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Effect of milling time on dynamic permeability values of reduced carbonyl iron filled composites

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ABSTRACT

Flaky-shaped carbonyl iron fillers were fabricated using ball-milling and followed by annealing. Their morphology and particle size distribution, static and high-frequency magnetic properties were studied.

For flaky-shaped filler composites, the permeability significantly enhances, as compared with sphere-shaped filler composite. The maximum real and imaginary permeability, μ' and μ'', increase from 5 to 8 and from 2 to 5.3, respectively, while resonance is shifted to lower frequency, from 7 GHz to about 5 GHz. The increase in μ' and μ'' has its origin in the flaky shape of carbonyl iron fillers. The composites with ball-mill time of 48–96 h have the optimum high-frequency properties. Also, the effect of volume concentrations on static and dynamic magnetic properties is studied for sphere-shaped carbonyl iron filler composites.

1. Introduction

Typically, for practical use in microwave magnetic applications, i.e. microwave attenuation, electromagnetic interference (EMI) shielding, etc., composite materials consisting of the metal particles embedded into a nonmagnetic polymer matrix are preferable over the bulk materials due to their low weight, high corrosion resistance and their ability to be easily fabricated into various shapes. The design of such composite materials, especially highly filled ones, requires that one should achieve a particular balance between the processing ability and the properties of the obtained composites for a given range of applications. The primary purpose of the polymer matrix in magnetic composites is to bind the filler particles together, while the filler particles are responsible for the electromagnetic performance of the composites and, dependence on the volume fraction of the filler, chemical composition, particle shape and size may vary. The main technical requirements for good absorbing performance are as follows: matching of complex permeability $\mu* = \mu' - i\mu''$ (μ' is the real part of magnetic permeability, μ'' is the magnetic loss or imaginary part of magnetic permeability) and complex permittivity $\varepsilon* = \varepsilon' - i\varepsilon''$ (ε' is the real part of dielectric permittivity, ε'' is the dielectric loss or imaginary part of dielectric permittivity), broad bandwidth, small thickness, light weight and low cost [1–4]. The thickness of the composite materials is derived as

$$d_a = \frac{c}{2\pi f \mu''} \tag{1}$$

where c is the velocity of light and μ'' is the maximum of magnetic loss [5]. Thus, in order to fabricate thinner microwave absorbers, filler particles with higher values of magnetic losses are required.

Carbonyl iron powders are one of the most promising materials to be used in microwave magnetic applications due to their high initial magnetic permeability, high saturation magnetization and high Curie temperature. In recent years the attenuation properties of carbonyl iron composite materials had been intensively explored [6–14]. However, most investigations were performed on primary carbonyl iron powders regardless of their particles' microstructure. In our previous work, a significant difference in the permeability spectra of composites filled with primary and reduced carbonyl iron powders was revealed and mainly attributed to whether or not particles are characterized by onion microstructure [15]. Reduction of primary carbonyl iron powders (heat treatment in a steam of hydrogen) leads to the disruption of the amorphous layers of iron carbides and nitrides present in onion microstructure and formation of polycrystalline particle's microstructure. In its turn, polycrystalline microstructure results in the enhancement of domain wall motion and leads to significant increase in permeability values of composite materials filled with reduced carbonyl iron powders.

It should also be added that the size of the particles plays a significant role in the the microwave magnetic performance of magnetic composite materials. The eddy current losses in composites with sphere-shaped inclusions expressed as

$$\delta_{eddy} = 0.2\pi^2 \frac{d^2 \mu}{\rho p} \times 10^{-9} \tag{2}$$

where d is the particle diameter, μ is the permeability, ρ is the resistivity of the particles, and p is a loading factor, decrease the

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permeability values at high frequencies [16]. Consequently, particles with smaller sizes are preferable. Furthermore, it is well known that particle size should not exceed the skin depth much in a gigahertz range and it was shown that the skin depth of pure iron remains almost unchanged above 5 GHz and is about 1–2 μm [17].

Moreover, achieving higher values of μ^* through modification of the particle shape from spherical to flaky has become one of the most promising directions. In particular, particles with uniaxial anisotropy are governed by Snoek's limit which illustrates the relationship between the permeability at gigahertz range and resonant frequency:

$$f_r(\mu_r - 1) = \frac{2}{3}\gamma M_s \quad (3)$$

where f_r is the resonant frequency, μ_r is the relative initial permeability, γ=2.8 MHz/Oe is the gyromagnetic ratio, and M_s is the saturation magnetization [4,18]. Larger values of permeability can be obtained using flaky particles with planar anisotropy:

$$f_r(\mu_r - 1) = \frac{1}{2}\gamma M_s \left(\frac{H_\theta}{H_\varphi}\right)^{1/2} \quad (4)$$

where H_θ and H_φ are the c-axis anisotropy and basal plane anisotropy fields respectively [4,19,20]. One of the most commonly used methods for the fabrication of flaky particles is high energy ball-milling [20].

