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Original Research Paper

Structure and magnetic properties of ZrO_2-coated Fe powders and Fe/ZrO_2 soft magnetic composites

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Fe particles were coated with ZrO_2 nanopowders using mechanical milling method combined with high temperature recovery annealing process. The effect of milling time on particle size, phase structure and magnetic properties of the core-shell structure powders was studied. Scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD) revealed that the surfaces of the composite powders comprised thin and uniform layers of ZrO_2 insulating powders after milling. Also, the SEM images showed the morphology of micro-cellular structured compacts with cell-body of Fe particles and indicated that Fe particles were well separated and insulated by thin ZrO_2 layers. The Fe/ZrO_2 soft magnetic composites displayed much higher electrical resistivity, lower core loss than that of the pure Fe powder cores without ZrO_2 layers at medium and high frequencies. The preparation method of ZrO_2-insulated Fe powders provides a promising method to reduce the core loss and improve the magnetic properties for soft magnetic composite materials.

1. Introduction

Soft magnetic composites (SMCs) consisting of ferromagnetic particles separated by electrical insulating materials have attracted considerable attention recently due to their high electrical resistivity, three-dimensional isotropic ferromagnetic behavior and relatively low total core loss [1–3]. Generally, core loss in magnetic cores mainly consist of hysteresis loss (W_h), eddy-current loss (W_e) and residual loss (W_r) [4]. About 9% of electrical energy is lost during electromagnetic transmission and distribution mainly because of eddy-current loss, especially at medium and high frequencies [5]. Therefore, a key challenge to improve energy efficiency for power conversion is to prepare soft magnetic composite with better magnetic properties and lower core loss.

The eddy-current loss could be reduced significantly by eliminating the electrical conducting path or increasing the electrical resistivity between Fe particles in magnetic materials [6,7]. And substantial numbers of insulating materials have been applied in SMCs for separating the conductive Fe particles including organic materials [8,9], inorganic materials [10,11] and in-situ passivation coatings [12,13]. Unfortunately, most of the insulating materials could not endure high temperature and would be decomposed or evaporated, leading to a sharp deterioration in mechanical and magnetic properties of the magnetic cores during subsequent annealing process. Thus inorganic oxides, such as SiO_2, Al_2O_3 and MgO [14–16], with high thermal stability and electric resistance are alternative insulating materials to decrease core loss in SMCs.

ZrO_2 is also one of the most important oxide ceramics with high chemical inertness, refractory properties and high dielectric constant. It is capable of electrically insulating iron powders, even after high temperature treatment, to eliminate eddy currents, and at the same time is effective to keep the original magnetic properties. There are several routes to prepare such composite powders. Myagkov et al. [17] synthesized ferromagnetic Fe-ZrO_2 nanocomposite thin films by using a thermite reaction between Zr and Fe_2O_3 layers and found that the synthesized Fe-ZrO_2 nanocomposite films possess soft magnetic behavior, high magnetization, high resistivity and good chemical stability. de Resende et al. [18] investigated the formation of Fe-ZrO_2 nanocomposite powders by reduction in H_2 of a totally stabilized $Zr_{0.9}Fe_{0.1}O_{1.95}$ solid solution. Protsenko et al. [19] investigated electrodeposition of iron and composite iron-zirconia coatings from a methanesulfonate electrolyte. Zulhijah et al. [20] reported α''-$Fe_{16}N_2$ phase formation of plasma-synthesized core-shell type α-Fe nanoparticles and the prepared nanoparticles with a thin shell exhibited an enhanced magnetic performance over α-Fe nanoparticles.

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However, most of the reported methods for the production of nanocomposite materials are quite complex in preparation route or applicable only in film form. In recent years mechanical milling has demonstrated the ability to produce composite granular powders. This technique of mechanical milling has some advantages over sol-gel route, chemical reduction, thin film deposition or nitridation since large quantities of material may be produced quickly, efficiently and cheaply [21,22]. Furthermore, the particle size of the constituent materials and the component content can be easily controlled by varying the milling parameters.

In this study, a novel soft magnetic composites insulated by ZrO_2 coatings were prepared. Our work provided a simple and effective method to prepare high-performance ZrO_2-insulated Fe powders. The coating method described here can be achieved by mechanical milling of the mixture of pure Fe powders and ZrO_2 nanopowders. Not only the practicability of ZrO_2 nanopowders to coat Fe powders was confirmed, the effect of milling time on structure and magnetic properties of the composite powders was also investigated. We show, through a combination of structural identification and chemical analysis cooperated with magnetic property testing, that these composite powders have homogeneous ZrO_2 layers which are capable of diminishing eddy-current loss, and possessing enhanced magnetic properties.

