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Innovative ferrite nanofibres reinforced soft magnetic composite with enhanced electrical resistivity

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ABSTRACT

Soft magnetic materials with an excellent performance are desired for functional applications. We present an innovative method for manufacturing the soft magnetic composites that may pave the way for magnetic cores with improved electromagnetic properties. In this paper, soft magnetic composites based on FeSi powder coated with the hybrid organic-inorganic coating composed of boron phenol-formaldehyde resin and $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite fibres were fabricated to investigate the effects of ferrite nanofibres on the structural and electromagnetic properties. A uniformity of hybrid organic-inorganic coating is reflected in a high value of the electrical resistivity. A low porosity and extraordinary high values of mechanical hardness and flexural strength were found in prepared soft magnetic composites.

1. Introduction

Magnetic materials made of soft magnetic composites (SMCs) are extensively developed as a viable alternative to the laminated steel materials in a range of new applications, such as transformers, inductors, sensors, fast switching solenoids and electrical motors. In comparison with laminated soft magnetic materials, SMCs based on the ferromagnetic powder materials and dielectric coatings allow for revolutionized design of electromagnetic devices with improved efficiency and reduced weight and costs, without sacrificing magnetic performance [1]. Basically, the SMCs are designed as a ferromagnetic powder surrounded by a thin electrically insulating layer [2], which exhibit unique magnetic properties such as an isotropic magnetic behaviour, low eddy-current loss, as well as, a relatively lower total core loss at medium and high frequencies. Till now, the most used ferromagnetic core materials for designing of SMCs are Fe [3–5] or Fe-Si alloys [6,7], which are characterized by high electrical resistivity, Ni-Fe alloys [8,9] with high permeability and Fe-Co alloys [10] with high magnetic saturation magnetization.

Generally, the dielectric coatings are divided to organic or inorganic materials. The advantages of organic coatings lie in simple coating process, what leads to a creation of uniform insulation of particles ensuring production of the materials with high density and high electric resistivity of final green compacts [11]. The main disadvantages of SMCs with organic component are the thermal treatment, which is strictly limited by the thermal resistance of the organic insulating material. On the other side, for application of core materials where the higher temperature is needed in the preparation process, it is more desirable to use the pure inorganic coatings (electric motors, batteries, house appliances, machine tools etc.). Moreover, inorganic coatings including phosphates [12], oxides [13], silica [14], sodium silicates [15] or ferrites [16] and other ceramic compounds ensure that a final thermal treatment is adequate to remove residual stress after compaction and a preparation of green compacts. The common disadvantage of all inorganic coatings is creation of shrinkage during heat treatment leading to formation of cracks and possibility of metal-on-metal contacts yielding to final exfoliation of inorganic coatings. Another feature of inorganic coatings is formation of bi-layered coating because of nature of ferromagnetic core, which can interact with coating at high temperature during synthesis procedure [17]. Several efforts have been conducted to form hybrid organic-inorganic coatings in SMCs, e.g. by the sol-gel-prepared nano-sized SiO_2 in the phenol-formaldehyde resin [18,19], by direct addition of SiO_2 nanoparticles in the epoxy-modified silicone resin [19] or by the incorporation of the mixture of SiO_2 and Fe_3O_4

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particles into epoxy-modified silicone resin [20]. Such the modifications tend to the enhanced mechanical strength, electrical resistivity and magnetic properties. Chemical routes of in-situ preparation of SiO_2 nanoparticles in the organic coatings allows to induce the chemical bonding between inorganic and organic part of the coating and finally cause the homogeneous formation of coating [18] and improved thermal stability [19]. The challenging task remains the preparation of hybrid SMC with ferrite coating for industrial applications. Ferrites are well-known ferrimagnetic materials, which possess unique electromagnetic properties, high electrical resistivity, controllable saturation magnetization, moderate thermal expansion coefficients, energy-transfer efficiency [21]. There is a variety of physical or chemical methods employed to prepare the spinel type ferrite: sol-gel autocombustion method [22], chemical precipitation [17] or mechanical mixing procedure [23]. However it is known that basic magnetic characteristics of spinel-type ferrites can be controlled by changing the type of divalent cations in a crystal structure [24] or by the size and shape of ferrite nanoparticles [25–27]. One-dimensional nanostructures in the form of fibres have received considerable attention due to their tunable mechanical properties such as high mechanical strength, toughness and Young's modulus. By the preparation of hybrid organic-inorganic coatings, it is possible to combine the benefits of both types of coatings and prepare the new family of SMC with desirable properties.

In this work, it is reported the preparation of soft magnetic composite based on FeSi powder coated with the hybrid organic-inorganic coating composed of boron phenol-formaldehyde resin (PFRB) and $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite fibres. PFRB was synthesized by polycondensation reaction of phenol and formaldehyde in the presence of boric acid and the synthesis, characterization and advantage of thermal resistance was reported previously in detail [28]. The needle-less electrospinning was used for preparation of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ soft magnetic fibres in large scale. The hybrid coating was deposited on a surface of spherical FeSi powder and processed by PM technology for a bulk sample for mechanical, electrical and magnetic tests. The morphology of prepared ferrite fibres as well as final SMCs samples were characterized by SEM, TEM, XRD and EDX analysis. Electro-magnetic properties were studied and the complex permeability and core losses dependence of hybrid organic-inorganic coatings composition are discussed.

