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Chemical synthesis of nickel ferrite spinel designed as an insulating bilayer coating on ferromagnetic particles

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ABSTRACT

Soft magnetic core–shell particles were designed by coating FeSi and permalloy powders with ferrite nanoparticles. The permalloy-type powder particles were prepared by mechanical alloying process of 80 wt% of Ni, 14.7 wt% of Fe, 4.4 wt% of Mo, 0.5 wt% of Mn and 0.3 wt% Si. $NiFe_2O_4$ cuboidal nanoparticles were synthesized by the chemical precipitation of hydroxides by alkaline treatment of the dissolved metal in aqueous chloride solution and the same process was used for a deposition of $NiFe_2O_4$ nanoparticles on both substrates. The average size of $NiFe_2O_4$ nanoparticles, crystallinity and spinel structure were determined by TEM and XRD techniques. The deposited coating was created in a bilayer form. The composition of individual layer was analyzed by XRD and TEM using 100-nm lamella extracted from the coating by focused ion beam. The chemical composition of individual layers was analyzed by EDX analysis. The specific electric resistivity measurement has confirmed a good insulating character of the designed bilayer coating, whereas the prepared core–shell powders and relevant green compacts belong to soft magnetic materials.

1. Introduction

Soft magnetic composites (SMCs) are basically designed as a ferromagnetic powder surrounded by a thin electrically insulating layer. In comparison with laminated soft magnetic materials, SMCs prepared by powder metallurgy (PM) methods have unique magnetic properties such as an isotropic magnetic behavior, low eddy-current loss as well as a relatively lower total core loss at medium and high frequencies [1]. PM technologies are able to produce SMCs with a high enough density and sufficiently stable mechanical properties, whereas an insulating layer between magnetic powder particles ensures a high electrical resistivity minimizing the overall magnetic losses [2]. The increase of electrical resistivity without any noticeable degradation of magnetic properties is also desirable for some electromagnetic applications including the ones in a microwave-frequency range. One of the most promising approaches for the preparation of nano- and microstructured SMCs is based on a modification of metal powders (mostly Fe and Fe-base alloys like permalloy, Vitroperm, FeSi) through organic or inorganic coatings. Permalloy is an alloy with approximate content 80% of nickel and 20% of iron. It is a soft magnetic alloy with exceptionally high magnetic permeability of about 100,000, which is much higher than the magnetic permeability of electrotechnical steel (several thousands) [3]. Permalloy has a low coercivity, nearly zero magnetostriction and significant anisotropic magnetoresistance. The low magnetostriction is extremely important for industrial applications, since variable stresses in thin films would otherwise cause extraordinary large variations in magnetic properties. Permalloy's electrical resistivity can vary as much as 5% depending on a strength and direction of an applied magnetic field. Permalloy-type alloys with the nickel content of about 80% usually have the face-centered-cubic crystal structure with a lattice constant of approximately 0.355 nm. A disadvantage of permalloy is that it is not very ductile or workable. Permalloy is especially useful in designing highly sensitive input and inter-stage transformers, where signals are extremely low and DC currents are not present. It is also useful in current transformers where losses must be kept to a minimum and high accuracy is a necessity. Permalloy is distributed by many commercial companies in the form of powder, shot, pellets and ingots [4]. The nanocrystalline Vitroperm alloys are based on Fe with a small addition of Si, B, Nb and Cu. Vacuumschmelze GmbH&Co global manufacturer develops a rapid solidification technology resulting in the production of two-phase structure with fine crystalline grains embedded in an amorphous phase. The nanocrystaline cores are widely used as switched mode power supplies, solar inventers, frequency converters, EMC filters, welding equipments, wind generators, inducting cooking, automotive application, uninterruptible power supplies [5].

