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Electromagnetic properties of core–shell particles by way of electroless Ni–Fe–P alloy plating on flake-shaped diatomite ☆

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ABSTRACT

Flake-shaped diatomite particles coated by Ni–Fe–P alloy were prepared by electroless plating technique and processed by heat treatment. The samples were characterized by SEM, EDS and XRD. The results indicated that the magnetic diatomite particles had continuous and homogeneous Ni–Fe–P coating, and the phase constitution of the Ni–Fe–P coating was transformed from an amorphous structure to a crystalline structure during heat treatment. The measured electromagnetic parameters and the calculated reflection loss suggested that heat treatment was able to enhance the microwave absorption performance of the paraffin wax based composites. In a word, the Ni–Fe–P coated diatomite particle obtained in this paper is a promising candidate for lightweight microwave absorbing inclusions.

1. Introduction

Recently, microwave absorbing materials filled with ferromagnetic metallic particles have attracted considerable attention in both civil and military applications due to their high saturation magnetization [1–5]. However, the conventional ferromagnetic metallic particles have some drawbacks in terms of simple shape and great density. In order to reach full microwave absorbing potential, particles prepared by depositing ferromagnetic metal or metallic alloy on non-metallic template can provide electromagnetic absorbents with various shapes and low density [6–9].

Diatomite particles are typical biological siliceous rocks containing mass of frustules. They are formed from the action of natural environment on remains of single-celled diatoms deposited in the sea bed, and inherit characteristics of shape and structure of diatoms. Diatomite particles have various shapes including spherical, laminar, annular, cylindrical and navicular along with particular substructures such as porous and spinous [10]. Furthermore, diatomite particles possess good thermal resistance and chemical stability for its chemical composition is mainly amorphous SiO_2. These make them an excellent non-metallic template.

Permalloy is an excellent soft magnetic material and has been widely used in microwave absorbing materials. Ni–Fe–P alloys could be deposited onto the non-metallic template by electroless plating technique [11–13]. A small amount of non-metallic elements (P or B) could improve the synthetic electromagnetic properties of the coating by increasing its electrical resistivity [14]. Moreover, the phase constitution of coating prepared by electroless plating could be adjusted by heat treatment to enhance the electromagnetic properties [15].

In this paper, the flake-shaped diatomite was used as non-metallic template to fabricate core–shell ferromagnetic particles by way of electroless Ni–Fe–P alloy plating technique, and then the obtained particles were processed by heat treatment for phase constitution adjustment. Besides, the electromagnetic properties of the coated diatomite particles before and after heat treatment were investigated in details.

2. Experimental details

2.1. Materials

Diatomite is a kind of low cost mineral. The flaked-shaped diatomite used in this research belongs to *Coscinodiscus* Ehrenberg,

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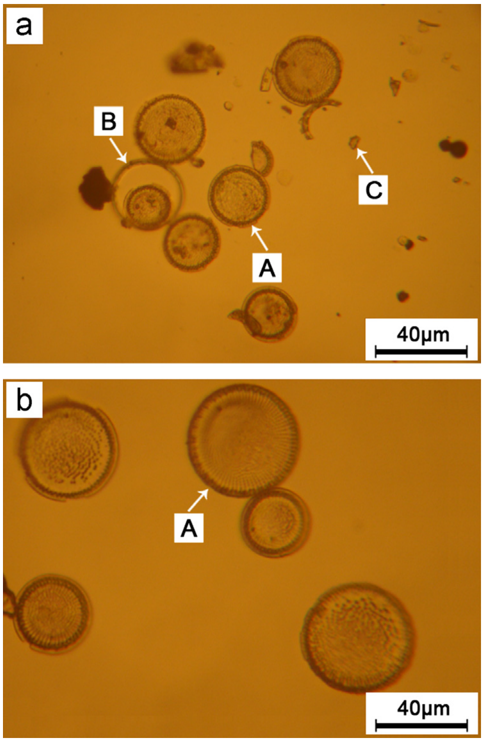

Fig. 1. Optical micrographs of diatomite particles: (a) original diatomite and (b) extracted diatomite valves.

which was purchased from Linjiang Sailite Diatomite Co., Ltd. The diameter is about 20–40 μm, the thickness is about 2–10 μm, the specific gravity is about 2.15, and there are many micropores on the surface. Fig. 1 shows the optical micrographs of the diatomite particles. It is found that most diatomite particles have been separated into diatomite valves (arrow A), girdle bands (arrow B) and fragments (arrow C), which result from nature long-term destructions and calcinations in the production process. The diatom valves, possessing bigger specific surface area than girdle bands, are the contributing parts of the diatomite particles. According to the method in the literature [10], the girdle bands were isolated from the diatomite particles before they were taken as templates.

