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Soft magnetic composites based on hybrid coated Fe-Si nanocrystalline powders

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ABSTRACT

The preparation and characterisation of soft magnetic composite compacts based on hybrid coated nanocrystalline Fe-Si powder are presented. The Fe-Si powder was prepared by mechanical milling of Fe-Si electrical steels sheets up to 20 h. The hybrid coating consists in an electrically insulating phosphate and a polymer layer that covers the Fe-Si particles. The influence of phosphating duration on the particles surface was investigated by SEM, EDX, XRD, and FTIR investigations. The saturation magnetisation of the powders phosphated for 60 s decreases with 17% as compared to the uncoated powder. The influence of the compaction pressure, as well as the phosphating duration, on initial relative permeability and power losses of the compacts was investigated. It was found that increasing the compaction pressure leads to the increase of the compact's permeability and a decrease of the hysteresis losses. A shorter phosphating duration leads to a partial coating with phosphate of the Fe-Si particles and to compacts with higher density characterised by high magnetic permeability.

1. Introduction

Soft magnetic materials play a major role in numerous electrical and electronic devices that are part of our everyday life. The market of soft magnetic materials is dominated by Fe-Si steels (laminated sheets), the largest part of electrical motors and transformers being actually realised by a stack of laminated electrical steels. Among electrical steels, soft magnetic ferrites ($MeFe_2O_4$) are also industrially produced and used as magnetic cores especially for AC (alternative current) applications.

Each class of soft magnetic materials above mentioned have a specific set of electric and magnetic characteristics and a specific field of applications as follows [1]: (i) electrical steels sheets are characterised by high flux density and relatively high permeability; they have the main drawback of having excessive core losses at higher frequencies (electrical steels applications are limited to a few hundred Hertz). (ii) soft magnetic ferrites ($MeFe_2O_4$) have low core losses in the high-frequency region (due to their high electrical resistivity), but their main drawback is the requirement of large cores due to their low magnetic flux density. As compared to the above-mentioned classes of soft magnetic materials, soft magnetic composites (SMC) is a relatively new and promising class of materials. SMC's cover the regions were electrical steels and soft ferrites cannot be used. Typically, an SMC consists of electrically insulated ferromagnetic particles that are compacted into 3D finished parts [1,2]. The SMC offer a series of advantages over electrical steels and ferrites such as: magnetic and thermal isotropy, relatively low total core losses at low and medium frequencies, very low eddy current losses, high electrical resistivity, reduction in size and weight, complex designs through the use of traditional powder metallurgy techniques etc. [2]. As a ferromagnetic material, pure Fe powder is the most used but different Fe-based, Ni-based or *Co*-based powder alloys (in the polycrystalline, nanocrystalline or amorphous state) are also intensively investigated [3–5]. Concerning the insulating layer (the dielectric), organic and inorganic coatings are utilised to insulate the ferromagnetic particles so that eddy current losses will be reduced. The organic coatings that are generally used are thermoset polymers, such as epoxy resins, polyester powder, acrylic powder etc. The inorganic coatings such as phosphates, sulphates or ceramics (such as ferrites or Al_2O_3), offer the advantage of allowing higher temperature heat treatments used to release the stresses induced by compaction process [6]. For example, classic sintering at 1100 °C for 2 h or spark plasma sintering at 1050 °C for 10 min under an axial pressure of 30 MPa was used to prepare high density soft magnetic composites. Fe-Si based powder was used as ferromagnetic phase and SiO_2 or Al_2O_3 as insulating phase. The composite cores prepared by these routes present good magnetic and electric properties [7–9].

A new approach was recently proposed that consists in coating the ferromagnetic powder with a ferrimagnetic material like Fe_3O_4, MnZn or NiZn ferrite, Ni ferrite and subsequently sintered by spark plasma

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sintering (SPS) [10–14]. Also, recent studies propose the use of a double insulating layer formed by an inorganic layer and an organic polyepoxy resin on the surface of ferromagnetic particles. Such an insulation layer minimises eddy currents and improves magnetic permeability of compacts [15].

The aim of this study is to present a sustainable route to produce SMC using Fe-Si powders prepared by milling of the out of use Fe-Si magnetic cores. The hybrid insulating layer, that covers the particles, was designed is such a way that, the two coatings (inorganic and organic) are complementary. The paper presents the following aspects: powder preparation, powder coating, characterisation of inorganic coating, SMC compacts preparation and AC magnetic characterisation of the compacts.

2. Experimental

The Fe-Si powder was prepared via dry mechanical milling using laminated electrical steel (the magnetic core of an old transformer) as raw material. The Si content of the used electrical steel is 1 wt%. Firstly, the insulating layer that covers the faces of the laminated sheets was removed by polishing. The resulted sheets were cut into small pieces having approximatively the size of 10 mm × 10 mm. A quantity of 100 g of electrical steel was subjected to high-energy milling process using a planetary ball mill (Fritsch Pulverisette 6). The vial rotation speed was set to 350 rpm and the duration of the milling experiment was 20 h. The milling bodies (balls and vial) were manufactured from tempered steel. The diameter of the milling balls was 14 mm, and the ball to powder ratio (BPR) was 8:1. This led to a filling factor of 60%. In order to avoid oxidation, the milling process was performed in high purity argon atmosphere. After milling, the powder was subjected to a heat treatment at the temperature of 350 °C for 2 h in vacuum (10^{-2} Torr) in order to release the stresses induced by milling.

