liberation of water. The reaction is generally catalysed by the addition of acids or bases.

A range of coating formulations were prepared with different TEOS:MTMS ratios as shown in Table 1. Depending on the composition, two different base sol formulations were necessary for the sol-gel syntheses, an aqueous based medium for the formulations with MTMS up to 40 mol.% and an alcohol based system for containing higher levels of MTMS. The water based formulations comprised distilled water (1 mole):ethanol (0.05 moles):mixed TEOS/MTMS (0.1 moles):H_3PO_4 catalyst (0.002 moles). The "alcohol based" formulations comprised distilled water (1 mole):2-propanol (0.56 moles):mixed TEOS/MTMS (0.25 moles):H_3PO_4 catalyst (0.005 moles).

The organic content is calculated as the mass % of the final coating composition comprising CH_3, assuming the ideal reactions given in Eqs. (1) and (2) for the relevant additions of TEOS and MTMS.

For convenience, the TEOS/MTMS hybrid comprising e.g. 80 mol.% of TEOS was named as T80. Hybrids with other molar ratios were named in the same way.

Portions of each of the coating sols were then cast onto glass and retained for characterisation/analysis. The remaining materials were used to prepare dielectric coatings on magnetic iron powder as described below.

Powder coating

The powder coating process was carried out as follows. Appropriate amounts of a commercially produced high

Table 1 Coating formulations and properties used in dielectric coating development trials

Formulation designation	TEOS (mol.%)	MTMS (mol.%)	Methyl (Mass%)	Xerogel appearance	
				As dried	600 °C × 1 h, N_2
T100	100	0	0.0	Transparent	Transparent
T80	80	20	4.9	Transparent	Transparent
T60	60	40	9.6	Transparent	Opaque
T40	40	60	14.0	Translucent	Opaque
T20	20	80	18.3	Translucent	Opaque
T0	0	100	22.4	Transparent	Translucent

purity iron powder (ATOMET 1001HP, QMP Metal powders GmbH, Germany) together with the above described hybrid SiO_2 sols were well mixed in a flask with vigorous stirring for 10 min. The mixture was then transferred into a fluid bed dryer (Christison Scientific, UK) and quickly dried by blowing hot air. The coated powders were then recovered and stored in a closed container. The loading levels of coating material were in the range from 0.05 to 3.0 wt%.

Powder compaction and sample preparation

Following the coating process, the coated powder was then used to prepare compacted test specimens for characterisation. This was carried out using a tool steel cylindrical pressing die, with twin plungers. Compaction was performed uniaxially at constant pressure of 900 MPa using a manual hydraulic press. Approximately 4.5 g of powder was added to the die, with the resultant dimensions of the compacts being 13 mm diameter by approximately 5 mm height. Paraffin wax solution was used as a die wall lubricant. In addition a number of alternative sample dimensions were prepared for mechanical and magnetic property characterisation, using a similar technique. These comprised cylindrical test specimens of 60 mm diameter and 5 mm thickness, compacted under 700 MPa for magnetic property characterisation, and rectangular bars of dimension $5 \times 5 \times 36$ mm also compacted under 700 MPa used for mechanical testing.

Following the compaction process samples were heat treated in a tube furnace under a flowing nitrogen atmosphere at a temperature of 500 °C for 30 min to simulate the effects of thermal annealing of a magnetic core.

Characterisation

FTIR analyses were carried out on portions of the dried coating material using a Mattson 3000 spectrometer (Unicam Ltd., England). Spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} and averaging 64 scans. Prior to the measurement being performed, the material was dried at 75 °C for 1 week and blended with KBr at the level of ca. 3 wt% and pressed into a disc according to normal IR procedures. The microstructure of both the hybrid coating material and coated iron particles was observed using a field emission gun scanning electron microscope (FEGSEM) (model LEO 1530 VP), with Energy Dispersive X-ray Analysis (EDX capability), which was used to perform two dimensional elemental mapping and line scanning of compositional profiles.

To investigate the effect of heat treatment on the coating material thermogravimetry and differential thermal analyses (TGA–DTA) were carried out on a 2690 Simultaneous TGA–DTA analyser (TA Instruments). Measurements were taken under air atmosphere at the ramp of 10 °C/min. Both coated iron powder samples and samples of the cast coating materials were tested. Coating material samples were dried at 75 °C for 24 h, while the hybrid-coated iron powders were dried under vacuum at room temperature for 48 h before testing.