2.2. Electroless plating

During the process of electroless Ni–Fe–P plating, the process parameters (bath constituents, temperature, plating time, load, stirring rate, etc) have much effect on surface morphology, phase constitution and electromagnetic property. Therefore, the process conditions of electroless Ni–Fe–P plating should be optimized in advance. The optimized processing steps and the corresponding technical parameters of electroless Ni–Fe–P plating are shown in Table 1. The coating thickness is approximately 1.55 μm and the density of the coated diatomite particles is about 4.67 g/cm^3 by testing and analyzing. During the whole plating process, the thermostatic water bath was adopted for heating the solution, and the mechanical stirring was used to avoid the agglomeration of diatomite particles and in favor of obtaining uniform Ni–Fe–P coating.

2.3. Heat treatment

The heat treatment was carried out in the nitrogen-based atmosphere furnace. The coated diatomite particles were treated at 400 °C, 450 °C and 500 °C for 1 h, 3 h and 5 h, respectively, and then cooled quickly to room temperature in nitrogen atmosphere.

2.4. Morphology characterization

The morphologies of the diatomite particles were examined by a XSY-1 optical microscope with SONY DSC-H50 photographic camera and a scanning electron microscope (SEM, Cambridge CamScan CS3400). The chemical composition was determined by energy dispersive spectrometer (EDS, Oxford INCA). The phase constitution was characterized by employing the X-ray diffraction (XRD, Rigaku D/max-3) with Cu-Kα radiation at a voltage of 40 kV, a current of 40 mA, step size 0.02°, scanning rate 8°/min and wavelength 1.5418 Å.

2.5. Electromagnetic properties

The electromagnetic parameters (complex permeability and complex permittivity) were measured by using a vector network analyzer (AV3627, CETC) in the frequency range of 2–18 GHz. The measured composites were made into toroidal shape with outer diameter of $7^{+0.03}_{-0.02}$ mm, inner diameter of $3^{+0.05}_{0}$ mm and thickness of 2 mm. Fig. 2 shows the schematic diagram of measurement device. In order to investigate the heat treatment effect on the electromagnetic properties of composites, the coated diatomite particles were mixed with paraffin wax matrix at volume fraction 40%.

3. Results and discussion

Fig. 3 shows the SEM micrographs of diatomite particles after electroless Ni–Fe–P plating. It can be seen in Fig. 3(a) that there are few agglomerations which indicate good dispersion of the diatomite particles in the solution during the electroless plating process. It is found in Fig. 3(b) that the Ni–Fe–P coating is continuous and the micropores on the diatomite surface are completely covered by the coating. Fig. 4 shows the EDS spectrum of the Ni–Fe–P coating on the diatomite surface. Beside with the main Ni, Fe and P peaks, C, Si and O peaks are also found in the spectrum. The Si and O elements are the principal components of diatomite particles. The quantitative analysis result is shown in Table 2, which shows that the coated diatomite is comprised of about 64.67 wt% (36.83 at%) Ni, 8.92 wt% (5.15 at%) Fe, and 5.07 wt % (5.48 at%) P. Meanwhile, it can be found that the Ni content is a little high and the Fe content is a little low, and the molar ratio of Ni to Fe in the coating is much higher than that of Ni^{2+} to Fe^{2+} in the solution. The reason may be that the catalytic activity of Ni is higher than that of Fe.

Fig. 5 shows the XRD patterns of the coated diatomite particles before and after heat treatment. It can be found that there is a diffuse peak between $2\theta = 40°$ and 50°, which indicates that the as-prepared coating is mainly composed of amorphous Ni–Fe–P, and some shape peaks emerge after heat treatment. It means that heat treatment can promote the transition of the coating structure from an amorphous state to a crystalline state. According to the XRD patterns, the strongest peak is attributed to the formation of $(Fe, Ni)_3P$ phase and the other weaker peaks are caused by formations of Ni_3P and Fe_2NiP phase.

Fig. 6 shows the complex permittivity (ε', ε'') and the complex permeability (μ', μ'') of the paraffin wax based composites containing the coated diatomite particles heat-treated at 400 °C for different times. It can be found that the complex permittivity (ε', ε'') increases with the heat treatment time, but the change trend of complex permeability is a little confused especially for the real part (μ') which increases on the whole with the heat treatment time but along with decline, and the imaginary part (μ'') increases firstly and then decreases with the heat treatment time. We also investigated the complex permittivity (ε', ε'') and the complex