Proceedings of the 17th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 3–7, 2019

Preparation and Characterization of Fe Based Soft Magnetic Composites Coated by SiO_2 Layer Prepared by Stöber Method

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Atomised iron powders of two different particle sizes (particle size below 63 μm and 75–100 μm) were coated with an SiO_2 insulating layer by a chemical procedure, also called Stöber's method, and then have been used as the basis material to form a compact Fe/SiO_2 soft magnetic composite (SMC) using warm compaction techniques. It turned out that a more coherent coating was formed on particles sized below 63 μm rather than on those with size between 75 and 100 μm. This observation was confirmed by SEM images, as well as by higher value of electrical resistance of iron-based SMCs with lower Fe particle size. Annealed Fe/SiO_2 SMCs showed an increased of the value of relative initial permeability (from 100 to 120), and a decreased of the value of coercivity (from 480 A/m to 310 A/m).

DOI: 10.12693/APhysPolA.137.872

PACS/topics: soft magnetic material, composite, powder coating, powder consolidation, magnetic properties

1. Introduction

Recently, soft magnetic composites (SMCs) have attracted even greater attention, especially for their exceptional magnetic properties, including stable permeability at higher frequencies, low energy losses, magnetic anisotropy and relatively high magnetic saturation [1]. They are suitable for various AC and DC applications, like cores for transformers and electric motors, but they find use also in sensors, low frequency filters or magnetic shielding [2]. SMCs should be described as ferromagnetic powder particles coated by an insulating layer (to prevent contact between metallic particles), and pressed to the desired shape. They are manufactured using conventional powder metallurgy (PM) which usually consists of: milling of metallic powder, pressing the powder, annealing to remove internal stress generated during pressing, and secondary operations [3, 4]. Annealing is usually performed at high temperatures (iron-based SMC materials are recommended to be heated at a temperature range of 570 °C to 770 °C) [5, 6]. To make this possible, the insulating coating must be resistant to high temperatures without cracking or chemical decomposition, in order to prevent the composite degradation. The insulating materials can be divided into three groups in terms of chemical composition [7]. The first group consists of organic coatings (such as thermoplastics, thermosets) which form a uniform layer on the surface of the particles, but their major weakness is a low temperature resistance, because even the most heat-resistant organic coatings decompose at 500 °C [8]. Another alternative group consists of hybrid, organic-inorganic coatings (for example resin with embedded SiO_2 particles), but as the pure organic coating, they also can not withstand high temperatures [9]. For this reason, more attention is drawn to the group of coatings based on inorganic compounds, such as Al_2O_3 [10], ZrO_2 [11], SiO_2 [12], and more. It is very likely, that layers made of inorganic oxides, e.g. SiO_2, will be a suitable candidate to produce heat-treated SMC materials, giving the possibility to improve their resulting magnetic properties.

This paper focuses on the preparation of Fe/SiO_2 based SMC material using the Stöber method [13], and also on determination of the appropriate coating process time.

2. Experimental

2.1. Materials and reagents

The sponge iron powder (grade ABC 100.30), supplied by Höganäs AB Sweden, was used as the core material. Two different particle sizes were chosen for experiments (particle size below 63 μm and 75–100 μm). To prepare the coating the tetraethyl orthosilicate (TEOS, 98 wt.%), aqueous ammonia (NH_4OH) isopropyl alcohol, and deionised water was used. All chemicals were of analytical grade and were used without further purification as received.

2.2. Preparation of SiO_2 coating on Fe substrate

In this synthetic procedure, 10 g of iron powders were dispersed in a solution of 320 ml of isopropyl alcohol and 64 ml of deionised water. After few minutes of mechanical stirring 8 ml of ammonia and 32 ml of TEOS

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were added to the solution. Then, the mixture was stirred for 7 h and 24 h. After synthesis the coated powders were washed 3 times in acetone, and dried at room temperature.

2.3. Preparation of Fe/SiO_2 soft magnetic composite

The coated powders were compressed in a press into a ring shaped pattern (outer diameter 24 mm, inner diameter 18 mm, height 2.5 mm). The pressing components were treated by spray lubricant Loctite 8191. The compaction was carried out under an argon atmosphere at a temperature of 400 °C, and a pressure of 700 MPa. The holding time at the sintering temperature was 5 min. After compaction the samples were annealed at 700 °C for 90 min under argon protective atmosphere to remove residual stress.