Atomic force microscopy (AFM) imaging was performed using a Veeco Explorer microscope fitted with a Wollaston wire thermal probe (the resolution is of 1 μm for thermal scan). The thermal probe acts as both heating element and thermal detector, and allows the thermal conductivity difference of different regions on sample surface to be exploited to generate an image [9]. For this test, the dielectromagnetic compact was first polished with 1 μm diamond paste. Images were recorded using tapping mode under ambient conditions.

Measurements of electrical resistivity of the coated and compacted powder samples were carried out before and after heat treatment. Prior to measurements, the surface of the specimens was ground using 400-grade silicon carbide abrasive paper, to obtain a clean, non-oxidised surface for electrical testing. Measurements were carried out using a simple two point contact method, using brass foil contacts across the faces of the cylindrical specimens applying a fixed pressure using a spring to ensure good contact. A current of 10 mA was passed through the specimen and the voltage drop between the faces measured using a digital electrometer (Keithley 6517) with DC measurement range 10 μV to 210 V. Typical values of voltage drop were in the range 1.0–1000 mV over the 5 mm thickness of the specimen corresponding to resistivity values of 5–5000 mΩ-m. It should be noted that these measurements should be considered indicative only due to the potential effects of contact resistance on the measurements, but are adequate to provide an initial evaluation of the relative effectiveness and continuity of the various dielectric coating formulations.

Finally, the coated powder was used to prepare test specimens for preliminary magnetic characterisation. A MAG-TD200 computerized measuring system was used [10]. Tests were performed under both alternating magnetic fields at frequency of 50 Hz and a standardised maximum magnetic induction of $B_m = 1.20$ T.

Results and discussion

Coating material

Properties of the hybrids

Compositions and properties of the TEOS/MTMS hybrids are summarized in Table 1. The two components are miscible in a wide range of compositions according to the transparency of xerogel films. The T40 and T20 specimens tended to form translucent rather than transparent films. This may be the consequence of phase separation of the two components at the ratios. In all cases, the xerogel appearance remained unchanged after firing at 500 °C. After heating at 600 °C for 1 h in nitrogen, however, the samples containing up to 20 mol % MTMS remain transparent, but in the case of the formulations containing between 40 mol% and 80 mol% of MTMS, a colour change to light grey occurred. This grey colouration suggests that these coating materials contained some residual carbon after heat treatment at this temperature, originating from the decomposition of the methyl group. The following FTIR and thermal characterisations support this explanation.

Processing of the hybrid coating formulations

During the development of the coating process, it was noted that the process conditions required to prepare and apply the coating sol were very different depending upon the respective proportions of TEOS/MTMS used in the formulation. Coating formulations containing up to 40 mol% MTMS (T100-T60) could be processed essentially in aqueous systems, with the addition of a small amount <10% of alcohol as a mutual co-solvent for the reactants. By contrast the coating systems with higher organic content (T40-T0) could only be processed using primarily organic (alcohol) solvents. For this reason, systems T100-T60 were considered of particular interest. Two systems were thus chosen for further investigation: T60, which was the system containing the highest level of organic content compatible with an aqueous based processing route, and the completely inorganic coating T100, which was used as a control to determine the effect of the organic addition in the coating.

FTIR analyses

FTIR was used to characterise the hybrids synthesised and heated at various temperatures, corresponding to the heating conditions at different stages in the processing of dielectromagnetics.

Figure 1 shows the FTIR spectra of the dried hybrid materials T100 (no organic content anticipated according to reaction (1), and T60 (9.6 wt% organic content from MTMS). The absorption bands characteristic of the organic methyl groups are indicated by arrows. In the high frequency range, the very broad absorption band from 2700 to 3820 cm^{-1} results from the vibration of the Si–OH group associated with absorbed water [11] or unreacted silanol groups from the sol-gel reactions (1) and (2). The weak bands from 2860 to 3000 cm^{-1} are assigned to symmetric and asymmetric stretching of C–H bond in the organic group [12]. These absorption bands were sometimes also found in the hybrids containing only TEOS, indicating the hydrolysis was not entirely complete. In the low frequency range, the sharp absorption at 1276 cm^{-1} characterises the methyl group, and the bands at 1160 and 780 cm^{-1}, can be attributed to Si–C bond vibration [12]. These absorptions overlap a second set of bands at 1080 cm^{-1} and 810 cm^{-1}, which can be attributed to Si-O-Si symmetric and asymmetric stretching [13].