Since highly filled composites are of interest in microwave applications, the problem of high conductivity occurs with the Ohmic contacts contribute to the eddy current effect. The use of flaky particles leads to the higher values of permittivity which are undesirable in matching of complex permeability and permittivity. Therefore, a surface modification of the particles is required. In general, particle coating with a uniform insulating layer had been proved to be efficient in improving thermal, electrical and magnetic performance of the particles [21]. One of the most commonly used types of coating is SiO_2 coating [22,23].

Considering all the factors mentioned above, the present paper deals with the investigation of the structural and magnetic properties sphere-shaped and flaky-shaped reduced carbonyl iron powders with polycrystalline microstructure and the smallest available particle size and the composite materials on the base of them. A detailed analysis of the changes in the morphology, structure and magnetic spectra of the flaky-shaped composites materials has been carried out at different stages of ball-milling process.

2. Experimental

2.1. Preparation

As a starting material, reduced sphere-shaped carbonyl iron powder SU (BASF, Germany) with polycrystalline microstructure (Fig. 1), containing iron (> 99.4%) along with carbon (< 0.1%), oxygen (< 0.5%) and nitrogen (< 0.01%) was used. The matrix material was a commercially available silicone elastomer (SYLGARD 184, Dow Corning, USA) consisting of polydimethylsiloxane and platinum-containing catalytic agent (mixing ratio 10:1) with durometer hardness – 50 Shore, tensile strength – 7.1 MPa, and elongation at break – 140%.

Spherical carbonyl iron particles were flattened in a PM 400 Retsch planetary ball mill with a ball to powder ratio 10:1 at rotation speed of 100 rpm. Ball milling was performed for 8, 12, 16, 36, 48, 72, 96, and 120 h in ethanol to avoid agglomeration. As-milled flakes were named SU-8, SU-12, SU-16, SU-36, SU-48, SU-72, SU-96 and SU-120 respectively. As-milled powders were then annealed using a vacuum furnace (Elite Thermal Systems; vacuum pump, Oerlikon Leybold, PT151). Annealing was performed at 400 °C. Iron powders were heated at these temperatures for 2 h and then cooled to room temperature in a vacuum furnace.

Excellent soft mechanical properties of the reduced SU powder make it possible to compact it by dry pressing under a pressure of 1.5 kPa into cylindrical and toroidal samples with an outer diameter of 6.8 mm, inner diameter of 3.02 mm and thickness of 1.5 mm for the measurement of static and dynamic magnetic properties.

Sphere-shaped SU composite materials of 10, 20, 30, 40, 50 and 55 vol% loadings and SU-8 to SU-120 composites with 40 vol% were prepared by a moulding method. The composite mixture was placed and moulded in a coaxial die with the outer diameter of 7 mm, inner diameter of 3.04 mm, and thickness of 1 mm at 65 °C for 4 h. The volume concentration of the filler was calculated using the density of carbonyl iron powder (~7.8 g/cm^3) and silicone matrix (~1.05 g/cm^3) respectively.

2.2. Characterization

The crystalline structures of the starting and as-milled powders were characterized by X-Ray Diffraction (XRD) analysis performed on Ultima IV, X-Ray diffractometer (Rigaku, Japan) employing Cu $K\alpha$ radiation (λ=1.54184 Å) with an angle 2θ ranging between 30° and 140° degrees with a scan rate of 0.5. All of the original and ball-milled samples are single phase with BCC structure, as shown in Fig. 2, and no second phases were found. The grain sizes are about 30 nm, which are obtained from Scherrer's formula [24].

The morphology of the starting and as-milled powders was examined by scanning electron microscopy (SEM) using JEOL JSM-6340F field emission scanning electron microscope. Particle size distribution and mean sizes of the particles were studied by Laser Scattering Particle Size Distribution Analyzer LA-950 HORIBA. A spherical particle can be described using a diameter, while flaky particles are described using multiple length and width measures.

Magnetization curves and hysteresis loops were measured using the vibrating sample magnetometer (VSM, EV9, ADE Magnetics, USA) at room temperature with an applied magnetic field up to 20 kOe.

The relative complex permeability $\mu^*=\mu'-j\mu''$ and permittivity $\varepsilon^*=\varepsilon'-j\varepsilon''$ values of the specimens were measured by two different methods, i.e. impedance and 7 mm coaxial line methods. An impedance method was employed in the frequency range of 1 MHz to 3 GHz by using an RF Impedance/Material Analyzer (Agilent 4991A). Coaxial line measurements were carried out using an APC-7 coaxial transmission line fixture and Agilent N5230A vector network analyzer. Toroidal samples with inner diameter of 3.04 mm and outer diameter of 7 mm were inserted into a coaxial line and the scattering parameters (reflection coefficient S_{11}, transmission coefficient S_{21}) were measured in the frequency range from 50 MHz to 18 GHz by a Vector Network Analyzer (VNA). The complex permeability and permittivity were calculated from the scattering parameters.

3. Results and discussion

3.1. Magnetic spectra of the sphere-shaped SU and its composite materials

The dispersion curves of the complex permeability for sphere-shaped SU pressed sample measured by two different techniques, viz. impedance and 7 mm coaxial line methods are shown in Fig. 3. It can be seen that a good agreement between two independent