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Microwave absorption properties of FeSi flaky particles prepared via a ball-milling process

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ABSTRACT

Flaky FeSi alloy particles with different aspect ratio were produced via ball-milling and a subsequent annealing. The microstructure and the morphology of the particles were examined by XRD and SEM. The dc resistivity, the static magnetization properties and electromagnetic properties were measured. Particles with high aspect ratio were found possess high permittivity and permeability. On the other hand, the variation of grain size and defects density was found influence the permittivity and permeability. High specific area was believed contribute to the intense dielectric loss and the high shape magnetic anisotropy lead to high permeability in the target band. Increased electromagnetic parameters compel the absorption peak's shift to lower frequency. Coating using flaky FeSi particles milled for 12 h as fillers presented a reflection loss of −10 dB at 2 GHz and a matching thickness of 1.88 mm. The flaky FeSi alloy particles prepared through ball-milling and annealing can be promising candidates for EMA application at 1–4 GHz band.

1. Introduction

With the fast development of wireless communication, the problem of electromagnetic interference (EI) and electromagnetic pollution (EP) has become more and more serious, especially in the 1–4 GHz band at which most communication systems work [1]. To absorb the harmful electromagnetic wave is an effective way to eliminate EI and EP problems, which basically rely on the application of electromagnetic wave absorbing (EMA) materials. Ferromagnetic metal/alloy powder of micro scale is the most promising candidate for EMA applications in the 1–4 GHz band since this series of materials possesses a unique potency of presenting a combination of high permeability and high permittivity [2]. To exert the potency of this series of materials is then a basic step to design high-performance EMA materials.

High and commensurate electromagnetic (EM) properties (the complex permeability and the complex permittivity) ensure small matching thickness and good impedance matching [3,4], which is crucial for obtaining high EMA performance in 1–4 GHz band. A lot of researches have then been carried out to obtain high EM properties. Among these efforts, particles with flaky shape and thin thickness have attracted intense attention, since they provide a possibility to obtain high permeability in 1–4 GHz band. The Snoek's limit demonstrates [5,6] that it is essentially difficult to increases the permeability and the resonance frequency (fr) simultaneously, revealing the obstacle to achieve high permeability in GHz band. This limit, however, could be exceeded by introducing easy-plane anisotropy via using flaky particles [7–10]. Additionally, thin thickness is believed helpful to suppress the negative effects from the eddy current in metal or alloys particles [11,12]. The eddy current induces reversed magnetization in particles and also reduces the effective volume due to the skin effect, which then leads to deteriorated permeability.

Han et al. [13] flattened spherical iron particles into fine flakes and observed that particles with aspect ratio (AR) of 5 presented much higher permeability than that of spherical ones. A minimum reflection loss (RL) of −26 dB was observed at 3.5 GHz in a thin (2.0 mm) coating using flaky iron particles as fillers. Yang [14] prepared flaky Fe16Ni82Mo2 particles through a similar method and wherefrom achieved increased permeability and permittivity. The corresponding coating with a thickness of 2 mm presented a RL of −20.4 dB at 13.0 GHz. Liu et al. [15] prepared spherical FeSi alloy powders of various size by gas-atomization method and found that both the permeability and the permittivity increased as the particle size decreased. Among these studies, ball-milling was

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found an efficient method to prepare flaky metal/alloy particles and improved EMA performances were wherefrom obtained.

Most attention has been focused on the influence related to particles' shape/size in the previous research, the evolution in microstructure characteristics including the grain size, the defects density and so on, however has not been investigated systematically. In this paper, flaky FeSi alloy particles were produced by ball-milling commercial FeSi alloy powders in large quantity to examine the feasibility. Post-milling annealing was thereafter performed to tailor the microstructure of the powder. The morphology and microstructure of the particles were examined and their influence on EM properties and the EMA performance were investigated.

2. Experimental details

Commercially available gas-atomized FeSi alloy powder with mesh -400 was used as the raw material of the current study. Composition analysis indicated that the starting powder contain 6.31 wt% of Si, 0.07 wt% of Cr and allowance of Fe. The raw powder, certain content anhydrous ethanol and GCr15 steel balls were added into jars of 250 ml and then the ball-milling process was conducted in a planetary ball-mill at a rotation rate of 500 rpm for up to 20 h. Through the study, the ball–powder–ethanol ratio was set at 5:1:1. After the ball-milling completed, the product was collected, washed for three times with anhydrous ethanol and then dried for 8 h at 50 ºC in an oven. The product milled for 20 h was labeled ON500r20h for short and samples of other conditions were labeled in the same way. Some as-milled powder (ON500r20h) was transferred into annealing process. The power was heated in a furnace in hydrogen atmosphere at 800 ºC, hold for 2 h and then let cooled to room temperature naturally. The annealed powder was labeled as H500r20h.