Figure 2 shows the FTIR spectra of the T60, organic containing composition after heating at different temperatures. It can be noted that the organic methyl group

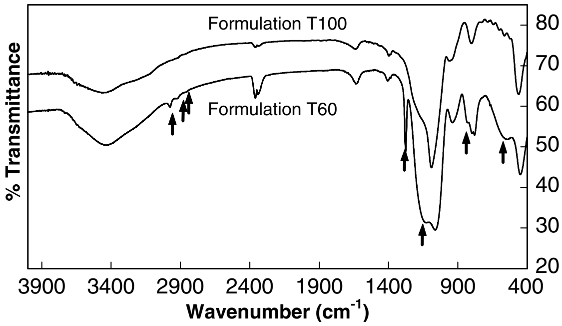


Fig. 1 The FTIR spectra of coating materials from T100 and T60 formulations after drying at 75 °C (arrows indicate the characteristic absorption bands of the methyl group. Note, baselines offset for clarity)

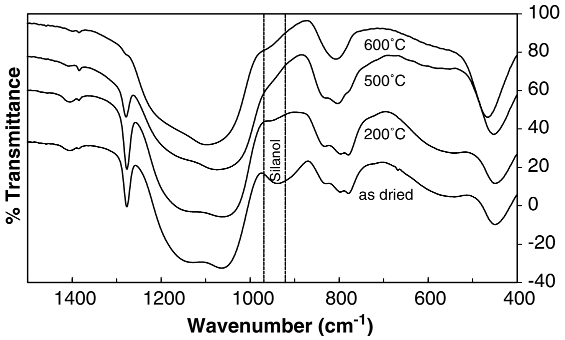


Fig. 2 FTIR spectra of coating formulation T60 after heating to different temperatures. (NB baselines offset for clarity)

is retained even after heating at 500 °C, but is almost completely eliminated after heating at 600 °C. This is consistent with both the TGA–DTA results (Fig. 3) and other studies of the decomposition of MTMS derived materials, which have reported that the elimination of methyl group begins and accelerates with increasing temperature between 500 °C and 600 °C [14]. In addition, the absorption band at 950 cm^{-1}, characteristic of the stretching vibration of free silanol [13], reduces with increasing temperature. This absorption band is still apparent even after heating at 200°C, but is eliminated in the samples heated to 500 °C. This finding, which is consistent with previous studies [15] suggests that the sol gel polycondensation reactions are not complete for these materials during ambient processing, but rather the dried hybrids undergo further polycondensation during the processes of drying and heating. This also explains why the dried hybrids cannot be re-dissolved.

TGA–DTA analyses

Figure 3 shows the TGA–DTA results obtained from the samples of the coating materials of formulation T100 and T60. The two materials exhibit similar thermal behaviour at temperatures up to 500 °C. The initial weight loss up to 160 °C in the TGA study relates to the loss of the absorbed water. The weight losses during this stage are 2.79% for T60 and 3.79% for T100. Therefore, the magnitude of this loss is significantly smaller, and the onset and end temperatures about 30 °C lower for the T60 material containing organic functionality, which is consistent with the anticipated lower hydrophilicity (or increased hydrophobicity) of this material. The endotherm observed at the same temperature range in the DTA results also provides confirmatory evidence, with the smaller endothermic peak for the T60 sample being consistent with the removal of a smaller amount of water. Afterwards, the steady weight loss up to 500 °C originates from the polycondensation of the xerogels, with gradual release of water. The expected reactions for the hydrolysed TEOS ($Si(OH)_4$), and MTMS ($SiCH_3(OH)_3$) precursors are given in Eqs. 3 and 4, respectively

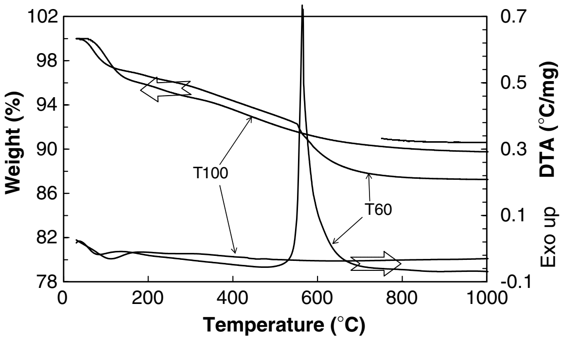


Fig. 3 TGA–DTA curves for the T100 and T60 coating formulations

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \tag{3}$$

$$2CH_3Si(OH)_3 \rightarrow 2CH_3SiO_{3/2} + 3H_2O \tag{4}$$

The polycondensation mass loss continues at a gradually decreasing rate with increasing temperature until a temperature of approximately 900 °C for the inorganic T100 composition, at which point the mass stabilises, suggesting that the residual silanol groups are eliminated by this temperature.

