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Magnetic and electromagnetic properties of Fe_3O_4/Fe composites prepared by a simple one-step ball-milling

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ABSTRACT

In this study, an extremely simple one-step ball milling has been applied to fabricate the flaky Fe_3O_4/Fe composites. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), and vector network analysis (VNA). It is acknowledged that the ball-milling process has huge influence on the morphology and electromagnetic absorption capability. Compared with the raw Fe_3O_4, the saturation magnetization of Fe_3O_4/Fe composites improved greatly. When the thickness is just 1.25 mm, the reflection loss values below −10 dB can be achieved from 13.8 to 18 GHz, with a maximum reflection loss of −25.9 at 16.1 GHz. Obviously, the Fe_3O_4/Fe composites can be used as magnetic microwave absorbers due to its simple synthesis for the mass production standards. Moreover, this study also gives new enlightenment to design other magnetism/magnetism composites that can be applied to Ku-band such as satellite communications.

1. Introduction

Nowadays, the rapid development of wireless technique has created serious electromagnetic wave interference pollution, which harms the health of human beings and disorders the manipulation of electronic equipment [1–3]. Thus, the requirement for electromagnetic absorbers is imperative over the past years. The desired microwave absorbents not only need to have strong reflection loss and broad absorbing frequency, but also demand a thin coating thickness [4,5]. It is well known that the magnetic materials have great potential to be outstanding microwave absorbers due to its magnetic and dielectric loss [6–11].

As a vital kind of functional materials, magnetite (Fe_3O_4) has been wildly studied as microwave absorber with easy acquisition and low cost. However, it also sustains some disadvantages such as low dielectric loss that could result in poor and narrow absorption and heavy density, which restrict its further applications [12,13]. For carbonyl iron powders, it has many strengths including high saturation magnetization (*Ms*), high Curie temperature and magnetic loss ability. Nevertheless, the strong eddy current and effect of skin depth confine its development as microwave absorber [14,15]. Therefore, combining magnetite with strong magnetic materials such as carbonyl iron may be a good strategy, because it can not only improve integral dielectric loss ability, but also enhance impedance the matching behavior. For instance, Ding et al. prepared nanocomposites of graphene oxide with embedded Fe_3O_4/Fe nanorings through chemical hydrothermal process which showed a minimum reflection value of −23.09 dB at 9.16 GHz [16]. The oriented flake carbonyl/epoxy resin composite with enhanced microwave absorption properties and broad absorption bandwidth had been prepared by a magnetic field [17]. Heterostructured nanorings of Fe_3O_4/Fe@C composites were synthesized by a controllable two-step process which exhibit an absorption of 6.7 GHz and a minimum RL value of −28.18 dB at 4.94 GHz [18]. In addition, Our group also reported Fe@MFe_2O_4 (M = Zn, Fe, Co, Ni) flaky core-shell structure through a two-step process including the ball-milling and hydrothermal method, which shows decent microwave absorption properties and broad absorption bandwidth [19]. Meanwhile, the inferior reflection loss at small coating thickness (d < 1.5 mm) and the complicated synthetic process may limit its practical application. Hence, design of a plain method to prepare Fe_3O_4/Fe composites with strong microwave absorption capability at thin coating thickness (d < 1.5 mm) is urgently demanded.

As a simple process, ball-milling is wildly applied in

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mass-produced industrial manufacture [20]. Herein, we present a simple ball-milling to prepare Fe_3O_4/Fe composites. Fe_3O_4 nanoparticles uniformly distribute on the flaky carbonyl iron after the ball-milling process. Compared with raw Fe_3O_4 and carbonyl iron powders, the microwave absorption capability of the Fe_3O_4/Fe composites improved a lot, which can be mainly attributed to the increase of dielectric loss and strong magnetic loss.

2. Experimental section

2.1. Synthesis of flaky Fe_3O_4/carbonyl iron mixture

The Fe_3O_4/Fe mixture was fabricated by a simple wet ball-milling process. Firstly, 6 g Fe_3O_4 and 4 g carbonyl iron powders were added into 100 mL steel pot that contains 100 g stainless steel ball (4 mm in diameter). The mass ratio of powders to steel ball was maintained at 1:10. Next, 40 mL of absolute ethanol was transferred to the pot as solvent. Then, the rotation speed of the planetary ball mill was 500 rpm and the time of ball-milling process was set to 12 h. Finally, the obtained products were dried in air at ambient temperature. The raw materials of Fe_3O_4 (purchased from Aladdin Industrial Corporation) and carbonyl iron powders were acted as contrastive sample, respectively.

2.2. Characterization

The samples of X-ray diffraction (XRD) patterns were measured with Bruker D8 ADVANCE X-Ray diffractometer employing Cu Kα radiation (λ = 0.154718 nm with 40 kV scanning voltage and 40 mA scanning current). A Hitachi S4800 type scanning electron microscope (SEM) was used to observe the morphology features. The saturation magnetization was tested by a vibrating sample magnetometer (VSM, Lakeshore, Model 7400 series) at room temperature. And the electromagnetic parameters of complex permittivity and complex permeability ranged from 2 GHz to 18 GHz were obtained by Agilent PNA N5224A vector network analyzer by the coaxial-line method. The toroidal ring was yielded by homogeneously mixing paraffin wax with 70 wt% products and pressing into toroidal-shaped samples (Φ_{out}: 7.0 mm, Φ_{in}: 3.04 mm).

