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Electromagnetic wave absorption properties of composites with micro-sized magnetic particles dispersed in amorphous carbon

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ABSTRACT

Composites with micro-sized magnetic particles dispersed in amorphous carbon were fabricated conveniently and economically by carbonizing polyacrylonitrile (PAN) fibers mixed with micro-sized iron particles under different temperatures. The composites were characterized by X-ray diffraction (XRD) and scanning electric microscope (SEM). The electromagnetic (EM) properties were measured by a vector network analyzer in the frequency range of 2–18 GHz based on which analog computations of EM wave absorption properties were carried out. The influences of temperature on phase composition and EM wave absorption properties were also investigated, indicating that the composites had good electromagnetic absorption properties with both electrical loss and magnetic loss. Effective reflection loss (RL < -10 dB) was observed in a large frequency range of 7.5–18 GHz with the absorber thickness of 2.0–3.0 mm for the paraffin samples with composite powders heated up to 750 °C and the minimum absorption peak around -40 dB appeared at approximately 10 GHz with matching thickness of 2.0 mm for the paraffin sample with composite powders heated up to 800 °C.

1. Introduction

Electromagnetic (EM) wave has been applied in more and more fields from mobiles and computers in everyday life to radars and missiles in defense industry with the development of electronic technology, meanwhile, with which many problems have come along. EM wave absorption materials have been drawing much attention of researchers for their importance in solving electromagnetic interference (EMI) and making stealth weapons. EM wave absorption materials are those that can absorb or attenuate EM wave by transferring EM energy to heat or that can make EM wave interfere to counteract. Carbon based materials have been applied to microwave absorption for a long history and the improvement of their properties is still a focus of research [1–6]. Carbon fiber is a new generation of enhancement fiber which can be made by polyacrylonitrile (PAN), asphalt or viscose fiber, among which PAN is the mainstream. Carbon fiber is usually good conductor of electricity so as to reflect EM wave strongly but may have absorbing properties only after special treatment. The manufacture of carbon fiber is the process of gradual removal of un-carbon atoms such as nitrogen and oxygen and enrichment of carbon element. Resistance of electricity and dielectric constant of carbon fiber and the chemical reaction in the process of its preparation can be well controlled by adjustment of conditions, for structures and properties of carbon fiber are closely related to conditions especially temperature [7–13]. In this work, PAN fibers were carbonized in lower temperatures (700 °C/750 °C/800 °C) compared with the normal practice (over 1000 °C) in order to obtain relatively low conductivity of electricity and permittivity and, meanwhile, the micro-sized iron particles added into PAN fibers reacted with active oxygen and nitride atoms to become iron oxides or iron nitrides which contribute to the improvement of permeability. As a result, good electromagnetic match and effective EM wave reflection loss (RL) were achieved by lowering permittivity and improving permeability.

2. Experiments

First of all, PAN was synthesized by solution polymerization method. 100 ml acrylonitrile(AN), 260 ml dimethyl sulfoxide (DMSO), 6 g itaconic acid (IA) and azodiisobutyronitrile (AIBN)

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were fed into a conical flask and then stirred homogeneous. The conical flask was kept in a water bath kettle at 60 °C for 24 h to accomplish polymerization. Then the PAN solution with 3.8 g micro-sized iron particles added was stirred for 15 min at the speed of 75 r/min to become homogeneous. The PAN solution with iron particles was spun into PAN fibers with iron particles by a piece of equipment made by our laboratory. The PAN fibers with iron particles were carbonized within protective atmosphere of pure N_2 (> 99.99% in purity) in a carbide furnace manufactured by our laboratory and the temperature control strategy was as Table 1. Finally, the carbonized composites were milled into powders with a mortar as EM wave absorber.

The phase identification of the composites obtained was performed by X-ray diffractometer (XRD) with Cu Kα radiation under 40 kV and 50 mA during the analysis, and microstructures of the carbonized fibers were analyzed by using a scanning electron microscope (SEM, SU-70). Toroidal shaped samples (⌀ out=7.00 and ⌀ in=3.04 mm) of 75 mass% of powders mixed in paraffin which is transparent for EM wave were made in a special die. The EM parameters for these paraffin samples were measured by the coaxial method using a vector network analyzer (Agilent E8363B) at 2.0–18 GHz frequency range. The relative complex permittivity ($\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$) and permeability ($\mu_r = \mu_r' - j\mu_r''$) were evaluated by these parameters, and the EM wave absorption properties were calculated as a frequency dependence of RL at a thickness by using relative complex permittivity and permeability according to the following equations [1,14,15]:

$$Z_{in} = Z_o \sqrt{\frac{\mu_r}{s_r}} \sqrt{\frac{\mu_r}{s_r}} \tanh\left\{ j\left(\frac{2\pi f d}{c}\right) \sqrt{\frac{\mu_r}{s_r}} \right\} \quad (1)$$

$$RL = 20\lg\left|\frac{Z_{in} - Z_o}{Z_{in} - Z_o}\right| \quad (2)$$

where f is the frequency of the microwave, d is the thickness of an absorber, Z_o is the impedance of air and c is the velocity of the light.