The behaviour of the T60 composition shows a similar (but reduced) mass loss due to polycondensation. However this composition also exhibits a substantial mass loss of 4.66% of its original mass in the temperature range 550–750 °C with a corresponding large exothermic event in the DTA data. This can be attributed to the removal of the organic methyl groups from the material by pyrolysis according to the following reaction

$$2CH_3SiO_{3/2} + 4O_2 \rightarrow 2SiO_2 + 3H_2O + 2CO_2 \tag{5}$$

This decomposition process commences at 480 °C and reaches its most rapid rate at 560 °C according to the DTA curve. Due to the uncertain degree of polycondensation of the initial xerogels, a better estimation of the extent of this reaction can be obtained by comparing the mass changes against the final mass of the DTA sample and the assumption that this should have the stoichiometric composition SiO_2. According to Eq. (5) the theoretical mass loss for this reaction should be 11.67% of final mass of SiO_2 for a pure MTMS precursor, and hence in the case of the T60 composition containing 40 mol% MTMS the theoretical weight loss should be 4.67%. The actual mass change was 4.66% in the range of 550–750 °C as obtained from the TGA curve, while that of T100 was 1.34% in the same temperature range, however this represents the mass loss due to both reactions (4) and (5). The mass changes due to organic loss (reaction 5) of the hybrid coating can be separated from the effects of polycondensation (reaction 4) by subtracting the corresponding changes occurring in the organic free T100 material from those in the organic containing hybrid (T60 in this case) in this temperature range. In this case this results in a calculated organic mass loss of 3.32% (4.66%–1.34%) due to burnout of methyl group with the remaining 1.34%

being attributable to mass loss from the polycondensation reaction. Shifting the high temperature portion of the T60 TGA curve by this amount shows almost identical behaviour for both compositions above 750 °C (Fig. 3), whilst the curves for temperatures below 550 °C are also almost identical, except for slightly greater mass loss at low temperatures associated with the higher content of absorbed water of the T100 composition. The difference between the calculated organic mass loss from above (3.32%) and the theoretical value of 4.67% confirms that not all the organic moiety was burnt out, as might be anticipated from the observed colour changes in these materials. The presence of residual carbon in pyrolysed silica hybrid gels containing non-hydrolysable organic has been previously reported and indeed used as a route to prepare carbon containing glasses [16, 17].

The total weight loss observed for the T60 formulation during heating (12.75%) is larger than that for the T100 formulation (10.24%) as might be anticipated due to the additional mass losses associated with above%. However, it should be pointed out that these values are much lower than those of theoretical calculation from the Eqs. (3) and (4), which are 28.72% (40.39%)% for fully hydrolysed MTMS, 33.99% (38.66%)% for T60 and 37.50% for T100 (fully hydrolysed TEOS), Figures in brackets include effect of calculated mass loss due to reaction (5). These substantially lower total weight losses imply that the polycondensation reactions were largely completed during initial synthesis and drying of the coating formulations as normally occurs in sol-gel processing.

Analyses of the hybrid-coated iron powders

Stability

As outlined previously, one potential advantage of this coating system is its potential benefit in terms of improved storage stability of the coated iron powders due to the hydrophobic nature of the organic containing coatings. The un-coated and hybrid-coated iron powders were exposed to high humidity condition in an attempt to observe the protective effectiveness of coatings in an accelerated test. As shown in Fig. 4, the weight increase of the uncoated powder is very fast due to wet corrosion of the high surface area iron powder. The inorganic coated powder (T100) shows some initial improvement in stability but after 20 days exposure the effect is limited. Most probably the corrosion process occurs initially at small cracks or pinholes in the coating surface gradually exposing increasing amounts of surface as the process continues. By contrast, the organic containing (T60) coated powder shows excellent protective effects, with only a minor weight increase in the time span. These results confirm the supposition that the hybrid coating formulations would provide significant benefits in this regard due to its hydrophobicity and greater resistance to crack formation.

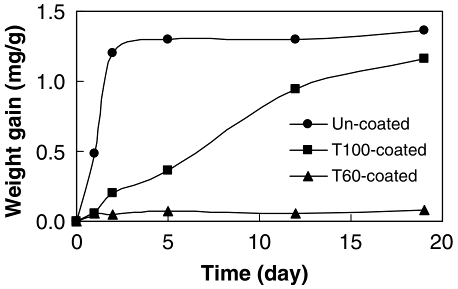


Fig. 4 Mass gain profiles of the uncoated and 0.1% hybrids coated powders under 100% relative humidity at 38 °C

Microstructure

SEM observation was used to observe the surface morphology of coated iron powders in attempt to get detail microstructure of coatings. The particle shape and surface morphology of the uncoated iron powder used are shown in Fig. 5. It is seen that the particles have an irregular shape and very uneven surface with some asperities and cracks.

