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Review

Magnetic properties and microwave absorption properties of carbon fibers coated by Fe_3O_4 nanoparticles

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ABSTRACT

Fe_3O_4 nanoparticles were plated on carbon fibers from nitrate and dimethylamine borane solution at 90 °C for 1 h. The structures and morphologies of the composite were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The thickness of the Fe_3O_4 films is about 1 μm. The saturation magnetization of the Fe_3O_4/CFs composites reaches 39.5 emu/g and coercivity reaches 166.9 Oe. The reflectivity of Fe_3O_4 nanoparticles covered carbon fiber (2.90–5.12 mm in thickness) is less than −10 dB over the range of 3.52–10.01 GHz and −20 dB over the range of 5.49–7.75 GHz. The lowest reflectivity of the Fe_3O_4/CFs composites is −35 dB at 6.37 GHz for a layer of 4.41 mm in thickness.

Contents

1. Introduction

The microwave absorption materials have attracted a lot of attention in recent years because of their potential applications in wireless data communication, local area network, satellite television and heating system [1]. Magnetic materials especially play a leading role in the investigation and application of microwave absorption materials [1–3]. However, the conventional microwave absorption materials, such as magnetic metal and ferrite, are very heavy which restricts their applications in many fields. One of the ways to solve the problem is to couple the magnetic absorption materials with low density substrates. Carbon fibers (CFs) are suitable to be the substrates due to their low density, high strength and excellent electrical property [4,5]. Many treatments have been used to enhance the absorbing property of carbon fibers, including changing the cross-section shape and size of carbon fibers [6–8], modifying the carbon fiber surface such as coating the surface with a layer of metal or other oxide [6–10]. The composites of carbon fibers and magnetic materials not only have a lighter weight but also possess good conductivity and strength. Fe_3O_4 nanoparticles exhibit excellent microwave absorption property and have been widely used in many fields [11–13]. However, very little work has been done for combining Fe_3O_4 nanoparticles with CFs.

Additionally, in recent reports, the CuO/CFs and CuO/Co/CFs composites exhibited strong electromagnetic wave absorption

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property, the strongest reflection loss (RL) of the composites reaches a maximum of −29.6 dB at 7.9 GHz and −42.7 dB at 10.8 GHz, respectively [6,7]. The RL of nickel-coated carbon fiber (NCF) composites reaches a maximum of −14 dB at 18 GHz [9]. The RL of the 70% volume fraction of Fe_3O_4-carbon sphere composite exhibits a broad microwave absorption ranging from 2.5 to 18 GHz [11]. The Fe_3O_4 coated with Ni–B alloy films exhibit better absorption performance than the pure Fe_3O_4 in the range of 2–18 GHz [3].

Various preparation techniques, including sputtering, vacuum evaporation, and sol–gel method have been employed for preparing ferrite composites [14]. In these work, post-heat treatments or high deposition temperature are required to obtain the desired crystalline phases which may result in the non-stoichiometric of the products [14,15]. However, the low-temperature wet chemical preparation method can overcome the disadvantage of the traditional methods. Izaki et al. prepared Fe_3O_4 film at low temperature by immersing a Pd/Ag-catalyzed substrate in aqueous iron nitrate and dimethylamine borane (DMAB) complex solutions [16]. This method was also employed to prepare n-type transparent wurtzite ZnO film [17].

In this paper, low-temperature wet chemical preparation method was employed to prepare Fe_3O_4 covered carbon fibers by immersing Ag-catalyzed carbon fibers into the nitrate-DMAB system at 90 °C for 1 h. The magnetic and microwave absorption properties of the Fe_3O_4/CFs composites were investigated.

2. Experimental details

The carbon fibers with a diameter of 5–10 μm were used to prepare Fe_3O_4/CFs composites by wet chemical method. Prior to the surface treatment, the carbon fibers were cut into 2–3 mm in length. The pretreatment involved four steps: (1) the carbon fibers were immersed into acetone for 2 h and then washed by distilled water; (2) the carbon fibers were treated with nitric acid [HNO_3] for 5 h and then washed by distilled water; (3) the carbon fibers were treated with stannous chloride and ammoniacal silver solution. The Sn/Ag activation process includes: (i) the surface of the CFs was sensitized by dipping into a conventional sensitizer containing 30 g/l stannous chloride dihydrate [$SnCl_2{\cdot}2H_2O$] and 1.6 mM hydrochloric acid [HCl] and then rinsed by distilled water; (ii) the surface of CFs was activated using an activator containing 5–10 g/l silver nitrate [$AgNO_3$] and 2.1 mM ammonia monohydrate [$NH_3{\cdot}H_2O$], the formation of Ag granules on the carbon fibers can be expressed by reactions (1) and (2); (4) finally, the pre-treated CFs were immersed into aqueous solution containing 10 mM iron nitrate 9-hydrate [$Fe(NO_3)_3{\cdot}9H_2O$] and 30 mM dimethylamine borane complex (DMAB) [$(CH_3)_3N{-}HBH_3$] at 90 °C for 1 h. The deposition process of the Fe_3O_4 nanoparticles can be briefly described by reactions (3)–(9) [15,18]:

$$C + Sn^{2+} = CSn^{2+} \quad (1)$$

$$CSn^{2+} + 2Ag^{+} = CAg_2 + Sn^{4+} \quad (2)$$

$$Fe(NO_3)_3 \rightarrow Fe^{3+} + 3NO_3^{-} \quad (3)$$

$$(CH_3)_2NHBH_3 + 2H_2O \rightarrow BO_2^{-} + (CH_3)_2NH + 7H^{+} + 6e^{-} \quad (4)$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (5)$$

