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Microwave properties of surface modified Fe–Co–Zr alloy flakes with mechanochemically synthesized polystyrene

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ABSTRACT

Polystyrene coated Fe–Co–Zr alloy flakes have been prepared from gas atomized powders and styrene monomer by high energy ball milling. The effective complex permittivity and complex permeability of flakes/paraffin composites within 3.95–12 GHz were measured to assess the application potential of these products used as microwave absorbers. It is found that both the real and imaginary parts of complex permittivity substantially decrease with the increasing amount of reactant styrene. For the complex permeability, the real part of polystyrene coated samples is larger than those of the as-milled sample in high frequencies, however, the imaginary part exhibits a decline while resonance frequency shifts to high values. The calculated reflection loss curve suggests that a proper thickness of coating can redound to improve the absorbing performance of polystyrene coated Fe–Co–Zr alloy flakes in high frequency range.

1. Introduction

To achieve low reflection for electromagnetic wave absorbing materials, excellent attenuation and impedance matching characteristics should be simultaneously required at a given frequency and thickness. In the design of absorbing materials based on magnetic materials, high value of complex permeability ($\mu_r = \mu' - j\mu''$) and complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) can yield large magnetic loss and dielectric loss to attenuate electromagnetic wave, and a proper ratio between them can realize electromagnetic wave entering into absorbing materials by the greatest extent [1–3]. Soft magnetic metallic thin flakes are promising for the application of GHz absorbing materials because of their desirable complex permeability and complex permittivity, which originates from their large saturation magnetization and particle shape. For these materials, a common method is to use small particles dispersed in insulating materials such as resin or rubber, yet there exist problems in their practical use. For example, the electric conductivity of metallic flakes is generally high, which leads to the decrease of the high-frequency permeability due to the eddy current loss. Moreover, the complex permittivity is overlarge comparing with the magnetic permeability, which induces impedance mismatching [4–9]. Therefore, it is necessary to suitably reduce the permittivity of metallic flakes. It has been reported that vinyl monomers such as methyl methacrylate (MMA) and styrene could polymerize mechanochemically by the resulting activity from the grinding of inorganic solids [10,11]. With the purpose of simultaneously flattening metallic powders and modifying their surfaces, we put forward a method of mechanical milling to fabricate polystyrene coated metallic flakes on the basis of mechanochemical polymerization of styrene.

In the present work, we characterize the structures and electromagnetic parameters of polystyrene coated Fe–Co–Zr alloy flakes, respectively, which obtained from gas atomized Fe–Co–Zr powder and various amount of styrene monomer. The effects of the surface modification of alloy flakes on the microwave properties are investigated in detail.

2. Experimental

2.1. Sample preparation

As a typical metallic magnetic material, the Fe–Co–Zr alloy powder with composition of x mass% Co – 5 mass% Zr – (95-x) mass% Fe (x is an intervenient value between 5 and 30, particle size $\leq$100 μm) was produced by gas atomization using argon. All the starting chemical materials are of analytical pure grade and are purchased from commercial sources. Silane coupling agent ($CH_2{=}CHSi(OCH_3)_3$) was employed to introduce the reactive functional groups on the surface of the alloy powder. The styrene monomer was distilled under reduced pressure with nitrogen to remove the inhibitor before polymerization. The azobisisobutyronitrile (AIBN) was used as an initiator, and absolutely ethanol was chosen as the solvent.

The Fe–Co–Zr alloy powders and ethanol were loaded together with multiple diameter steel balls in a steel container. The weight ratio of powder and ball charge was 1:20. Meanwhile, for the coating procedure, three different amounts of styrene monomer (the mass fraction of styrene to powder is 9%, 18% and 27%, respectively), proper amount of AIBN and silane coupling agent were added into the container. The mechanical milling was performed using a QM-1SP4 planetary mill for 5 h at