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The main advantage of widely used organic binders lies in a smart preparation of composites, a high density of final green compacts and a thermally undemanding curing process [6]. However, the thermal treatment for these materials is strictly limited by a thermal resistance of the insulating organic material, which is inadequate in order to remove plastic deformations created during a preparation of green compacts [7]. The sufficient heat treatment of green compacts permits to obtain low volume fractions of defects, reduces distortions in the particles and lowers the dislocation density, which consequently lead to an increase of the magnetic permeability [8]. To achieve this goal, electrically resistant materials with acceptable magnetic properties like for instance ferrites are regarded as the most suitable candidates for a preparation of SMCs [7,9].

Ferrites have three possible crystal-structure symmetries: garnet, hexagonal and cubic. The actual crystal structure of ferrites is determined by the size and charge of the metal ions that balance the negative charge of oxygen ions, and they relative amounts. It is noteworthy that the spinel-type ferrites have the most important technological applications due to their outstanding optical, electrical, magnetic and catalytic properties. The spinel-type ferrites with a general formula MFe_2O_4 (M is divalent metal ion, e.g. Ni^{2+}, Co^{2+}, Cu^{2+}, etc.) involve two sites, i.e., the tetrahedral sites A and octahedral sites B occupied by the trivalent Fe^{3+} ions. According to a distribution of the divalent metal ions M^{2+} between A and B sites one recognizes two different types of the ferrites: the normal spinels $[M^{2+}]_A[Fe^{3+}Fe^{3+}]_BO_4$ in which the divalent metal ions M^{2+} occupy the tetrahedral sites and the trivalent Fe^{3+} ions occupy the octahedral sites and, respectively, the inverse spinels $[Fe^{3+}]_A[M^{2+}Fe^{3+}]_BO_4$ in which the divalent metal ions M^{2+} occupy the octahedral sites in contrast with the tetrahedral sites occupied in part by the divalent metal ions M^{2+} and in part by the trivalent Fe^{3+} ions [10]. Note furthermore that it is possible to control to a certain extent basic magnetic characteristics of spinel-type ferrites by changing the type of divalent cations [11], the size and shape of nanoparticles [9–14], which also have fundamental impact on a chemical composition and crystal structure [15,16].

Among the most versatile and technologically important spinel-type ferrites, one could mention $NiFe_2O_4$. $NiFe_2O_4$ ferrite synthesized as nano- or micro-sized powder is suitable material for a development of magnetic storage media [17,18], sensor materials [19,20], ferrofluids [21], anodes for lithium-ion batteries [22], etc. Up to date, a variety of physical and chemical methods have been employed in order to prepare the spinel-type ferrite $NiFe_2O_4$: sol–gel autocombustion method [23,24], solvothermal [12] or hydrothermal [25] synthesis, mechanical alloying [26,27], but only a little attention has been paid to the preparation of $NiFe_2O_4$ in the form of a thin coating by wet chemical methods. Several authors have tried to design a novel kind of SMCs by preparing the spinel-type ferrite, which has been subsequently used for a deposition on the surface of ferromagnetic particles by mechanical mixing procedure [7,9]. For the first time, Gunjakar *et al.* has reported the deposition of nano-sheet single-phase spinel $NiFe_2O_4$ films by a chemical deposition from alkaline bath on the glass substrates and characterized their structural, morphological and electrical properties [16]. The same authors described the modified bath deposition method to obtain $NiFe_2O_4$ thin film with required stoichiometry by immersing substrate into separately placed cationic and anionic precursors [28].

In the present work, we will report for the first time the deposition of nano-rectangular spinel coating $NiFe_2O_4$ by a chemical precipitation from an alkaline bath containing Ni^{2+} and Fe^{3+} ions. The designed coating is deposited on a surface of excellent soft magnetic powder particles such as commercial spherical powder particles FeSi or the powder particles 80Ni–14.7Fe–4.4Mo–0.5Mn–0.3Si prepared by a reactive milling. The preparation of $NiFe_2O_4$ ferrite coating has been accomplished by adapting the procedure developed in Ref. [22], where the ferrite was synthesized by low-temperature route without any surfactant and multiple steps. The spinel structure of $NiFe_2O_4$ ferrite powder will be confirmed by FTIR spectroscopy and TEM analysis. The size, structure, morphology and composition of synthesized ferrite coating will be verified by SEM, TEM, XRD and EDX analysis. It will be demonstrated that the coating designed in the form of a double layer has a high enough electrical resistivity, which is the principal technological requirement that is demanded for possible practical applications of SMCs. In addition, the magnetic properties of the prepared powder and bulk alloys are also investigated.