Table 1
Temperature control strategy.

Temperature (°C)	Heating up time (min)	Hold time (min)
190	20	10
270	90	10
350	8	2
400	8	2
500	10	2
700/750/800	30	10

3. Results and discussion

Fig. 1 shows SEM photographs of micro-sized iron particles before added into PAN solution from which we can know that the particles are farctate balls with smooth surface and diameter in a range of 1–5 μm. SEM photograph of carbonized fiber whose diameter was about 12 μm with particles dispersed in and incorporating well with the porous amorphous carbon matrix is shown in Fig. 2. The particles after heat treatment become clusters with rough surface composed of nano-sized particles.

Fig. 3 shows a set of XRD patterns for composites heated up to (a) 700 °C, (b) 750 °C and (c) 800 °C. The broad weak peeks with 2θ from 20° to 30° existing in all the three patterns were assigned to amorphous carbon. Fig. 1(a) shows that all the micro-sized iron particles had transformed to Fe_3O_4 in the composite heated up to 700 °C, for the active nitride atoms emitted from PAN matrix at 700 °C are not enough to enable the formation of iron nitride. With increasing temperature, Fe_3N and Fe_4N were found and Fe_3O_4 still existed in composite heated up to 750 °C according to Fig. 1(b) which may be explained by that the part of Fe reduced from Fe_3O_4 reacted with the active nitride atoms emitted from PAN. In Fig. 1(c), peaks of Fe_3N disappeared and the strong peak around $2\theta=44°$ and weak peaks at $2\theta=63°$ and 81° were indexed as (1 1 0), (2 0 0) and (2 1 1) reflections of α-Fe, respectively [16], for part of Fe_3O_4 was reduced to α-Fe and Fe_3N had all transformed to Fe_4N at 800 °C.

Fig. 4 shows the frequency dependence of real part of relative permittivity in the frequency range of 2–18 GHz for paraffin samples with powders heated up to different temperatures. It is obvious that the real part of relative permittivity increased with increasing temperature: the real parts of relative permittivity of the sample with powders heated up to 700 °C are around 5, 750 °C around 10 and 800 °C around 15. In addition, the real part of relative permittivity exhibited fluctuation variation with frequency and the higher temperature the powders were heated up to, the bigger was the amplitude of fluctuation. The frequency dependence of imaginary part of relative permittivity in the frequency range of 2–18 GHz for different samples is plotted in Fig. 5 which indicates that in most frequencies the imaginary part of relative permittivity increased and had bigger amplitude of variation with increasing temperature which is similar to the change rule of real part of relative permittivity. This is because higher temperature makes carbon content rise up and the arrangement of carbon atoms more periodic which can increase the circulation capability of electrons [7,8].

Fig. 6 shows the dependence of real part of relative permeability on frequency in the frequency range of 2–18 GHz for paraffin samples with powders heated up to different temperatures. Real part of relative permeability exhibited fluctuation variation around 1 with amplitude of fluctuation growing with

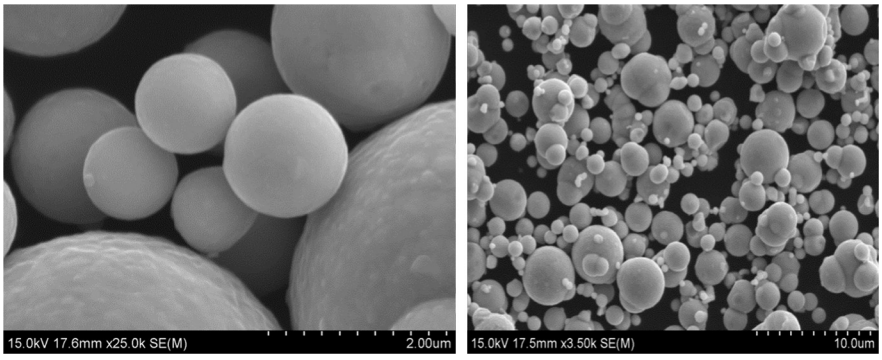

Fig. 1. SEM photographs of the micro-sized iron particles.