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Electroless plating preparation and electromagnetic properties of Co-coated carbonyl iron particles/polyimide composite

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ABSTRACT

To solve the serious electromagnetic interference problems at elevated temperature, one thin microwave-absorbing sheet employing Co-coated carbonyl iron particles and polyimide was prepared. The Co-coated carbonyl iron particles were successfully prepared using an electroless plating method. The microstructure, composition, phase and static magnetic properties of Co-coated carbonyl iron particles were characterized by combination of scanning electron microscope (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). The electromagnetic parameters of Co-coated carbonyl iron particles/polyimide composite were measured in the frequency range of 2–18 GHz, and the electromagnetic loss mechanism of the material-obtained was discussed. The microwave absorption properties of composites before and after heat treatment at 300 °C for 100 h were characterized in 2–18 GHz frequency range. It was established that composites based on Co-coated carbonyl iron demonstrate thermomagnetic stability, indicating that Co coating reduces the oxidation of carbonyl iron. Thus, Co-coated carbonyl iron particles/polyimide composites are useful in the design of microwave absorbers operating at temperatures up to 300 °C.

1. Introduction

Carbonyl iron particles have long attracted researchers' attention as magnetic components of polymeric composites for a number of applications, such as magnetic storage media and plastic encapsulated inductor cores [1,2]. Carbonyl iron is still now the main component of polymer composites developed for application in the design of magnetic type electromagnetic wave absorbers (EWAs) [3–7]. Moreover, it is possible to control complex permeability dispersion of composites filled with carbonyl iron by proper choice of the carbonyl iron type, namely particle size and shape, as well as microstructure (onion-like or polycrystalline) [8]. Due to a favorable form of frequency dependence of complex permeability, and a proper ratio between the permeability and permittivity, carbonyl iron particles with polycrystalline structure have the potential to be developed as a super-thin (below 1 mm) microwave absorber [9].In a practical application, the wave absorption performance of onion-like carbonyl iron is inferior to the polycrystalline one. For this reason, more and more researchers devote themselves to the polycrystalline carbonyl iron.

Polycrystalline carbonyl iron particles filled in polymers were also used at elevated temperature [10] for the high absorbing capacity of electromagnetic energy in the radar wave band. The thermomagnetic stability and the heat-resistance of carbonyl iron-based polymeric composites are the main factors determining the carbonyl iron used at high temperature. However, a common drawback of the carbonyl iron particles is their oxidation at high temperature to form Fe_3O_4 [1,11], which leads to the decrease in magnetic property of carbonyl iron particles. As is well known, microstructure of carbonyl iron determines the thermomagnetic stability of materials. Carbonyl iron with onion-like structure is characterized by more environmental and thermal stability (due to the presence of carbides and nitrides of iron) than carbonyl iron with polycrystalline structure [12]. Therefore, it is quite important to explore the antioxidation method of the polycrystalline structure carbonyl iron. Carbonyl iron particles are generally utilized as an auxiliary absorbent in other materials or after surface treatments [13–15].

It is well known that electroless plating is widely applied in preparation of metal composites, due to its advantages such as low cost, simple process, high shielding efficiency of coating, excellent environment stability and other notable features [16–18]. In recent years, various microwave absorption materials were successfully prepared by electroless plating technology [19–25]. In our previous works, the Ni coated carbonyl iron composite particles have been prepared successfully by electroless nickel plating, which possess higher microwave absorption than raw carbonyl iron

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particles [26]. Comparing to Ni, Co has higher Curie temperature and better magnetic property [27].What's more, thermogravimetric (TG) property exhibited a significant difference in the obvious weight gain temperature between uncoated and Co coated carbonyl iron particles [28]. As we know, polyimide is considered an ideal matrix for radar absorbing materials at higher temperatures because of its high decompose temperature, good dielectric properties, superior thermal stability, and high strength [29]. Therefore, the carbonyl iron particles after electroless plating Co coating were filled in polyimide to explore the heat resistance property.

In this paper, raw carbonyl iron/polyimide and Co-coated carbonyl iron/polyimide composites were prepared. The influence of Co coating on the morphology, electromagnetic, related microwave absorption properties of carbonyl iron particle/polyimide composite was discussed. In addition, the electromagnetic property after heat treatment at 300 °C for 100 h was also investigated.

2. Experimental and characterization

2.1. Materials

The carbonyl iron particles used in this study was fabricated by the decomposition of $Fe(CO)_5$ and purchased from Xinghua chemical Co. Ltd, Shaanxi province, China. The main characteristics of the FCI particles are: the content of α–iron >99.5 wt%, thin flakes of 1~5 μm in diameter and below 1 μm in thickness, and polycrystalline microstructure. Poly (amic acid) solution (PAA) was supplied by Changchun Institute of Applied Chemistry, and the solids concentration was 40%.