Figure 6 shows the surface morphology of iron particles coated with various addition levels of the T60 formulation coating. It is well known that existence of cracks is a common problem in sol-gel derived coatings, particularly at thicknesses above around 1 μm because of their inherent rigidity and the high volumetric shrinkage occurring during their processing. However, it is possible to produce such crack-free coatings provided that the thickness is controlled. In this case, experiments were carried out to attempt to determine the maximum addition of coating and hence coating thickness achievable without excessive cracking. In the case of the formulation T60, the maximum coating addition on this basis was found to be 0.3% with these coatings remaining intact and complete even after heating to 500 °C 30 min. EDX analysis of spot and general area scanning indicates the presence of silicon and carbon over the whole sample, implying the hybrid coating covers iron surface very well. However, cracks appear for coating additions ≥1 mass %. The samples were observed both before and after heat treatment and it was noted that cracking was apparent prior to heat treatment. Heat treatment at 500 °C did not appear to result in the creation of additional cracks, but rather increased the size of the cracks,

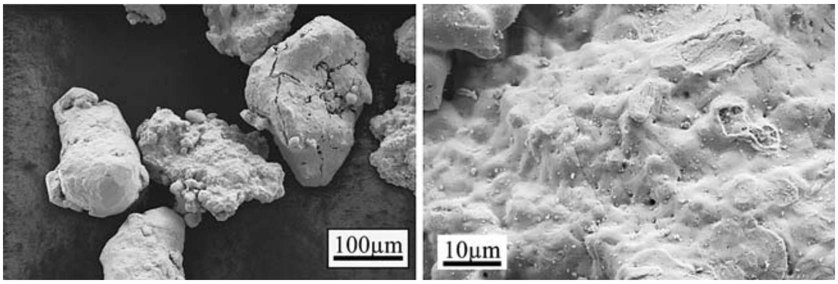
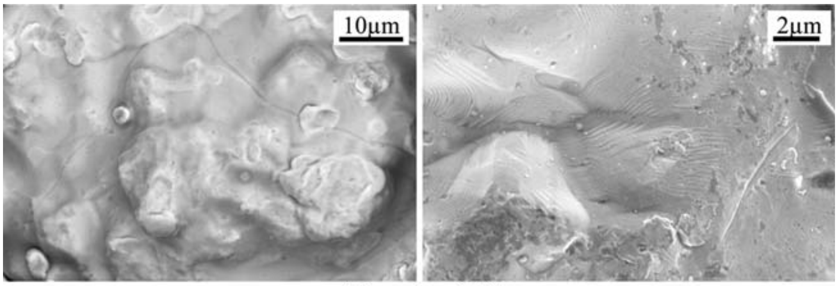
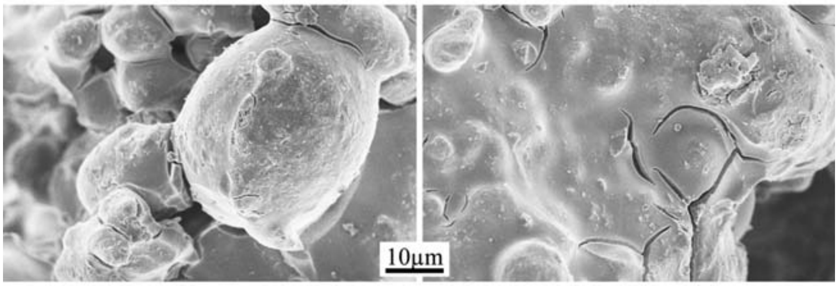


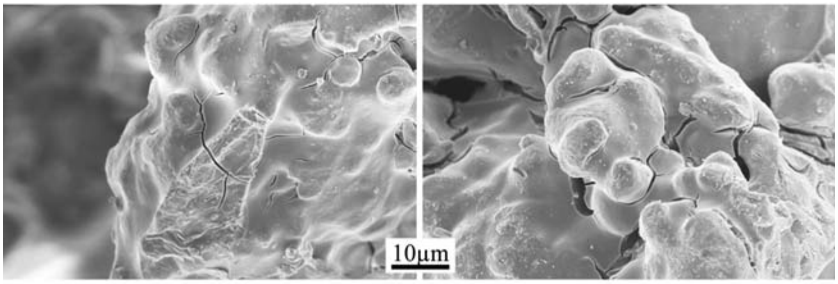
Fig. 5 Particle morphology and surface feature of uncoated Fe powder



(a) coating 0.3%



(b) coating 1.0%



(c) coating 2.0%

Fig. 6 Surface morphology of Iron particles coated with various addition levels (mass %) of coating formulation T60. (Left: as coated; Right: heated 500 °C × 0.5 h)

presumably as a result of coating shrinkage caused by dehydration/polycondensation and sintering processes in the material.