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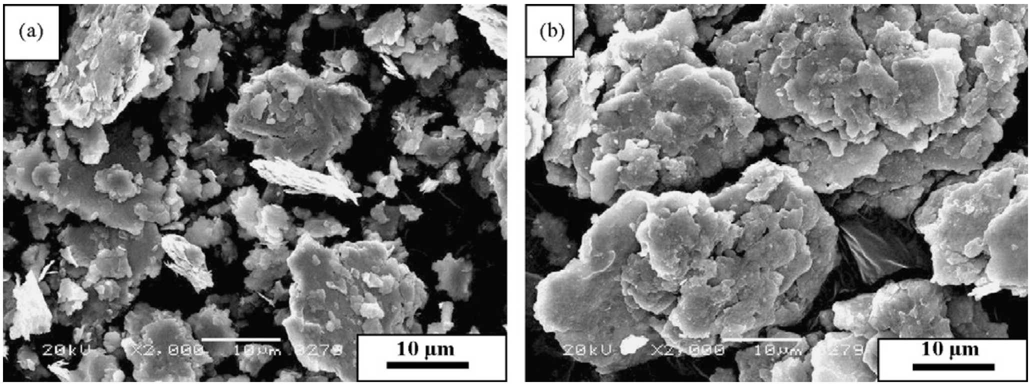

Fig. 1. SEM micrographs of the samples: (a) S0, and (b) S3.

450 rpm. The acquired powders were rinsed with ethanol and dried in a vacuum oven at 80 °C to remove free organic component. The as-milled powders and those coated with various amounts of reactant styrene were named sample S0, S1, S2 and S3, respectively, as shown in Table 1. It is aimed at improving the thickness of surface coating on Fe–Co–Zr alloy flakes by increasing the mass fraction of styrene to powder.

2.2. *Characterization*

The morphology of the as-milled and polystyrene coated Fe–Co–Zr alloy powders was observed by a JSM-5610LV scanning electron microscopy (SEM). X-ray diffraction (XRD) (Philips X' Pert PRO; Cu Kα, λ = 0.1542 nm) was used to characterize the phases in the as-milled powders. Infrared transmission spectrum for the polystyrene coated specimen was characterized by a VERTEX 70 Fourier transform infrared spectroscopy (FTIR). Thermal property of polystyrene coated powders was studied by thermo gravimetric apparatus (TG) and differential scanning calorimetry (DSC) in an argon atmosphere.

The prepared powders were homogenously dispersed in paraffin with a mass fraction of 80% (powder) and then formed into a cylindrical sample (7 mm in outer diameter and 3 mm in inner diameter) with a coaxial mould, respectively. The effective complex permittivity and permeability of these composites in the frequency range from 3.95 to 12 GHz (in C, XC and X-band) were measured using an Agilent 8722ES network analyzer.

3. Results and discussion

Fig. 1 shows the SEM micrographs of sample S0 and S3. The as-milled powders (Fig. 1a) exhibit a typical microstructure of mechanically milled materials, that is, thin flake shape and a relatively broad distribution of particle size (the thickness is about 1 μm and the length is smaller than 30 μm). To distinctly show the microstructure changes by the addition of styrene, we select sample S3 to investigate. It can be seen from Fig. 1b that some of the flakes are agglomerated each other, probably due to the conglutination of the formed polystyrene.

Fig. 2 shows the XRD pattern of the as-milled Fe–Co–Zr flakes (S0). The prominent diffraction peaks correspond to the (1 1 0), (2 0 0) and (2 1 1) planes of α-Fe. Their intensity maintains at a relatively high level although mechanical milling leading to a reduction of grain size and an increase of internal strain in the alloy powders [7]. It suggests that the prepared Fe–Co–Zr alloy flakes almost have crystalline characteristics with the present milling process. Similar diffraction peaks were also observed in the sample S1, S2 and S3, respectively.

Fig. 3 shows the FTIR spectra of the samples coated with 9 mass% (S1) and 27 mass% (S3) of initial reactant styrene monomer, respectively. It is found that polystyrene in the two samples is characterized by the C–H aromatic stretching vibration at 3024 and 2923 cm^{-1}, the phenyl ring stretching vibration at 1491 and 1450 cm^{-1}, and the ring out-of-plane bend at 698 cm^{-1} [12]. This indicates that polystyrene should be bonded to the Fe–Co–Zr particle surface since the free organic component has been removed. Furthermore, we find the intensity of the absorption bands is obviously enhanced with the increase of reactant styrene.

Fig. 4 shows the TG-DSC curves of polystyrene coated Fe–Co–Zr flakes with 18 mass% of reactant styrene (S2). It can be seen clearly that a broad exothermic peak in the temperature range from 100 to 650 °C, except for a large endothermic peak within 360–444 °C, came from the grain growth of Fe–Co–Zr alloy crystal and the pre-

Table 1
The RL peak intensity and corresponding frequencies of the composites.