2. Experimental

2.1. Preparation of ferromagnetic powder

Two different types of ferromagnetic powder particles were used for coating process. The commercial spherical particles FeSi (97 wt% of Fe, 2.8 wt% of Si, 0.003 wt% of C, 0.04 wt% of O and 0.01 wt% of N) with a granulometric fraction from 45 μm to 150 μm were obtained from Högänes Corporation [29]. The permalloy-type powder particles (80 wt% of Ni, 14.7 wt% of Fe, 4.4 wt% of Mo, 0.5 wt% of Mn, 0.3 wt% of Si) were prepared by mechanical alloying process from atomic and pre-alloyed powders during 72 h using planetary ball mill Pulverisette P-6 (Fritsch). The milling was carried out in hardened steel vial with 1inch steel balls in air atmosphere. The ball-to-powder ratio was 15:1 and rotational speed of main disc was 350 rpm.

2.2. Preparation of microcomposite sample

The nano-structured ferrite $NiFe_2O_4$ coating was synthesized from alkaline water solution involving chloride salts of Ni^{2+} and Fe^{3+}. To adjust pH of the solution, we have used NH_3 (Aldrich, 26% aq.), as a complexing agent. The Ni^{2+} and Fe^{3+} molar ratio was kept as 1:2. To achieve this ratio, 1,9439 g of $NiCl_2$ (Centralchem SK, 97%) and 4,8659 g of $FeCl_3$ (Centralchem SK, 99.8%) were dissolved in 30 ml distilled water using magnetic stirrer for 1 h. The obtained clear solution was poured to the solution of 50 ml 4 M NaOH and continuously stirred (300 rpm) for 0.5 h. The brown precipitate of hydroxides immediately resulted from the relevant chemical reaction. Subsequently, 20 g of ferromagnetic powder was immersed into the prepared colloidal solution, and pH was adjusted to 10 by a slow dropping of NH_3. The obtained suspension was kept at 45 °C for 6 h and occasionally stirred. The resulting product was decanted three times with 200ml of distilled water, collected on filter and then washed with 20ml of ethanol. The covered particles were annealed at 500°C for 3 h on the air in muffle furnace. The final core–shell powder was pressed at 600 MPa in the cylindrical die ($d = 10$ mm, $h = 3$ mm), for electrical resistivity measurement. The 20 ml of filtrate containing pure $NiFe_2O_4$ particles was withdrawn from suspension after 6 h in order to confirm a crystal structure of the spinel-type ferrite.

2.3. Methods of characterization

The structural analysis was carried out using X-ray diffraction (XRD, X´Pert Pro PanAnalytical) within the 2θ range 10–115° with the scanning rate of 2°/min and Fourier transform infrared spectroscopy (Shimadzu, IRAffinity, KBr pellets 1 mg sample + 300 mg KBr). The thermal degradation of $NiFe_2O_4$ particles was analyzed by differential scanning calorimeter (METTLER 2000 °C). The sample was heated up to 900 °C in air at a heating rate of 10 °C/min. The microstructure and morphology of all the samples were examined by the scanning electron microscope (SEM, JEOL 6460 with Oxford Instruments INCA Energy EDX) equipped with the energy dispersive X-ray analyzer (EDX). The size, structure and morphology of as-prepared $NiFe_2O_4$ particles and the coating of $NiFe_2O_4$ were analyzed by the transmission electron microscopy (TEM, JEOL 2100F). Focused ion beam (FIB, Tescan LYRA 3 XMU FEG/SEM) was used for extraction of 100 nm thin film from a designed double coating for the purpose of identification of individual ferrite layers. The electrical DC resistivity measurement was carried