It should be noted that the coating material remains essentially pore free for all compositions after heat treatment, as shown in Fig. 7. The fine texture on the surface is an artefact of the gold coating applied to image the samples. The appearance of the dried films was essentially identical in all cases being very similar in appearance to that of the heated T100 composition. In the case of T60 composition, the bright contrasting regions apparent after heat treatment are believed to be due to phase separation on heat treatment. EDX analysis of these regions shows them to be relatively carbon rich compared with the bulk of the material.

Although the coating thickness could not be easily determined directly, an estimation of this was obtained based on an assumption that the powder comprised spherical iron powder particles of diameter 75 μm (the mean particle size). On this basis, the calculated coating thickness at 3.0, 1.0 and 0.3 mass % addition levels are 1.3 μm, 435 nm and 130 nm, respectively. In practice the actual coating thickness should be somewhat lower since iron particles exhibit irregular shapes and uneven surface, and thus possess larger surface area than spheres. As a comparison equivalent coatings

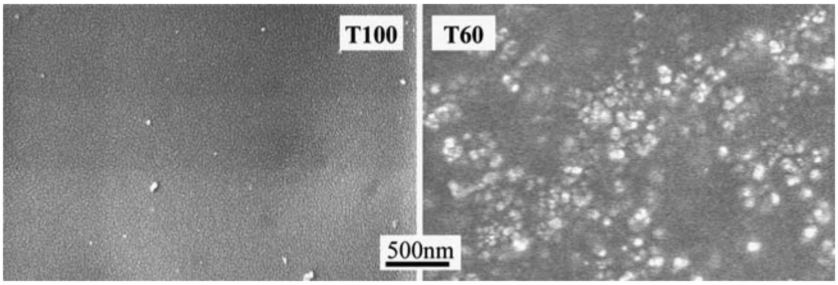


Fig. 7 The film of coating materials after heating at 500 °C for 0.5 h

were prepared on a flat iron surface, at a thickness of circa 400 nm. Interestingly, these coatings remained crack free, suggesting that the cracks are most possibly developed from inconsistent coating thickness because of the rough surface of iron particles.

SEM and EDX analyses were carried out in order to investigate the microstructure of compacted pellets made from the hybrid-coated iron powders and the distribution of the coating within them. Fracture surfaces of the compacted dielectromagnetic composites were polished to obtain flat surfaces for this measurement. As shown in Fig. 8, the iron particles are highly deformed and generally well packed, although there are some voids in the compacted pellets (Fig. 8). The density of the compacts was similar for both the T100 and T60 coated compositions after pressing at 700 MPa, being in the range 7.1–7.2 for 0.3% coating additions, this being around 93% of theoretical density. It should be remembered that these materials are unsintered and thus the values are effectively green density values, modified by the effect of the low-density coating.

As shown in Fig. 8, the particle boundaries/interfaces are clearly distinguishable in these polished specimens. Line scanning across a boundary confirms the existence of coating material between the two particles (Fig. 8b and c). However, it is noticed that the gap measured by Fe-profile is wider than that by Si-profile. This may be due to the tilt of the gap with respect to incident electronic beam or emitted X-ray. It is also possible that the boundary is not fully filled with coating material possibly as a consequence of the sample preparation process, which might be expected to fracture these brittle coatings. Nevertheless, the coating thickness appears broadly consistent with the value predicted by the calculation method previously described (circa 1 μm in this case).

Thermal Atomic Force Microscopy (AFM) was used to further explore the microstructure of compacted pellets made from the coated iron powders. Results are shown in Fig. 9. The height signal image (left) gives the topographic feature of the sample surface under analysis. The thermal conductivity signal image (right) shows the difference in the thermal conducting property of the different surface areas. This signal can be used to distinguish different compositions on the surface. By comparison with the topographic image, it is seen that