Sample	S0	S1	S2	S3
Styrene/powder (mass%)	0	9	18	27
RL peak intensity (dB)	−4.15	−8.5	−11.88	−11.82
RL peak frequency (GHz)	4.0	4.4	6.24	7.04

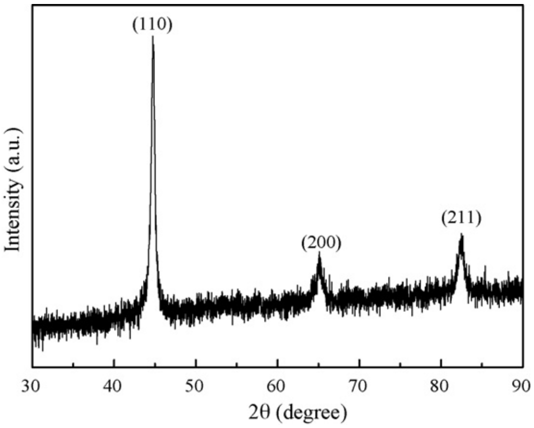

Fig. 2. XRD pattern of the as-milled Fe–Co–Zr flakes (S0).

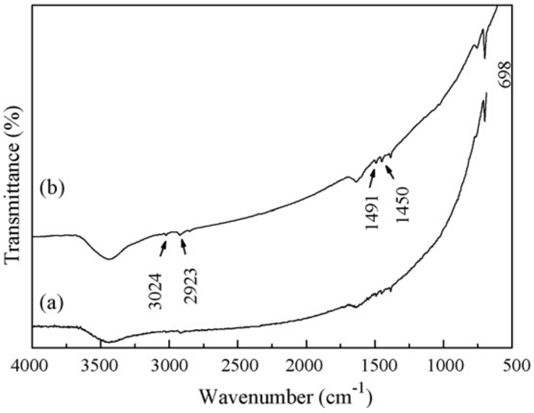

Fig. 3. FTIR spectra of the samples: (a) S1, and (b) S3.

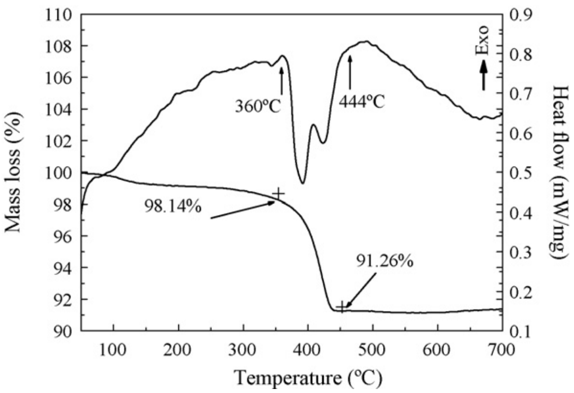

Fig. 4. TG–DSC curves of polystyrene coated Fe–Co–Zr flakes (sample S2).

cipitation of Fe from alloy [13]. In addition, the endothermic peak is due to thermal decomposition of polystyrene. The corresponding TG curve could be roughly divided into three stages. The first stage was from room temperature to 360 °C, a mass loss of about 1.86% was observed, which could be attributed to the evaporation of the adsorbed water and other chemicals. The second stage was from 360 to 444 °C, where the large mass loss was observed and was about 6.88%. This was assigned to the thermal decomposition of polystyrene in the Fe–Co–Zr flakes. Above 444 °C, there was almost no change in mass due to the complete decomposition of organic components.

These results confirm that polystyrene coating has been performed successfully on the Fe–Co–Zr flakes, and the thickness of polystyrene layer increases with the increase of reactant styrene, although we can not provide the quantitative thickness of polystyrene layer for each sample from the structure analysis results.