2.4. Characterization of coated powders and Fe/SiO_2 rings

The nature of the formed coating was analysed by scanning electron microscope (JEOL JSM 7000F) equipped with analytical units EDX and EBSD (Oxford Instruments). The density of cores was calculated using the well-known formula, while the resistivity was measured by 4-point method. The initial relative permeability was measured by impedance spectroscopy, with an impedance analyser (HP 4194 A, from 100 Hz to 40 MHz). The coercivity was obtained by Foerster Koerzimat 1.097 HCJ [14].

3. Results and discussion

3.1. SEM microscopy and EDX analysis

SEM images, as well as EDX analysis for Fe/SiO_2 particles (below 63 μm) coated for 7 h (Fig. 1a) and for 24 h (Fig. 1b) are presented. One can notice that a coating of about 100 nm in thickness occurred on the surface. This is confirmed also by EDX. Due to the sponge-like shape of the iron powder this coating is incoherent. More preferable is when the coating is trapped on the particle irregularities due to its tendency to smooth the surface.

SEM images, as well as EDX analysis for Fe/SiO_2 particles (75–100 μm) coated for 7 h (Fig. 2a) and for 24 h (Fig. 2b) are also presented. One can see that in this case the layer was much thinner than that on smaller Fe particles. It is evident that the amount of TEOS in the solution was insufficient to produce a thicker layer. In spite of this, there have occurred clusters of SiO_2 spherical nanoparticles, mainly located in gaps on the Fe surface.

3.2. Magnetic measurements and electrical resistivity

Electro-magnetic properties (specific resistivity, coercivity and maximum values of real part of relative initial permeability), and density for green compacts and for

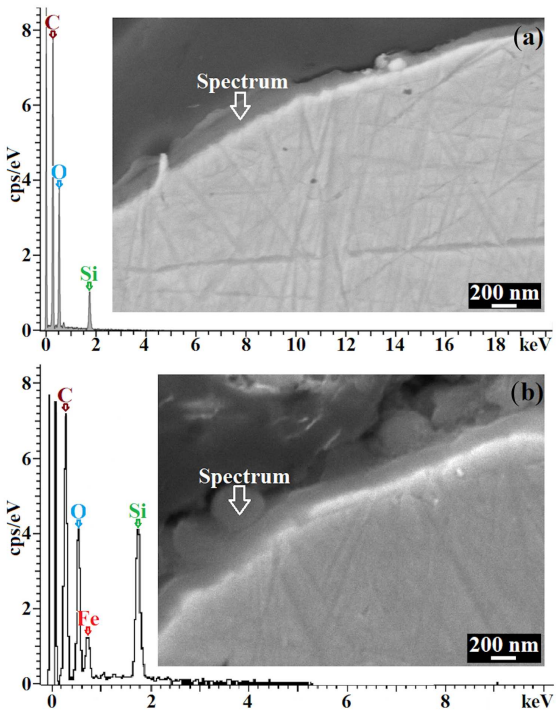

Fig. 1. (a) Surface view on the Fe particle (below 63 μm) with corresponding EDX analysis of formed coating after 7 h. (b) Surface view on the Fe particle (below 63 μm) with corresponding EDX analysis of formed coating after 24 h.

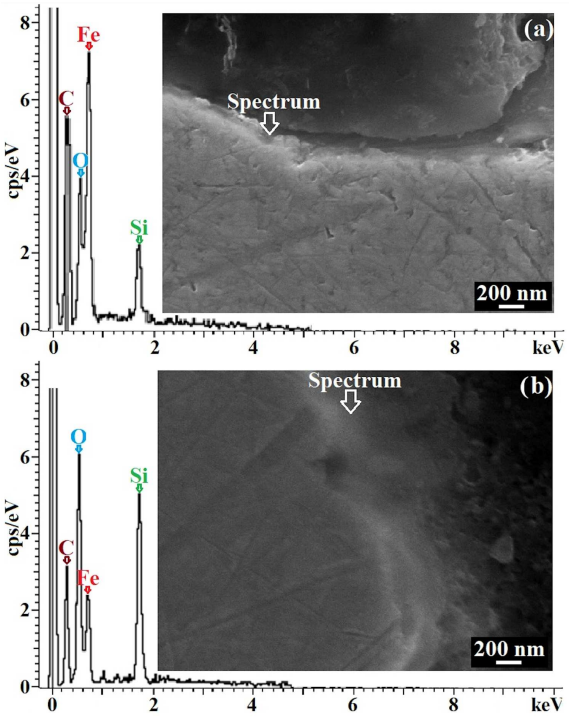

Fig. 2. (a) Surface view on the Fe particle (75–100 μm) with corresponding EDX analysis of formed coating after 7 h. (b) Surface view on the Fe particle (75–100 μm) with corresponding EDX analysis of formed coating after 24 h.