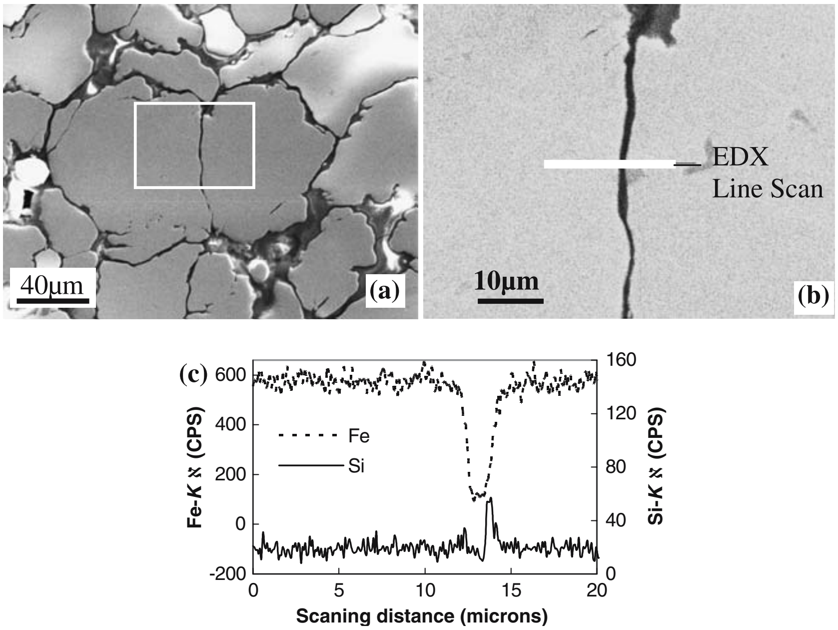


Fig. 8 EDS line-scanning measurement of polished fracture surface of a compacted pellet made from 3 wt% coated iron powder. (**a**) basic SEM micrograph, (**b**) line scanning location and (**c**) Silicon and iron K_α-profiles along the scanning line

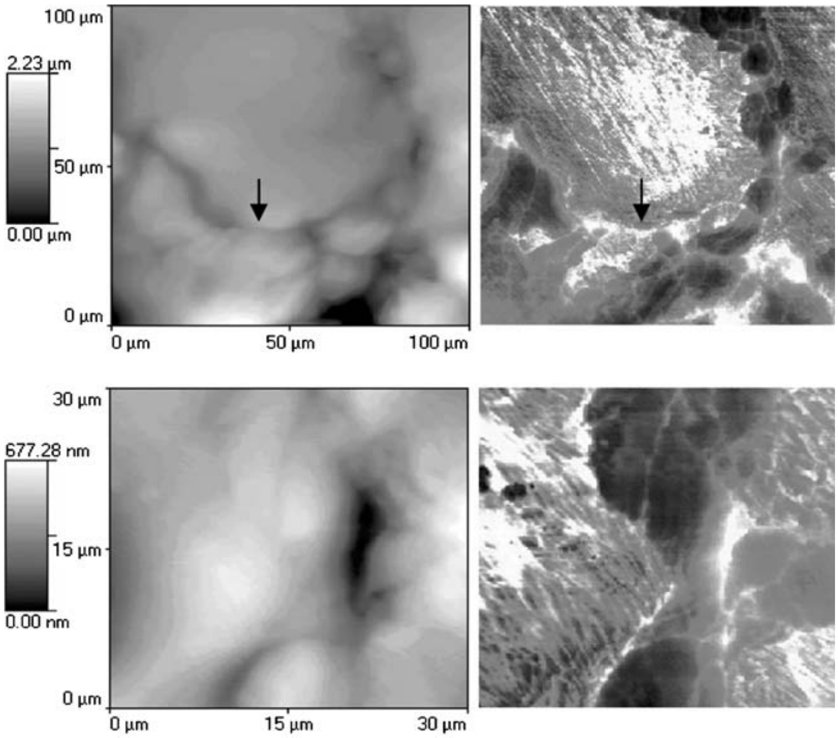


Fig. 9 Thermal-AFM images at two different scales for the polished fracture surface of the same sample as in Fig. 8. Signal channels: height (L), thermal conductivity (R)

some parts of surface area are topographically high (the lighter regions in the left image), but have relatively lower thermal conductivity (the darker regions in the right image). These parts should be the hybrid coating material or the iron particles covered by the hybrid since iron has much higher thermal conductivity than the hybrid materials. In addition, this comparison can also give some information on the particle boundaries. The arrows in the images point at a boundary of two iron particles as shown in Fig. 9. The interface is clearly seen in the height image, while it shows high conductivity in thermal conducting signal, implying there is little hybrid present between the two iron particles. These results indicate that the hybrid coating is not evenly distributed between the iron particle boundaries.

Mechanical, electrical and magnetic performance

Although not a critical parameter in most soft magnetic applications, the mechanical strength of the compacts can be significant, particularly with regard to handling and assembly operations of the magnetic cores. Mechanical testing on 3-point bending of the optimum 0.3% T60 coated formulation was carried out, and indicated flexural strength values of approximate 40 MPa. This is considered to be adequate for this application and is similar to other commercial soft magnetic composite systems [18].