2. Experimental

2.1. Materials for core-shell composite powder

The commercial powder of FeSi spherical particles distributed by Höganäs Corporation was used as the base ferromagnetic material, which is available in the granulometric fraction from 45 μm to 150 μm. Phenol (Ph, 99%, Aldrich), formaldehyde (F, 37% aq., Aldrich), ammonia (NH_3. 26% aq., Aldrich), and boric acid (H_3BO_3 99.5% Lachema) were used for the synthesis of boron modified resin (PFRB). The initial molar reaction ratio of $Ph/F/NH_3/H_3BO_3$ was 1/1.5/0.35/0.1. The $Ni_{0.3}Zn_{0.7}Fe_2O_4$ nanofibres were prepared by use of 7 wt% water solution of polyvinyl alcohol (PVA Acros Organic, $Mw = 146.000–186.000\ g\ mol^{-1}$) with appropriate amount of metal nitrates (Acros Organic, $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$. $Fe(NO_3)_3.9H_2O$). The molar ratio of $Ni^{2+}/Zn^{2+}/Fe^{3+}$ was set to 0.3/0.7/2 in order to maintain the molar ratio in the resulting ferrite $Ni_{0.3}Zn_{0.7}Fe_2O_4$. Subsequently, 0.03 vol% of acetic acid (Sigma Aldrich. 99.7%) was added to the prepared solution.

2.2. SMCs preparation

The composition of studied samples is summarized in Table 1. The preparation of core-shell powder was as follow: PFR was dissolved approximately in 10 ml of absolute ethanol. The predetermined amount of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ fibres were mixed in this solution until achieving of the uniform distribution of fibres in PFRB solution. FeSi powder was added to the PFRB/$Ni_{0.3}Zn_{0.7}Fe_2O_4$/ethanol solution and mixed after complete evaporation of the solvent. The dried core-shell particles were pressed at 800 MPa in the cylindrical die 10 × 3 mm (d x h), and Vickers hardness test HV10 (STN-EN-ISO 6507-1 (42 0374) MPIF 43) was performed. The flexural strength TRS (transverse rupture strength) (STN (42-0891-4) MPIF41) was detected on prism-shaped samples of dimensions 5 × 4 × 2 mm (w x h x l). Electromagnetic measurements were recorded on the toroid-shaped samples with the outer diameter of 24 mm. The inner diameter was 17 mm and the height 2 mm. The prepared green compact samples with PFRB were slowly cured up to 220 °C and samples without PFRB were sintered at 800 °C with a heating rate of 10 °C/min for 1 h in air atmosphere.

2.3. Techniques for preparation and characterization

$Ni_{0.3}Zn_{0.7}Fe_2O_4$ fibres were produced by a needle-less electrospinning technology by mean of Nanospider ™ NS Lab (ELMARCO). PVA/metal nitrate solution was spinned at 80 kV of applied voltage with 130–140 mm of distance between spinning electrode and collector. The electrospinning was performed at ambient temperature with a relative humidity of 50%. After electrospinning, the electrospun nanofibre mats were dried at 90 °C for 15 min and then annealed at 800 °C for 4 h in air at atmospheric pressure, with a heating rate of 10 °C/min. Densities of powder and bulk composites were measured by He-pycnometer AccuPyc II 1340. The prism-shaped samples were used to evaluate elastic properties represented by Young modulus (E) by impulse excitation method and software Buzz-o-Sonic and transverse rupture strength (TRS) measured by 3-point bending test using universal testing machine Tiratest 2100. The cylindrical shaped samples were used to measure the hardness tests using TUKKON 1102 hardness tester. The structural analysis was carried out using X-ray diffraction (XRD, X'Pert Pro Pan Analytical) in Bragg-Brentano geometry, with CoKα radiation, linear detector and β-filter in incident path. The microstructure and morphology of all the samples were examined by the scanning electron microscope (SEM/FIB. ZEISS AURIGA COMPACT) equipped with the energy dispersive X-ray analyzer (EDX). Complex permeability spectra were measured on ring samples with few turns of insulated wire by impedance spectroscopy using an impedance analyzer HP 4194 A from 1 kHz to 40 MHz with the contact electrodes in two-terminal connection configuration. The AC hysteresis loops were measured at the frequency range from 100 Hz to 13 kHz and at maximum induction of 0.1 T by two different AC hysteresisgraphs - in the frequency range from 100 Hz to 1.2 kHz by an AC/DC Permeameter AMH-1K-S, and in the frequency range from 1 kHz to 13 kHz by a MATS-2010SA hysteresis graph. The electrical resistivity was measured from DC to 20 MHz by means of a standard four-wire method, with good voltametric and amperometric electrical contacts ensured by indium strips sandwiched, at the ends of a cut ring sample, between the polished sample surface and copper leads subjected to uniform pressure. The cylinder samples were used for measurement of coercivity by Foerster Koerzimat 1.097 HCJ.

3. Results and discussion

3.1. Preparation of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ fibres

The needle-less electrospinning technique is the most versatile technique for preparation of ferrite nanofibres in large scale. The