Structural characterisation of the powders was made by X-ray diffraction (XRD) using an Inel Equinox 3000 diffractometer. The diffraction patterns were recorded in the angular range of 2θ = 30–110° and the cobalt radiation Kα (λ1 = 1.788965 Å + λ2 = 1.792850 Å) was used. The particles morphology and chemical homogeneity were investigated by scanning electron microscopy (SEM) and X-ray microanalysis, using a Jeol-JSM 5600 LV scanning electron microscope equipped with an EDX spectrometer (Oxford Instruments, Inca 200 soft).

The Fe-Si powders were subjected to a phosphating process using analytical reagents and deionized water as phosphating bath. The reagents were: manganese carbonate (99.9%), phosphoric acid (85.8 wt %, nitric acid (65.7%). Sodium hydroxide was used to adjust the pH of the bath. Phosphating of the powder samples was carried out by immersion in 300 ml of solution at 98 °C and pH = 1.5–2 in an open bath from 5 to 60 s and then they were rinsed with distilled water and dried in the oven at 80 °C for 15 min.

The chemistry of a phosphating process can be given by the following reaction:

$$3M + 6H^{+} + 2PO_4^{3-} \rightarrow 3M^{+2} + 2PO_4^{3-} + 3H_2.\ (M = Fe, Zn, Mn)$$

When an iron powder is immersed into a phosphating bath the following chemical reaction start:

$$5Fe + 4H_3PO_4 + 4H_2O \rightarrow Fe_5H_2(PO_4)_4{\cdot}4H_2O + 5H_2.$$

Before the phosphating process the powder was treated as follows: to carry out 10 min of ultrasonic cleaning, with the alkaline solution of pH = 9.5, and then 1–2 min pickling with the mixture of hydrochloric acid and nitric acid. The powders were immersed in the phosphating bath for 5, 15, 30 and 60 s in order to investigate the influence of the phosphating duration over the uniformity of the phosphate layer. The powder phosphated for 30 and 60 s were covered by a thin layer of polymer (Araldite AT 1). The polymer was dissolved in acetone in order to obtain a liquid solution. The magnetic powders were added into this solution and continuously mixed until complete evaporation of the acetone. In such a way, each individual particle is covered with a thin layer of polymer that represents 1% of the powders mass.

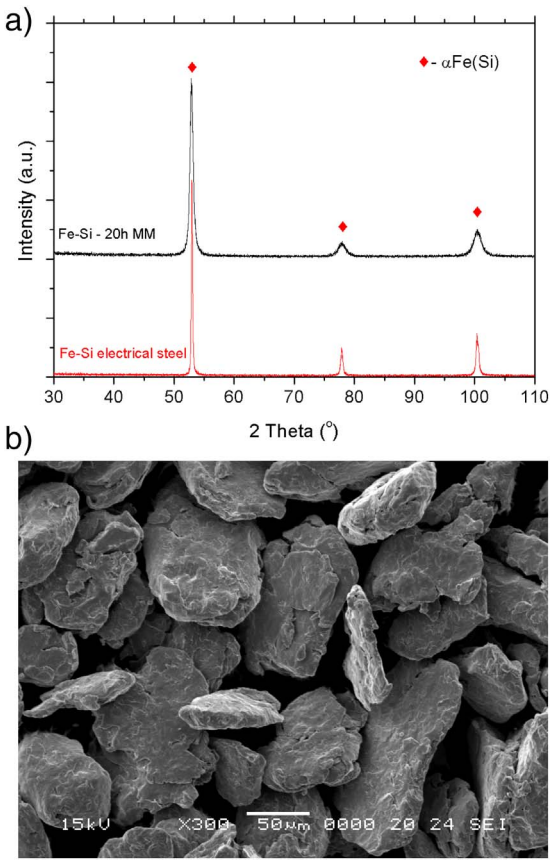

Fig. 1. XRD patterns of Fe-Si electrical steel and Fe-Si powders obtained after 20 h of MM (a) and SEM image of Fe-Si powders (b).

Fourier Transform Infrared (FTIR) Spectroscopy was performed for the phosphated samples using a Bruker Tensor 27 FTIR Spectrometer in ATR (Attenuated Total Reflection) mode. All spectra were normalised for the highest band in the 400–4000 cm^{-1} range. The thermal stability of the powders was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) on a Setaram Labsys apparatus using as reference high purity alumina powder. The measuring range was 20–900 °C, with a heating/cooling rate of 20 °C/min under high purity argon atmosphere. The DSC-TG equipment was coupled with a QMS 200 atmospheric sampling quadrupole spectrometer with an ionisation potential of 70 eV in the m/z = 10–90 range (m/z represents the ratio between the mass of the ion (m) to the number of elementary charges (e)).

The first magnetisation curves of the phosphated powders were recorded using a vibrating sample magnetometer (VSM) from Lake Shore Cryotronics Inc. The maximum applied field was 1400 kA/m.

The as-prepared powder was subjected to cold pressing at the pressure of 600, 700 and 800 MPa in order to obtain toroidal samples. The as obtained compacts were polymerised, according to the polymer specifications, through a heat treatment at the temperature of 180 °C for 1 h in air. The AC magnetic properties of the toroidal compacts (inner diameter of 12 mm, outer diameter of 18 mm and height of about 4 mm) were determined at a maximum flux density (B_{max}) of 0.1 T in the frequency range of 50 Hz–10 kHz, using a computer controlled Remagraph - Remacomp C - 705 hysteresisgraph produced by Magnet Physik Dr. Steingroever GmbH. The electrical resistivity of the samples was measured by 4-point probe method.