The effect of the different coating formulations on the resistivity of compacted pellets was determined initially at relatively high (3 mass%) addition levels of the various coating formulations in order to produce the clearest distinction between the data obtained with increasing MTMS content in the hybrids. The results show that the resistivity reaches a maximum at TEOS-to-MTMS molar ratio of 40/60 (T40), implying that this formulation of the hybrid coating is optimum in terms of coating effectiveness and dielectric behaviour. As the organic content of the coating is decreased, the hardness and brittleness of the coating layer increases and it is believed that coatings with lower levels of organic content are increasingly prone to damage during the compaction process as the metal powder particles are deformed. In addition, the amount of organic phase might be expected to directly contribute to the increase of resistivity of the coating material itself. Further increasing the MTMS component in the hybrids above 60 mol.% leads to decrease in resistivity. This may be due to the coatings being more flexible, so that they can be squeezed out from between the iron particle interfaces, reducing the insulating layer thickness and potentially allowing the formation of some metal-to-metal contacts (Table 2).

Table 2 Resistivity of 3 mass% coated iron powder compacts annealed 600 °C × 1 h

Formulation	T100	T80	T60	T40	T20	T0
Organic content (%)	0.0	4.9	9.6	14.0	18.3	22.4
Resistivity (mΩ-m)	6.64	57.32	88.09	>60000	4600.4	36.20

It can be seen from the above data that the selection of a coating formulation suitable for aqueous based processing places some constraints on the dielectric performance of the coating, with significantly improved resistivity being achieved for the alcohol based sol derived coatings containing 60 mol.% MTMS as opposed to 40 mol.% MTMS (T60) systems produced via the aqueous based process route, which were chosen for the bulk of this investigation. Nevertheless, the above figures should be seen in context. The resistivity figures of circa 6–90 mΩ-m are an order of magnitude greater than the minimum adequate values of resistivity of circa 10 $\mu\Omega$-m which previous published work has identified as being necessary to control, eddy currents in dielectromagnetic materials [2], and allowed the work to focus on the use of aqueous process routes.

Table 3 lists the properties of dielectromagnetics containing 0.3 mass% T60 dielectric. The presence of the T60 coating imparts effective insulation of iron particles, increasing the resistivity by almost 100 times, resulting in significant reduction of total and eddy current losses. Even the hysteresis losses have reduced to some extent. This may be due to the lower surface friction of coated powder, with a corresponding reduction of stress-hardening of the ferromagnetic particles. On the other hand, the T60 coating has a negative impact on compact density. Low density results in reduction of magnetic induction, $B(T)$ and the maximum permeability, $\mu_{\max}$. Although the density drop is inevitable when less dense coating material is introduced, an optimum comprehensive performance can be achieved by balancing various parameters, and this will be the subject of a subsequent paper.

Conclusions

Sol-gel derived inorganic SiO_2 and organic–inorganic hybrid silica coatings have been investigated for potential dielectromagnetic applications. The hybrid coating formulations have excellent properties as dielectric coating materials for coating iron powders and their properties can be adjusted simply by varying the ratios of TEOS-to-MTMS. The hybrid sols can be easily applied on iron particle surfaces to form a crack-free insulting coating when the coating amount is up to 0.3 wt%. Coatings containing 60 mol.% or more TEOS in the formulation can be processed by a predominantly aqueous process.

The hybrid xerogel films which comprise these coatings are thermally stable up to 500 °C in air as confirmed by FTIR and TGA–DTA analyses, and provide good electrical isolation of the iron powder particles.

The resistivity of pellets compacted from the hybrid-coated iron powders depends upon the coating composition and the maximum is obtained from the T40 coating formulation containing 60 mol.% MTMS. However, compositions with a lower level of MTMS, compatible with the aqueous processing route, also impart adequate resistance and are considered a more cost effective and commercially attractive option.

The coating materials remain intact, distributed along particle surfaces and without any pores both after high pressure compaction and after heat treatment at temperature up to 600 °C, and it can be concluded that the aqueous processed hybrid-coated iron powders developed in this paper have favourable properties for use as a new family of thermally stable dielectromagnetics.

Table 3 Electrical and magnetic properties of the base power and the dielectromagnetics containing 0.3 mass% T60 after annealing 500 °C × 0.5 h

Property	ρ, g/cm^3	R, μ Ω-m	$B(T)$ @10 kA/m	$\mu_{\max}$	ΔP @B = 1 T	ΔP_h @B = 1 T	ΔP_e @B = 1 T
Base powder	7.28	0.20	1.51	551	20.64	9.0	11.64
0.3% T60-coated	7.14	15.7	1.33	382	7.28	6.64	0.64

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