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Al_2O_3 "self-coated" iron powder composites via mechanical milling

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ABSTRACT

Electrically insulated ferrous powders permit isotropic magnetic flux, lower core losses, and structural freedom for state-of-the-art electromagnetic (EM) core and device designs. Many current coating materials are limited by low melting temperatures, which leads to insufficient insulation of powders, resulting in metal-on-metal contact. Use of a high-temperature coating material, such as alumina, could alleviate these issues. In this work, iron powder was mechanically milled with alumina media, to yield plastically deformed, alumina-coated iron particles with improved magnetic saturation, elastic modulus, and hardness. Various milling times and media ball sizes are investigated to maintain particle size, insulate powders uniformly, and optimize properties after compaction and curing. We found that longer milling times yielded more dense powder coatings and lower magnetic saturation.

1. Introduction

Soft magnetic composites (SMCs), used in various low power electromagnetic devices, incorporate magnetic, metallic particles (iron-, nickel-, or cobalt-alloys) coated with electrically insulating materials [1–5]. SMCs are advantageous over traditional steel laminates due to their lower core losses, 3D magnetic flux capabilities, and the structural freedom that allow for complex designs. These materials also possess good green strength and formability as well as high saturation magnetization and low coercivity.

The future of SMCs lies in higher frequency applications such as transformers, jet engines, and electric motors; however, the limiting factor for further advancements and implementation of these materials is the stability of the materials currently used as insulating coatings [6–8]. The conventional process of developing SMCs from coated powders requires high compaction pressures (> 800 MPa) to maximize density and heat treatment temperatures between 570 °C and 775 °C for proper iron stress relief [9,10]. Organic coatings such as epoxy resins or silicone polymers cannot withstand post-compaction heating above 450 °C before they begin to degrade, which results in low mechanical strength and metal-to-metal contact points that lead to large eddy currents and reduced magnetic permeability [11–14]. For this reason, inorganic coatings such as phosphates, MgO, Al_2O_3, Y_2O_3, and ZrO_2 are superior high temperature coating alternatives [15–18].

Inorganic, high temperature protective coatings are capable of electrically insulating iron powders even after compaction and heat treatment, to eliminate eddy currents and improve efficiency of devices. Phosphates and MgO are both limited by reduced resistivity after annealing temperatures below 600 °C [19–21]. Alumina (Al_2O_3), with its high melting point (2050 °C) is a strong candidate for high temperature coatings that confine eddy currents within individual iron particles after compaction and curing steps. The highly stoichiometric structure and large band gap of α-Al_2O_3 make electronic conduction extremely difficult, which is essential for reducing eddy currents in iron-based composites [22].

Several wet chemistry and dry coating techniques have been developed for coating iron-alloy powder surfaces with protective layers of alumina; however, uncontrollable phase transformations often led to degraded magnetic properties. For example, the formation of maghemite (Fe_2O_3) during the thermal decomposition of boehmite (γ-AlOOH), a precursor to alumina, led to decreased volumes of iron, which thus decreased the magnetic permeability [23,24]. Alumina-coated iron nanocomposites were also synthesized by wet chemistry; however, the magnetization suffered due to the formation of $FeAl_2O_4$ at reducing temperatures below 800 °C [13]. Both studies had extensive processing steps and led to

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undesired oxidation of the Fe core, which reduced magnetization. Dry coating methods, based on Van der Walls interactions between large (host) Fe powders and small (guest) Al_2O_3 particles, have also been developed. Jay et al. used a mechanofusion process to coat Fe powders ($d_{ave} = 150$ μm) with alumina particles ($d_{ave} = 9$ μm), then subsequently oxidize and heat treat the powders to study oxidation kinetics [25]. Due to cracks in the Al_2O_3 coating from the processing methods, iron oxide layers formed on Fe surfaces during the oxidation process, which would thus decrease magnetization due to reduced iron content. An additional form of dry coating, is mechanical milling (by high-energy ball milling), conventionally used for deformation and refinement purposes, but can also be used for an unique and simple coating method [26–28]. The mechanical forces introduced between the media material and iron powder during milling allow for powders to be internally stressed and externally coated while maintaining particle size improves mechanical strength [29]; but decreases the magnetic permeability by hindering domain wall motion [30]. Therefore, stress-relief temperatures are necessary to improve magnetic properties, but consequently hinder mechanical properties. These temperatures can be reached by using high temperature coatings such as alumina.

In this paper, we discuss the use of alumina media balls during mechanical milling to coat iron powder surfaces in the absence of additional powder. We show, through a combination of structural and chemical analyses along with magnetic and mechanical testing, that these "self-coated" powders possess uniform alumina coatings capable of minimizing eddy current losses, and have relatively strong magnetization and mechanical strength.