Phase structure of the particles, raw, milled and mill-annealed, was examined on a PANalytical X'Pert PRO diffractometer (XRD) using Cu Kα radiation. The grain size of the particles was calculated according to Scherer formula

$$D = K\lambda/B\cos\theta \quad (1)$$

where D is the average grain size, λ is the wave length of the incident X ray (1.5418 Å in the current research) and B is the width of the diffraction peak at half maximum for the diffraction angle 2θ, θ is the diffraction angle. Particles' morphology was observed with a scanning electron microscope (SEM, Philips FEI Siron). Specimens for electric resistivity measurement were fabricated by pressing FeSi powder into a mold with a pressure of 750 MPa and holding for 90 s. Fabricated specimens were 10 mm in diameter and around 2 mm in thickness. Electric resistivity was measured by a four-probe technique at room temperature on a source meter (Keithley 2400). For each condition, 3 specimens were used to measure the electric resistivity and the mean values were used in the study. Magnetic properties were measured with a Lake Shore 7404 vibrating sample magnetometer (VSM) at room temperature. Electromagnetic properties of specimens containing 75 wt% of FeSi particles as filler and 25 wt% of paraffin as matrix were measured on a vector network analyzer (VNA, Agilent N5230A) at 2–18 GHz band. The VNA specimens were coaxial toroidal with outer diameter 7 mm, inner diameter of 3 mm and thickness of 3–3.5 mm. Microwave absorption performance can be evaluated by the transmission line theory [4,16], and the related formulas are as follows:

$$Z_{in} = Z_0\left(\mu_r/\varepsilon_r\right)^{1/2} \tanh\left[j(2\pi fd/c)(\mu_r\varepsilon_r)^{1/2}\right] \quad (2)$$

$$\mathrm{RL} = 20 \log\left|(Z_{in} - Z_0)/(Z_{in} + Z_0)\right| \quad (3)$$

where μ_r and ε_r are the effective permeability and permittivity of composite specimen, respectively, f is the frequency of electromagnetic wave, d is the thickness of absorber layer, c is the velocity of light, Z_0 is the impedance of free space, and Z_{in} is the input impedance of absorber layer.

3. Results and discussion

3.1. Phase structure and morphology

Fig. 1 shows the x-ray diffraction patterns of FeSi alloy particles ball-milled for different time and milled-annealed. Three diffraction peaks are indexed to the (110), (200) and (211) planes of cubic α-Fe (Si) solid-solution, as is shown in the figure. No other diffraction peak can be identified, which indicates that neither phase transformation nor chemical reaction occurs during the ball-milling. Diffraction peaks become wider but the intensity decreases as the ball-milling time increases, as shown in the spectra, suggesting that the milling induces refined grains (more details about grain size is displayed in Table 1) and increased defects density. Similar phenomenon was previously observed in Refs. [17,18]. As shown in Table 1, the mean grain size decreases sharply from 39.4 nm to 17.3 nm in the first 10 h and remains at the level as the ball-milling further proceeds. Since the diffraction peak width increases persistently all through the ball-milling process despite the suspended grain refining, the broadening of diffraction peaks at the latter stage is believed attributed to the increase in defects density. On the other hand, diffraction peaks are found shift to higher angles as the ball-milling time increases, which suggests a decrease in the lattice size. The variation is believed results from the increase in the Si atoms' dissolving into the Fe matrix. Since the radius of Si atom (0.118 nm) is smaller than that of Fe atom (0.124 nm), it's replace of Fe induces a shrinkage distortion. This shrinkage enhances when increased replace occurs as the ball-milling progresses.

Diffraction peaks of H500r20h are narrower and higher, comparing to those observed in XRD pattern of ON500r20h. Also, a peaks' shift back to lower angle is observed, as shown in the figure. This reversion in the XRD pattern reveals that the annealing can help to reduce the defect density, release the lattice distortion and then perfect the crystal structure of particles.

The morphology of FeSi alloy particles of different condition is presented in Fig. 2. Raw particles are spherical with diameter ranging from 5 to 30 μm. Once milled, particles are flattened into flakes with increased diameter and decreased thickness. When the ball-milling time approaches to 10–12 h, flaky particles with the highest aspect ratio are fabricated. Max diameter of around 70 μm and the mean thickness around 1 μm is obtained, as seen in Fig. 2 (c). The thin thickness is helpful to suppress the eddy current effects since it is near or even below the skin depth (about 1 μm reported by Ref [19]).When the ball-milling further proceeds, flaky particles are struck and sheared to fine pieces with reduced diameters of 4–20 μm and thickness of a few microns. Fig. 2(e) shows that, some small pieces attach to each other and the surface of particles is quite rough. Through the process, the aspect ratio is found increases firstly and then decreases with the highest aspect ratio achieved through 12 h milling. Particles' shape and size changes little during the annealing, according to the comparison between the morphology in Fig. 2(e) and (f).

3.2. Electrical resistivity

The dc electrical resistivity of FeSi alloy particles are listed in