Fig. 5 shows the complex permittivity and complex permeability spectra of polystyrene coated Fe–Co–Zr flakes/paraffin composites. As shown in Fig. 5(a) and (b), for the as-milled Fe–Co–Zr flakes (S0), both the real part (ε') and imaginary part (ε'') of complex permittivity have relatively high values due to the large space-charge polarization between flakes with large surface area [3]. For polystyrene coated samples, both the ε' and ε'' substantially decrease and are inclined to be independent of frequency with the increase amount of reactant styrene for surface coating. These can be mainly ascribed to the decrease of electric conductivity of Fe–Co–Zr alloy flakes by the increase of polystyrene layer thickness. For a conductor-loaded composite, the real part (ε') and imaginary part (ε'') of complex permittivity can be expressed by the following equations [14]:

$$\varepsilon' = \frac{\varepsilon_m}{1+(\varepsilon_m-1)^{U_\varepsilon}}\left\{\left[\left(\frac{\sigma_f}{\omega\varepsilon_0}\right)^{V_f}(\varepsilon_m-1)^{1-V_f}\cos\left(\frac{\pi V_f}{2}\right)\right]^{U_\varepsilon}+1\right\} \tag{1}$$

$$\varepsilon'' = \frac{\sigma_{ac}}{\omega\varepsilon_0} \tag{2}$$

$$\sigma_{ac} = \left(\sigma_f-\sigma_m\right)\left\{\left[\frac{2\pi f\varepsilon_0(\varepsilon_m-1)}{\sigma_f}\right]^{1-V_f}\sin\left(\frac{\pi V_f}{2}\right)\right\}^{U_\varepsilon}+\sigma_m \tag{3}$$

$$U_\varepsilon = \frac{1}{2}\left[\frac{\coth(e)}{e}-\frac{1}{e^2}\right] \tag{4}$$

where ε_m is the dielectric constant of matrix (paraffin), ε_0 is the dielectric constant of free space, ω is the angular frequency, V_f is the volume fraction of the particles, U_ε is an order function that implicitly determines the dependence of ε on the geometric aspect ratio, σ_f and σ_m are the electric conductivities of the particles and matrix, respectively, and e(=$t/D-1$) is the eccentricity of the oblate

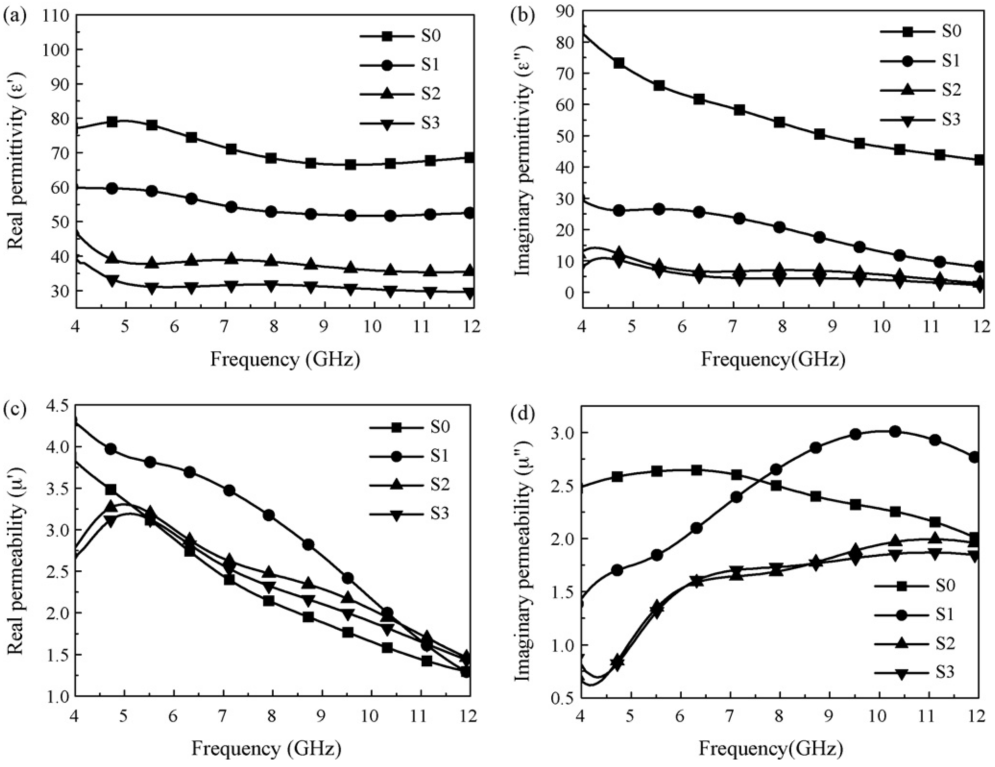

Fig. 5. Complex permittivity and permeability versus frequency of the composites.