2. Material and methods

Commercial sphere-shaped Fe powders (purity ≧99.5%, Tianjiu Metal Material Co., Ltd, China) with an average particle size of 75 μm and ZrO_2 powders (purity ≧99.9%, Jingrui New Material Co., Ltd, China) with an average particle size of 30 nm were used as starting materials. The specific experimental procedures to prepare ZrO_2-coated Fe powders and corresponding SMCs were as follows: (a) Fe powders and ZrO_2 nanopowders (the content of ZrO_2 was 5, 7.5, 10 and 12.5 wt.%, respectively) were pre-mixed in a V-type blender for 15 min, and then the mixture was dry-milled for various times (1, 2, 3, 4, 5 and 6 h, respectively) with a ball-to-powder ratio of 50:1 in a high-energy ball milling machine (1-SL, Qingdao Union Machinery Co., Ltd, China) under argon atmosphere. 304 stainless steel vessel (with a inner diameter of 220 mm) and 304 stainless steel balls (with a diameter of 5 mm) were used in this process; (b) the obtained composite powders were then annealed at 600 °C for 2 h in argon atmosphere to relieve internal stress; (c) the annealed Fe/ZrO_2 composite powders were mixed with 1.5 wt.% muscovite (purity ≧95%, Meryer (Shanghai) Chemical Technology Co., Ltd, China) and then compacted under 1000 MPa to form toroidal-shaped magnetic cores with 22 mm outer diameter, 12 mm inner diameter and 5 mm thickness as shown in Fig. 1; (d) the magnetic powder cores were annealed again at 650 °C for 2 h in flowing argon atmosphere. To investigate the effect of ZrO_2 insulating layers on magnetic properties, a pure Fe magnetic powder cores without any insulating materials was also prepared under the same conditions for comparison.

The particle size distribution of raw Fe powders and composite powders was measured by laser particle size analyzer (MS2000G, Malvern, England). The phase identification was analyzed by X-ray diffraction (XRD) (DX-2007, Dandong fangyuan Co., Ltd, China) operated at 30 kV and 30 mA using Cu-Kα radiation. The morphology and local chemical homogeneity of composite powders and compacts were examined by scanning electron microscopy (SEM) (Nova NanoSEM 450, FEI, USA) coupled with a energy-dispersive spectroscopy (EDS) (Ultra, EDAX, USA). The density of the SMCs was determined by using Archimedes principle with ethanol as the immersion fluid. The static magnetic properties of the powders were tested at room temperature by vibrating sample magnetometer (VSM) (Quantum Design, USA). Total core loss of the ring-shaped magnetic powder cores was measured at 0.02 T from 1 kHz up to 100 kHz by using a soft magnetic AC measuring instrument (MATS-2010SA/500k, Linkioin, China). The hysteresis loss of the compacts was measured by using a DC B-H loop tracer (MATS-2010SD, Linkioin, China).

3. Results and discussion

3.1. Effect of mechanical milling on particle size evolution and microstructure of the ZrO_2-coated Fe powders

Fig. 2 shows the particle size distribution of Fe powders before and after mechanical coating, and it can be found that the

Fig. 1. The toroidal-shaped magnetic cores of the Fe/ZrO_2 SMCs.

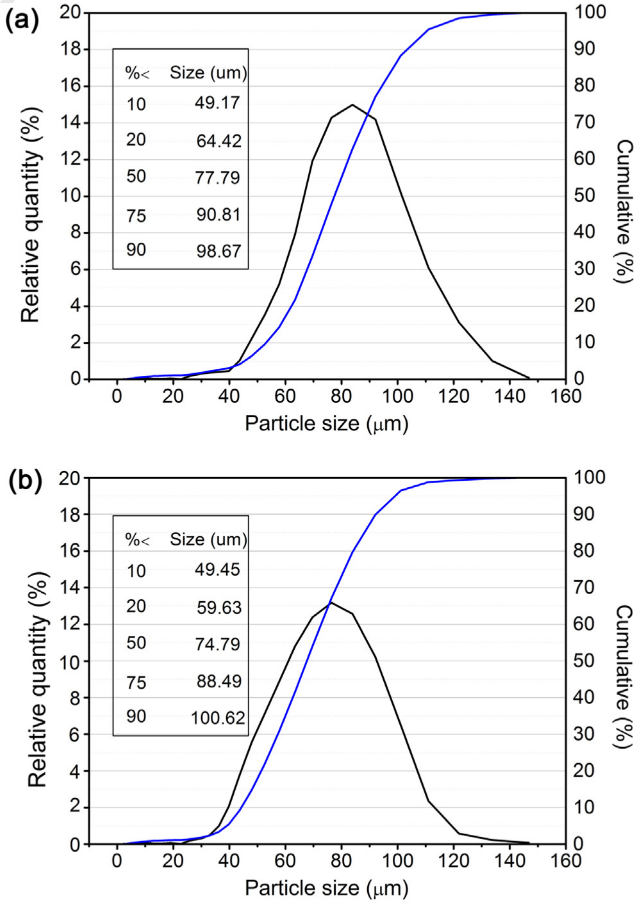

Fig. 2. Particle size distribution of the raw Fe powders (a) and composite powders (with 10 wt.% ZrO_2) after 2 h of mechanical milling (b).

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