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Microwave absorption property of the diatomite coated by Fe-CoNiP films

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ABSTRACT

A bio-absorbent of Fe-CoNiP coated on the diatomite was fabricated by way of electroless plating of CoNiP and subsequent chemical vapor deposition of Fe. The surface morphology and composition of the above-mentioned diatomite particles at different stage were characterized with the scanning electron microscopy and the energy spectrum analysis respectively, and the results showed that the diatomite was successfully coated with CoNoP and Fe (carbony iron). The complex permittivity and permeability of composites filled with the bio-absorbent and paraffin was measured in frequency range of 2–18 GHz, and then the microwave reflection loss (RL) and the shielding effectiveness (SE) were calculated. The results showed that the permittivity and the permeability were both enlarged as Fe films were coated onto the CoNiP-coated diatomite, which was attributed to the excellent electromagnetic property of carbonyl irons. The composites made with the Fe-CoNiP diatomite had a better absorbing property (minimum RL −11.0 dB) as well as the shielding property (maximum SE 5.6 dB) at thickness 2 mm. It indicated the absorption property was mainly due to the attenuation on the microwave, and the Fe-CoNiP diatomite could be an effective absorbent with low-density.

1. Introduction

Radar absorbing materials (RAM) have been widely used in both military applications and civil aspects, such as stealth technology, electromagnetic radiation reduction, electromagnetic interference (EMI) shielding, etc. There are mainly three types absorbing materials according to the absorption mechanism, including the dielectric loss material, the magnetic loss material and the conductive loss material [1–3]. Using absorbing materials in the form of coating or plate, the incident microwave will be attenuated in the absorbers due to the fact that part of the electromagnetic energy can be converted to the thermal energy, and the reflected microwave will become weaker. The promising absorbing materials should have high absorbing rate, thin thickness, wide absorbing band and light weight to meet different application needs.

Recently, the bio-limited technology which uses biological particles as templates to fabricate soft-core electromagnetic particles has been reported, such as NiFe/diatomite [9], NiFe/spirulina [10]. The soft magnetic alloys can be coated on the biological particle surface using various physical or chemical processes. The previous research has showed that these bio-absorbents have features of low density and high absorption performance due to their specific core-shell structure and optimized coating film composition. In addition, the carbonyl iron particles (CIPs) are extensively used as absorbents due to their large saturation magnetization and the large Snoek's limit at gigahertz (GHz) frequency. As the powders are shaped to flakes, the existing easy-plane anisotropy supports a solution on exceeding the Snoek's limit, and the permeability can be increased as well as the absorption [4–6]. The mechanical milling process is often an effective way to fabricate the flaky CIPs, but the milled absorbent is solid and owns a heavy density. If the flaky CIPs can be coated on the biological particle surface to fabricate core-shell particle, the density of the composite can be reduced. The potential improvement on the dielectric loss and magnetic loss can exist as the microwave-transparent materials are added, such as the SiO_2 coated on the Z-type barium ferrite [7], Z-type barium ferrite/silica coating polypyrrole composite [8].

In this paper, a new type of flaky core-shell bio-absorbent was fabricated with the diatomite as the template, CoNiP alloy and Fe was coated on the diatomite in sequence using two different chemical processes. Then the electromagnetic property of the coated particles was analyzed in detail, and the enhancement mechanism was discussed.

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Table 1
Composition of electroless CoNiP plating solution.

Composition	Agents	Concentration (mol/L)
Main salt	$NiSO_4{\cdot}6H_2O$	0.04
	$CoSO_4{\cdot}7H_2O$	0.06
Reducing agent	$NaH_2PO_2{\cdot}2H_2O$	0.2
	$C_4H_4Na_2O_5{\cdot}H_2O$	0.4
Complexing agent	$C_3H_2Na_2O_4{\cdot}H_2O$	0.3
	$C_4H_4Na_2O_4{\cdot}6H_2O$	0.5
Buffer	$(NH_4)_2SO_4$	0.1

2. Experiment

2.1. Materials preparation

The diatomite was purchased from Linjiang Sailite Diatomite Co. Ltd., Jilin province, China. All other chemical reagents used in the following sections were of analytic grade, which were bought from Beijing Chemical Reagents Factory. All the aqueous solutions were prepared with deionized water during the process of preparation. The morphology of the diatomite is shown in Fig. 1. Generally, the diatomite particles are in flake shape with a diameter range of 20–60 μm, thickness range of 2–10 μm. They are mainly composed of SiO_2 (70–90%), and their volume density is about 1.2 g/cm^3.