3. Results and discussion

As shown in Fig. 1, it is clearly found that the diffraction peak at 30.1°, 35.5°, 43.1°, 53.4°, 56.9°, 62.3° can be ascribed to the (220), (311), (400), (422), (511) and (440) crystal planes of Fe_3O_4 (JCPDS card No.07–0322). The carbonyl iron powders show peaks at 44.7°, 65.0° and 82.3°, which can be indexed to the (110), (220) and (211) of Fe (JCPDS card No.06–0696). Meanwhile, it is observed that the diffraction peaks of Fe_3O_4/Fe match well with raw materials of Fe_3O_4 and Fe. No other impurity peaks are discovered. It should be noted that the ball-milling process only mixed uniformly of Fe_3O_4 and carbonyl iron powders without forming other solid solution phase.

The morphological distinctions of the samples were observed by SEM. As displayed in Fig. 2a and inset, the raw material of Fe_3O_4 is made up of nanoscale particles with uniform size, which shows up a slight agglomeration. Carbonyl iron powders presents sphere-like feature with a glossy surface and the diameter distribute mainly about 0.6–3.3 μm (Fig. 2b and inset). After wet ball-milling, it is clearly seen from Fig. 2c and d that the morphology has a great change that the carbonyl iron powders was turned into flaky structure, on which evenly distributed Fe_3O_4 nanoparticles. There still exists a small part of Fe_3O_4 particles not on the flakes. Most importantly, the flake shape is an effective way to overcome the

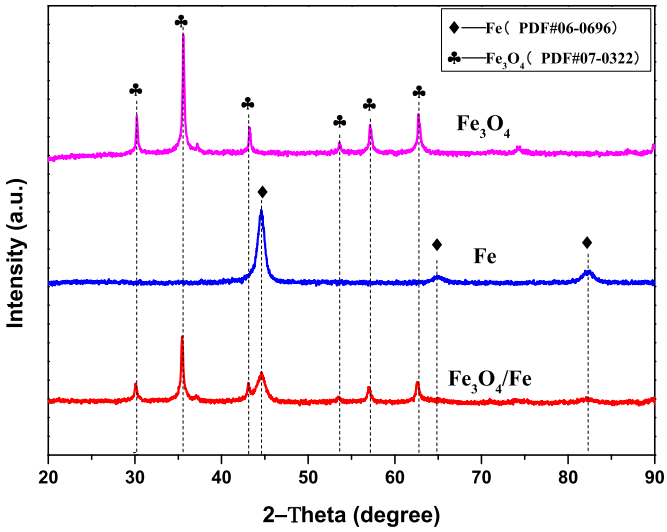

Fig. 1. XRD patterns of Fe_3O_4, carbonyl iron powders and Fe_3O_4/Fe flake composites.

Snoek limitation [21].

The hysteresis loops of samples were showed at Fig. 3. Obviously, the saturation magnetization values (Ms) of Fe_3O_4 and carbonyl iron powders are 54.8 emu/g and 189.1 emu/g, respectively. After ball-milling, the Ms (74.6 emu/g) of Fe_3O_4/Fe composites is larger than the raw Fe_3O_4 while smaller than carbonyl iron powers. According to the following equation [22,23]:

$$\mu' = 1 + (M/H)\cos\sigma \quad (1)$$

$$\mu'' = 1 + (M/H)\sin\sigma \quad (2)$$

where M represents the magnetization, H means the intensity of the external magnetic field, and σ is the magnetic phase lag angle behind the external magnetic field. It is discovered that the value of saturation magnetization is well-matched with complex permeability measured by vector network analyzer. The remanent magnetization and coercivity of Fe_3O_4, Fe_3O_4/Fe and Fe can also be read in the inset of Fig. 3, which are 8.7, 6.0, 3.8 emu/g for retentivity and 110.8, 87.7, 44.8 Oe for coercivity, respectively, which is similar to the previous report by Han R [24].

Fig. 4 shows the electromagnetic parameters of three samples. It can be seen from Fig. 4a that the carbonyl iron powders has the lowest ε' while the mixture of Fe_3O_4/Fe has the largest value of real permittivity on the frequency range. The ε' of raw Fe_3O_4 is about 8.5. It is well known that a good performance absorbent should have moderate value of real permittivity (10–20) which shouldn't be too big or too small [15]. It is interesting that the ε'' value of Fe_3O_4/Fe has an obvious tendency of increase over 2–18 ranged from 2–5, which can give a huge contribution on a thin microwave absorber. It is well interpreted by the 1/4 wavelength equation [25,26]:

$$t_m = nc/4f_m(\varepsilon_r\mu_r)^{1/2} \quad (3)$$

According to Equation (3), one can find that ε'' at high frequency will result in a small coating thickness (t_m), which can optimally explain the phenomenon of excellent microwave absorption capability at small thickness (1.25 mm). While the ε'' value of raw Fe_3O_4 and carbonyl iron powders are very small, which represent that poor dielectric loss ability (Fig. 4b). From Fig. 4c, we can observe that all of samples possess high μ' values