TABLE I

Comparison of electrical resistivity, coercivity, permeability and compact density between samples (green state and annealed state).

Powder size, coating time	Specific resistivity [Ω m]		Coercivity H_c [A/m]		Permeability μ_r		Compact density [g/cm^3]	
	Green state	Annealed state	Green state	Annealed state	Green state	Annealed state	Green state	Annealed state
< 63 μm, 7 h	1.9×10^{-6}	8.8×10^{-7}	480	310	100	120	7.5	7.6
< 63 μm, 24 h	2.2×10^{-6}	8.3×10^{-7}	510	360	70	95	7.2	7.4
(75–100) μm, 7 h	2.5×10^{-7}	2.0×10^{-7}	430	240	110	160	7.7	7.8
(75–100) μm, 24 h	8.4×10^{-7}	5×10^{-7}	430	270	94	120	7.7	7.5

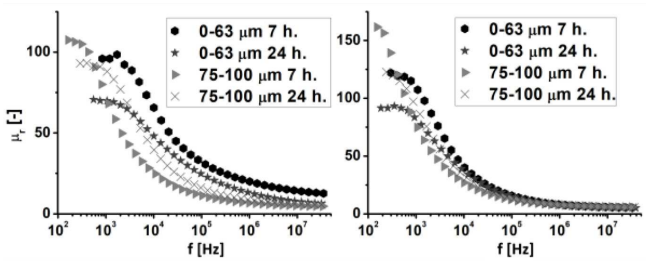

Fig. 3. (a) The frequency dependencies (frequency range 150 Hz–40 MHz) of real part of relative initial permeability μ_r (a) for green compacts, and (b) annealed samples.

annealed samples are introduced in Table I. Results shows that annealing generally improves the soft magnetic properties, reduces coercivity, and increases permeability.

We can assume that this is caused by the minimization of internal stresses of ferromagnetic component that were introduced at milling and compaction, acting as obstacles for domain wall displacement, and thus considered as an essential magnetization mechanism in this type of ferromagnetic material. The increased time for creation of insulating layer for green compacts leads to the increase of resistivity, coercivity, and to the decrease of permeability. This tendency was also evident for annealed samples by an increase of coercivity and a decrease of permeability.

The relative permeability decreases with increased frequency at relative low frequencies, as a consequence of low resistivity of the resulting material. However, on the other hand the maximum permeability is high for annealed samples. Comparing these results with that for similar iron rich materials [15], it is clear that the requirement for maximum permeability and the maximum frequency of the permeability decrease, are often opposed.

The relative permeability of all samples summarized in Table I can be followed in more details in Fig. 3. It is clear, that the best sample for low frequency application is sample 3 with larger iron particles, while for higher frequency application appropriate is sample 1 with smaller particles. The increased time for insulation layer preparation has not positive influence on relative permeability.

4. Conclusion

The iron-based soft magnetic composites coated by Stöber's method with SiO_2 insulation layer were prepared, and the influence of coating preparation time and various iron particle size on resulting electro-magnetic properties was studied. The 7 h and 24 h coating process was sufficient to form a protective layer on samples of both sizes. However, judging from SEM images and resistivity measurements, the formed coating on specimens of particle size below 63 μm was thicker, and so its insulation properties were better. The measurements of relative initial permeability have revealed that the sample with powder particle size below 63 μm and coated for 7 h, is more suitable for higher frequencies. In turn, the sample with grain size from 75 μm to 100 μm and coated for 7 h, is more suitable for lower frequencies. From the resulting electro-magnetic properties we can conclude, that increased time over 7 h for chemical reaction leading to creation of insulating layer does not improve the properties of resulting product. We expect that this layer can be further improved by re-coating of existing layer by several separated processes step-by-step.

Acknowledgments

This work was realized within the frame of the project "MACOMA" financed by Slovak Research and Development Agency under the contract APVV-15-0115, the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic, and the Slovak Academy of Sciences (VEGA 1/0143/20), the Internal Scientific Grant of the Faculty of Science, P.J. Šafárik University in Košice (vvgs-pf-2019-1038), and by the Development Operational Programme Research and Innovation for the project "New unconventional magnetic materials for applications", ITMS: 313011T544, co-funded by the European Regional Development Fund (ERDF).

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