2.2. Electroless plating of CoNiP

The electroless plating process of the CoNiP alloy on the diatomite is as followings: firstly, the diatomite was dispersed in ethanol and cleaned with the ultrasonic washer for 40 min to remove the impurities. Then, the gravity sedimentation and filtering was carried out to improve the consistency of the diatomite. Secondly, the sieved diatomite was transferred to the colloidal palladium-stannum solution and mechanically stirred for 15 min at 30 °C to make the diatomite activated. Thirdly, the activated diatomite is further accelerated with the solution containing sodium hypophosphite (30% in concentration) for 60 s at 30 °C to make the palladium particle exposed acting as the catalytic center for the coming electroless deposition. Finally, the pretreated diatomite was put into the preheated CoNiP electroless plating bath, to react for 30 min at 80 °C. The detailed composition of the bath is given in Table 1. The pH value of the solution is adjusted to 8.7–9.3 with sodium hydroxide. The mechanical stir is used during the whole electroless plating process to make the uniform plating on the diatomite. Then the coated diatomite is dehydrated in an alcohol series and dried in the vacuum drying chamber at 120 °C for 4 h.

2.3. Chemical vapor decomposition of CIPs

The CoNiP diatomite was further coated with carbonyl iron by the chemical vapor decomposition (CVD) process [11]. Fig. 2 shows the CVD system for depositing on the diatomite. According to the previous report [12], the heat temperature of the $Fe(CO)_5$ steam was 120 °C, which was much higher than the $Fe(CO)_5$ boiling temperature 103.5 °C. It would result in the fast and drastic decomposition process before the steam reaching the reactor, and a lot of free spherical CIPs could be formed. In addition, the thermal conductivity of the diatomite was inferior to the reactor, the $Fe(CO)_5$ steam did tend to decompose on the reactor surface easily. Therefore, in this work, the diatomite was pretreated with CoNiP film to achieve superior thermal conductivity, after they were added into the reactor, they were stirred with the mechanical stirring at velocity of 60 r/min; and the $Fe(CO)_5$ steam was added into the reactor by pre-heating in a water bath with temperature 90 °C. The reactor was heated to 300 °C at the N_2 atmosphere to make the $Fe(CO)_5$ decomposed and deposited onto the particles. After the reaction completion, the particles were cooled in the reactor directly to the room temperature. Then the obtained hybrid core-shell particles were dispersed in an alcohol series and dried in the vacuum drying chamber at 120 °C for 4 h. Finally, the dried particles were sieved to eliminate the free CIPs by a standard sieve with mesh number 500.

2.4. Sample measurement

The morphology of the coated diatomites was observed by the optical microscope and the scanning electron microscopy (SEM CamScan CS3400) to evaluate CoNiP or Fe films on the particle surface. The static magnetic property was then evaluated on a vibrating sample magnetometer (VSM, JDM-13), and the field reached up to 1.5×10^4 Oe. The compostion and phase structure of coating on the diatomite was estimated by the X-ray diffractometer (D/MX 2200) using Cu K-radiation (wavelength $\lambda = 0.154$ nm), scan step size was $0.02^\circ\ s^{-1}$ with 50 steps per degree. The complex dielectric permittivity and magnetic permeability of the composites were measured using the transmission method with an AV3627 vector network analyzer and a coaxial transmission line in the frequency 2–18 GHz. The testing sample for the electromagnetic (EM) parameter measurement was a toroidal shape with outer diameter 7.0 mm, inner diameter 3.04 mm and thickness 2 mm. The density of the coated diatomite was measured by drainage method, showing the CoNiP coating diatomite with density of 2.5 g/cm^3, the Fe-CoNiP coating diatomite with density of 3.5 g/cm^3 and Fe coating diatomite with density of 3.8 g/cm^3. Then they were mixed into paraffin with the weight content of 50%, respectively. Then the reflection loss (RL) and shielding effectiveness (SE) could be calculated. For an absorbing material, the RL of normal incident EM wave at the absorber surface can be defined as the ratio of reflected power to incident power by testing the absorbers backed by a perfect electronic conductor, and the SE can be defined as the ratio of transmitted power to incident power by testing the absorbers directly without the backed conductor. The parameters can be represented in the following equations [13,14]

$$\Gamma_0 = \frac{Z_{in} - 1}{Z_{in} + 1} \tag{1}$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left(\frac{2\pi d j \sqrt{\mu_r \cdot \varepsilon_r}}{\lambda}\right) \tag{2}$$

$$T = \exp\left(\frac{-2\pi d j \sqrt{\mu_r \cdot \varepsilon_r}}{\lambda}\right) \tag{3}$$

$$\mathrm{RL(dB)} = 20 \log \left|\Gamma_0\right| \tag{4}$$

$$\mathrm{SE(dB)} = -20 \log \left|\frac{(1 - \Gamma_0^2)T}{1 - T^2\Gamma_0^2}\right| \tag{5}$$

where Z_{in} is the input impedance of the absorbing material. Γ_0 is the reflection coefficient, while T is the transmission coefficient. ε_r, μ_r and ε_0, μ_0 are complex permittivity and complex permeability of the absorbing material and free space, respectively. λ is the wavelength of the microwave, and d is the thickness of the absorbing material.

3. Results and discussion

3.1. Characteristics of the particles

The mophology of the diatomite powders coated with CoNiP film and Fe-CoNiP film is shown in Fig. 3. It can be seen that the