2.2. Preparation of Co-coated carbonyl particle

Carbonyl iron particles were heat-treated at 600 °C for 30 min and then cooled to room temperature in a vacuum furnace to remove the residue organic layer on the surface of particles. Then the carbonyl iron particles were degreased in dilute solution of hydrochloric acid at the pH-value of 3 to remove the oxidation layer. The activated carbonyl iron particles were washed with distilled water and then introduced into an electroless plating bath. The composition of the plating solution and the reaction conditions were shown in Table 1. The chemical reaction process can be expressed as the following reaction:

$$CO^{2+} + H_2PO_2^{-} + 3OH^{-} \rightarrow Co + HPO_3^{2-} + 2H_2O \quad (1)$$

All the chemical reactants were analytical grade and used as received. The proportion of pre-treated carbonyl iron particles added to the plating bath was 10 g/L. The particles were put into the electroless plating solution when the temperature reached 90 °C and mechanically stirred with a rate of 300 rmp in order to mix sufficiently and homogenously. In general, the thickness of Co coating can be controlled by the plating time [30]. The plating time was maintained for 60 min in the present study. After electroless plating, the solution was filtered, washed and dried. Thus, the final coated particles were obtained.

Table 1
The compositions and RL of the raw and Co-coated carbonyl iron particles filled composites.

Sample	Absorber and content	Optimum RL (dB) and Absorber Thickness (mm)		
		−6 (more than 74.9% absorption)	−8 (more than 84.1% absorption)	−10 (more than 90.0% absorption)
a	raw carbonyl iron /polyimide	8.6–18 GHz 1.0 mm	6.6–12.9 GHz 1.5 mm	5.8–9.1 GHz 1.8 mm
b	Co-coated carbonyl iron/ polyimide	7.4–18 GHz 1.0 mm	5.8–12 GHz 1.5 mm	5.1–8.6 GHz 1.8 mm
c	Sample a after 300 °C 100 h	7.8–18 GHz 1.0 mm	6.3–11.7 GHz 1.5 mm	5.5–8.1 GHz 1.8 mm
d	Sample b after 300 °C 100 h	7.5–18 GHz 1.0 mm	5.7–11.8 GHz 1.5 mm	5–8.4 GHz 1.8 mm

2.3. Preparation of Co-coated carbonyl iron/polyimide composites

The Co-coated carbonyl iron/polyimide composite was fabricated by the following steps. Firstly, the PAA solution was mixed with 70 wt% Co-coated carbonyl iron by mechanical stirring for 3 h, and then the mixture was placed into vacuum oven followed by thermal imidization at 240 °C for 2 h to eliminate the solvent. Secondly, the resulting mixtures were ground into fine particles and sieved with 100 meshes, then the particles were placed in a stainless steel mold with the size of 120 mm × 120 mm and compressed at 270 °C with a pressure of 5 MPa. Lastly, the temperature and pressure were maintained at 370 °C for 1 h for cross-linking reactions and the composites are naturally cooled to room temperature. The 70 wt% raw carbonyl iron/polyimide composite was also prepared for comparison.

2.4. Characterization

The morphology of the raw and Co-coated carbonyl iron particles were examined under a scanning electron microscope (SEM; JEOL JSM-5800 LV SKANNING) attached with a Links Systems energy dispersive spectrometer (EDS). Magnetic measurement was conducted at room temperature using a vibrating sample magnetometer (VSM, Riken Denshi, BHV-525). Composites were characterized by X-ray powder diffraction (XRD, Philips, Netherlands, with Cu Kα). The effective complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) of the composites were measured using a network analyzer (Agilent technologies E8362B: 10 MHz–20 GHz).

3. Results and discussion

3.1. Morphology and structure

As shown in Fig. 1(a), the morphology of carbonyl iron particles is flake with diameters ranging in 1~5 μm and thickness below 1 μm. In addition, there are small globular granules. Fig. 1(b) shows the SEM image of the Co-coated carbonyl iron. As observed, the morphology of the Co-coated carbonyl iron is similar to the particles before plating. It is worth noting that there exist few micro-holes on the surface of Co-coated carbonyl iron particles, which may be contributed to the acid pickling process. From the insert of Fig. 1(b), the carbonyl iron particles are uniformly coated with Co coating, the thickness of which is below 0.2 μm, indicating the core-shell structure of the Co coated carbonyl iron particles.

Fig. 1(c) and (d) shows the surface morphologies of the composite embedded with 70 wt% carbonyl iron particles and Co coated carbonyl iron particles, respectively. It is revealed in Fig. 2(c) and (d) that homogeneous dispersion of carbonyl iron particles and Co coated carbonyl iron particles in the polyimide matrix appears and no obvious agglomerations are detected, which is important to be a good absorbent.

Fig. 1(e) and (f) are the EDS spectra of carbonyl iron before and after plating. It indicates that the coating is composed of Co and P. The spectrum peaks of Co and Fe elements have some overlapping phenomena. The main ingredient of the electroplated coating is