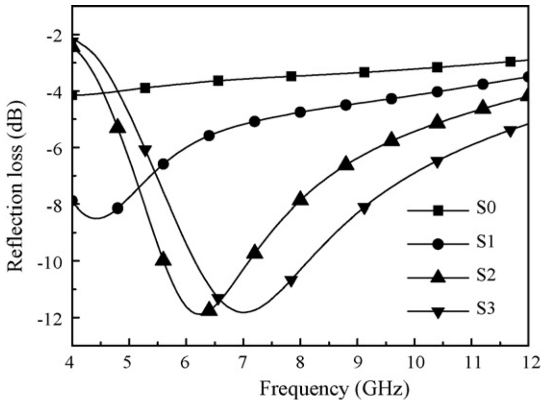

Fig. 6. Calculated reflection loss of the composites.

spheroidal particle. For alloy flakes, t and D are the thickness and the in-plane diameter, respectively.

Accordingly, it can be inferred that a low σ_f and high frequency are desirable for low values of ε' and ε'' when ignoring the effects of V_f and U_ε, since there should be little changes of the volume fraction, particle shape and size of the Fe–Co–Zr alloy flakes among the present composites.

As shown in Fig. 5(c), the real part (μ') of as-milled Fe–Co–Zr flake/paraffin composite shows a sharp decrease with an increase in frequency because of eddy current effect and ferromagnetic resonance [5]. The μ' of polystyrene coated samples are larger than that of as-milled one at high frequencies. This may be attributed to the increase of skin depth in virtue of the decrease of electric conductivity. For the imaginary part (μ'') of complex permeability in Fig. 5(d), all the samples exhibit a peak in a broad frequency range. It can be found that the μ'' decreases with the increase of reactant styrene while the resonance frequency shifts to a higher value. This decrease can be ascribed to the reduced magnetic content per unit volume against the increase of polystyrene layer. The shift of resonance frequency to higher value is probably due to the decrease of the demagnetization as a result of the eddy current loss decreasing with the decrease of electric conductivity [15].

Reflection loss (RL/dB) of a single microwave absorbing layer terminated by a perfect conductor can be calculated from the measured complex permittivity and complex permeability by the following equations [4]:

$$\mathrm{RL} = 20\ lg\left|(Z_{in} - Z_0)/(Z_{in} + Z_0)\right| \tag{5}$$

$$Z_{in} = Z_0(\mu_r/\varepsilon_r)^{1/2}\ \tanh\left[j(2\pi fd/c)(\mu_r\varepsilon_r)^{1/2}\right] \tag{6}$$

where Z_0 and Z_{in} is the impedance of free space and absorber, f the frequency of the electromagnetic wave, d the thickness of an absorber, and c the velocity of light. The impedance matching condition is determined by the combinations of ε', ε'', μ' and μ'' at a given thickness and frequency, and $Z = Z_0$ represents perfect absorbing properties.

The calculated reflection loss for the four composites at the thickness of $d = 1$ mm are shown in Fig. 6 and Table 1. It is evident that the RL peak shifts to high frequency with the increasing mass fraction of reactant styrene, meanwhile, the intensity of RL peak obtains obvious enhancement. These can be attributed to the improved impedance matching as a result of proper combination between modified complex permittivity and permeability by polystyrene coating. Additionally, the shift of RL peak to higher frequency is due to the decrease of the μ'' according to the relation $\mu'' f_m = 2\pi c d_m$ at a given thickness, where d_m and f_m are the absorber thickness and matching frequency [16]. However, the RL peak intensity of sample S3 is smaller than that of sample S2, probably because excessively thick coat results in too low dielectric and magnetic loss. It leads us to suggest that a proper thickness of coating can improve their absorbing performances at high frequencies.

4. Conclusion

The polystyrene coated Fe–Co–Zr flakes were successfully prepared by the method of mechanical milling. The dependence of the microwave properties of Fe–Co–Zr flakes on the polystyrene coating is discussed. Both the ε' and ε'' of the composites markedly decrease with the increasing amount of reactant styrene. Contrary to the μ'', the μ' of polystyrene coated sample shows larger values in comparison with the as-milled one at high frequency. The reflection loss peak shifts to high frequency with the increasing amount of reactant styrene and the peak intensity gradually enhanced except for the sample S3, as a result of too low dielectric and magnetic loss caused by polystyrene coating. Thus, it can be concluded that a proper thickness of insulating coating on metallic flake absorbers can improve their absorbing performances in high frequency range.

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