2. Experimental

High purity, Ancorsteel 1000C iron powders were provided by Hoeganaes Corp. (Cinnamonsin, NJ). Powders were sieved to produce large particle sizes of 250–400 μm. A high-energy SPEX 8000M shaker mill was used to ball mill iron powder in an alumina ceramic vial, with one of four alumina media ball sizes (0.5 mm, 1 mm, 2 mm, and 3 mm). Trials varied from 2 to 24 h with ball-to-powder weight ratios (BPRs) of 2:3. Powders were uniaxially compacted with 3 GPa pressure and cured for 1 h at 500 °C or 900 °C in an argon and hydrogen (3%) atmosphere. The experimental procedure is depicted in Fig. 1.

The phase identification and structural analysis of powder samples were characterized by x-ray diffraction (XRD) (Rigaku, Japan) with Cu-Kα radiation ($\lambda = 1.541$ Å). Williamson–Hall plots were used to analyze the crystallite size and microstrain of milled powders [31]. Magnetic properties were measured from Ref. ± 1.5 T at room temperatures using a Physical Property Measurement System (PPMS®) with a vibrating sample magnetometery (VSM) extension (Quantum Design, USA). The surface morphology and porosity of powder samples were observed by scanning electron microscopy (SEM) (FEI, USA) (Fig. 2) Additionally, powder compacts were traditionally polished and imaged via SEM coupled with energy-dispersive spectroscopy (EDS) for chemical analysis of powders and powder compacts. Mechanical properties were investigated by nanoindentation (MTS, USA) at 200 nm depth. Alumina-coated iron powders were analyzed for magnetic, mechanical, and structural property dependence of milling time and media ball sizes.

3. Results

3.1. Effect of milling time

Ball milled powders became coated directly from the alumina media and media balls; with no additional powder added. A "self-coated" surface was characterized by a textured morphology and sub-micron sized particles as seen in Fig. 3, for powder milled for 24 h. Powders milled for longer periods of time (> 12 h) exhibited an excessive amount of agglomerations of finer sized particles in outermost regions, which is an indication of coated surfaces.

X-ray diffraction patterns confirmed increased microstrain and alumina content on iron powders milled for 2–24 h (Fig. 4). Initial, unmilled iron powder displayed minimal peak broadening and no trace of alumina content as expected. As milling time increased, Fe peak broadening increased and peak intensity decreased as evident of reduced crystallite size and increased microstrain. Calculations using the Williamson–Hall technique confirmed the decrease in crystallite size and increase in microstrain. Al_2O_3 peaks began to emerge for powders milled for 4 h or longer.

Less deformed powders allowed for improved mechanical interlocking and higher densities (7.3–7.4 g/cm^3), compared to more deformed powders (~ 6.8 g/cm^3) using 3 mm balls or times greater than 16 h. Nanoindentation was performed on polished powder compacts to measure elastic modulus and hardness of iron after being milled, compacted, and cured. Fig. 5 illustrates as milling time increased to 16 h, the hardness of Fe increased slightly, indication of more stressed regions, and decreased at 24 h. Higher curing temperatures, nominally 900 °C compared to 500 °C led to decreased hardness. Elastic modulus remained relatively constant throughout the experiments.

Cross-sectional SEM images of powder compacts revealed a highly dense, alumina coating on iron powders. Powders milled for 24 h, compacted, then cured at 500 °C, are seen in Fig. 6, in which light gray regions represent Fe particles, while dark areas bordering iron particles portray Al_2O_3 coating as confirmed by XRD. The inset image of Fig. 6 represents the highlighted region depicting a Fe–Al_2O_3–Fe junction. Finer, sub-micron sized particles of alumina were found between iron powders with a layer thickness of roughly 10 μm.

Complimentary elemental mapping from a magnified region in Fig. 6 reveals aluminum and oxygen elements uniformly distributed on iron powder surfaces (Fig. 7a). The oxygen content found within the iron powder regions was most reasonably due to exposure to air after mounting and polishing. EDS images exhibit clear isolation of iron particles with oxygen and aluminum, which

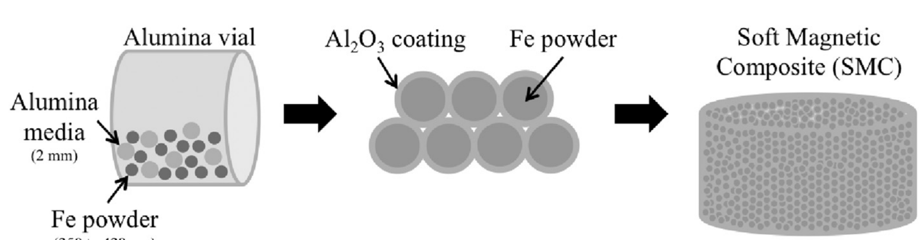

Fig. 1. Procedure for producing alumina coated iron powders via mechanical milling.