$$NO_3^{-} + H_2O + 2e \rightarrow NO_2^{-} + 2OH^{-} \quad (6)$$

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow (Fe^{2+}, 2Fe^{3+})(OH)_8 \quad (7)$$

$$(Fe^{2+}, 2Fe^{3+})_3(OH)_8 \rightarrow Fe_3O_4 + 4H_2O \quad (8)$$

The Ag layer plays an important role in the deposition of ferrite films. No Fe_3O_4 nanoparticles can be deposited on the bare fibers under the same reaction condition. Homma et al. found that the oxidation of DMAB preferentially proceeded in the electric double layer at the surface region of the deposited metal, and the metal surface enhanced the electron emitting reaction of DMAB due to its electron receptivity [19]. The reduction of NO_3^- ions to NO_2^- ions at the surface of the Ag layer is a key to raise the local pH value in reaction (6). In addition, heterogeneous nucleation is promoted by the presence of the Ag granules on the carbon fibers. Therefore, nucleation may take place at a lower saturation ratio on the Ag-catalyzed substrates than in solution. The surface of the Ag layer possesses high surface energy due to the large surface area of the fine Ag granules, which facilitates the ferrite nucleation.

The structure and morphology of the Fe_3O_4/CFs composites were characterized by X-ray diffraction (XRD) and field emission scanning electron microscope (SEM). XRD measurements were performed on a Rigaku D/Max-2400 X-ray diffractometer using Cu Kα radiation (40 kV, 60 mA) from 25° to 90° with a step width of 0.02° and a counting time of 3 s per step. The morphology and thickness of the Fe_3O_4 film were analyzed on a Hitachi S-4800 field emission scanning electron microscope (SEM) operated at an acceleration voltage of 5 kV. The magnetic properties of the Fe_3O_4/CFs composites were measured with a Lake Shore 7304 vibrating sample magnetometer (VSM) at room temperature. An Agilent E8363B PNA vector network analyzer was used to measure microwave absorption coefficient of Fe_3O_4/CFs composites. The Fe_3O_4/CFs composites were homogeneously dispersed into paraffin by ultrasonic method and pressed into a ring (external diameter 7 mm, internal diameter 3 mm) at 350 MPa. The weight fraction of the Fe_3O_4/CFs composites was 50%.

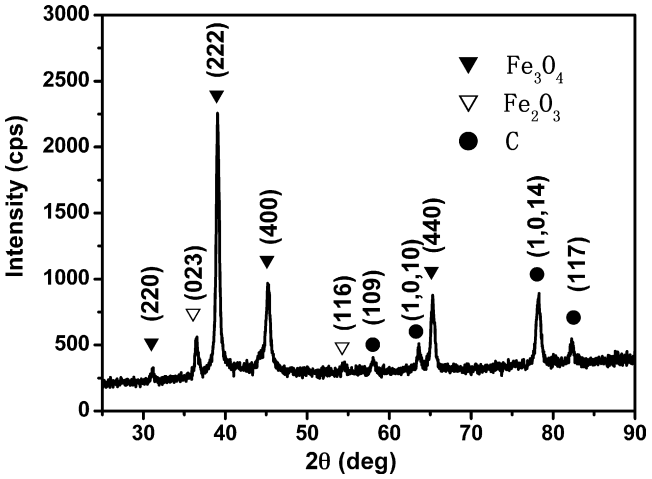

Fig. 1. XRD pattern of the Fe_3O_4/CFs composites.

The reflection loss (RL) of a microwave absorption layer backed by a perfect conductor was calculated by the following equations:

$$RL\,(\mathrm{dB}) = 20\log_{10}\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (9)$$

$$Z_{in} = \left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2}\tanh\left[j\left(\frac{2\pi fd}{c}\right)(\mu_r\varepsilon_r)^{1/2}\right] \quad (10)$$

where RL is a ratio of reflected power to incident power in dB. Z_{in} is the input impedance of absorber, d is the thickness of the absorber, and c and f are the velocity of light and the frequency of microwave, respectively. $\varepsilon_r = \varepsilon' - j\varepsilon''$ and $\mu_r = \mu' - j\mu''$ is the complex permittivity and complex permeability of the absorber material [7]. According to Eqs. (9) and (10) when the RL is −10, −20 dB and the attenuation of microwave absorption materials achieves 90%, and 99%, respectively.

3. Results and discussion

3.1. Structure and morphology of Fe_3O_4/CFs composites

XRD pattern of the prepared Fe_3O_4/CFs composites was measured and pictured in Fig. 1 The results show that Fe_3O_4 phases is obviously found in the products. The diffraction peaks between 10° and 25° (2θ) are from the carbon fiber substrate. The four diffraction peaks of the Fe_3O_4 can be indexed as the (2 2 0), (2 2 2), (4 0 0), (4 4 0) diffractions planes. The diffraction peaks of Fe_2O_3 (0 2 3) and Fe_2O_3 (1 1 6) can also be seen in the XRD pattern.

The surface morphology of the Fe_3O_4/CFs composites is shown in Fig. 2. Fig. 2a displays the SEM image of the untreated carbon fibers. We can see that the diameter of the carbon fibers is about 5 μm. The results show that all carbon fibers are completely coated by Fe_3O_4 nanoparticles (Fig. 2b). The high magnification SEM images of Fe_3O_4/CFs composites are shown in Fig. 2c and d. As we can see from the surface morphology, the carbon fibers are completely covered by Fe_3O_4 nanoparticles and the thickness of the Fe_3O_4 films is about 1 μm (Fig. 2c). Fig. 2e and f shows the high magnification FESEM images of the Fe_3O_4/CFs composites. It is found that small Fe_3O_4 granules are about 50–100 nm in size (Fig. 2f).