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Microwave absorption properties of multiwalled carbon nanotube/FeNi nanopowders as light-weight microwave absorbers

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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) and FeNi nanopowders have been facilely synthesized by a simple chemical method. Excellent microwave absorption properties have been obtained due to a proper combination of complex permittivity and permeability which result from the high resistivity of the sintered composite of MWCNTs and the magnetic FeNi nanopowders. The minimum reflection loss (*RL*) is less than −20 dB at 2.72–18.0 GHz with a thickness between 1.21 and 6.00 mm for 40 wt% MWCNT/FeNi composites, and a minimum *RL* value of −47.6 dB is observed at 12.09 GHz on a specimen with a matching thickness of 1.79 mm. The frequency of microwave absorption complies with the quarter-wavelength ($\lambda/4$) matching model. The MWCNT/FeNi nanopowders are a promising candidate for lightweight microwave absorption materials.

1. Introduction

In recent years, with the development of wireless communication and high-frequency circuit devices in GHz range, microwave absorbers have been widely researched to eliminate serious electromagnetic interference and microwave pollution problems [1–3]. As excellent microwave absorbers, it is not only required to possess low reflection loss (*RL*) value at definite frequency, but also it is demanded of them to be of light weight. Until now, magnetic loss microwave absorbers, dielectric loss microwave absorbers and magnetic/dielectric loss compound microwave absorbers have been deeply studied. For the light-weight requirement, carbonyl iron [4], Ni [5], FeNi [6] et al. as magnetic loss microwave absorbers, and ZnO [7], $BaTiO_3$ [8], MnO_2 [9] et al. as dielectric loss microwave absorbers have difficulty in achieving light-weight demands due to the high density of these materials. As other magnetic/dielectric loss compound microwave absorbers, magnetic material/serious type of carbon as light-weight microwave absorbers has been researched in-depth [10–16]. Among these microwave absorbing materials, firstly, 15 wt % multiwalled carbon nanotubes (MWCNTs) composite with 3 mm thickness have been found to exhibit a minimum *RL* of 10.5 dB at 3.85 GHz [17]. Lately, we reported that *RL* exceeds −20 dB from 2.04 to 3.47 GHz for thickness between 3.36 and 5.57 mm for 60 wt% MWCNT/Fe composites [18]. It is hard to decrease weight of microwave absorbers and maintain low *RL* value simultaneously with a certain layer thickness.

For the other microwave range requirement, most microwave absorbers can exceed −20 dB only in a limited microwave range and confined thickness range. The frequency dependence of microwave absorption obeys the quarter-wavelength ($\lambda/4$) matching model. According to the model, the minimum *RL* can be gained at given frequencies if the thickness of the absorber (t_m) satisfies [19,20]

$$t_m = \frac{n\lambda}{4} = \frac{nc}{4f_m\sqrt{|\varepsilon_r|}}|\mu_r| \quad (n = 1, 3, 5, \ldots) \tag{1}$$

where c is the velocity of light, f_m and t_m are the peak frequency and the matching thickness of minimum microwave absorptions, respectively λ is the wavelength in the materials, μ_r is the complex permeability at f_m and ε_r is the complex permittivity at f_m. Referring to eq. (1), the peak frequency f_m is inversely proportional to matching thickness t_m. Moreover, minimum *RL* can be obtained with a certain f_m and t_m. It is usual to obtain −20 dB value of *RL* with a narrow thickness range in a narrow microwave range [21]. Further, it is difficult to obain −20 dB for *RL* value with 1–6 mm thickness over 2–18 GHz.

In this work, for the requirement of light-weight microwave absorbers, MWCNT/FeNi nanopowders have been prepared by a simple chemical method. The complex permittivity and permeability of resin composites with 40 wt% are analyzed and the microwave absorbing characteristics are evaluated. The peak

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frequency dependence of the minimum *RL* and corresponding frequency on the sample thickness has been studied.

2. Sample preparation and measurements

In a typical synthesis, the MWCNTs with an average of 20 nm diameter were first placed in an ultrasonic bath containing vitriol and nitric acid (3:1) for 5 h to remove trace impurity and to open the cap of the tubes. After the samples were centrifuged, the remainder was dried in a vacuum oven at 60 °C for 12 h. The purified MWCNTs were dispersed in a solution whose molar ratio of $Fe(NO_3)_3 \cdot 9H_2O$ to $Ni(NO_3)_2 \cdot 6H_2O$ is 60/40, dealing with an ultrasonic bath. After draining excess water on a rotary evaporator with a vacuum pump and washing with distilled water, the resulting materials were reduced using H_2 at 900 °C. The mass ratio of MWCNTs with FeNi nanoparticles is 1:1.

The ratio of Fe to Ni was determined by inductively coupled plasma (ICP) spectrometer (ICAP 6000 SERIES) measurement. The image of MWCNTs was taken by a scanning electron microscope (SEM) (Hitachi S-4800) and a high-resolution transmission electron microscope (HRTEM, Tecnai G^2 F30, FEI, USA). The phase was examined using x-ray diffraction (XRD) with Cu $K\alpha$. radiation ($\lambda = 0.154056$ nm) on D/MAX-2500 diffractometer. Raman study of randomly oriented samples was performed with a Renishaw inVia Raman Microscope (wavelength = 514.5 nm). The epoxy resin composites for high-frequency magnetic properties measurement were prepared by epoxy resin with 40 wt% MWCNT/FeNi composites and pressing into toroidal shape (φ_{out}: 7.00 mm, φ_{in}: 3.04 mm). The scattering parameters (S_{11}, S_{21}) were measured on the toroidal-shape samples by a network analyzer (Agilent Technologies E8363B) in the range of 0.1–18 GHz. The relative complex permeability (μ_r) and permittivity (ε_r) values were determined from the scattering parameters to evaluate the electromagnetic wave absorption properties.

3. Results and discussion

ICP measurement shows that the ratio of Fe to Ni is 59.3:40.7. Fig. 1 shows the XRD patterns of MWCNT/FeNi nanopowders. It is clear that two crystal structures exist in the samples: γ-FeNi (fcc-structured) alloy and graphite carbon. The peaks at 43.6°, 50.8°, and 74.6° can be attributed to the (111), (200) and (220) reflections of γ-FeNi alloy, respectively. No individual peaks of Fe or Ni phase can be detected, confirming the absence of segregated Fe or Ni phase. According to the Scherrer formula, the average crystal size of FeNi nanopowders is deduced to be about 65 nm, which agrees with the result of SEM image.

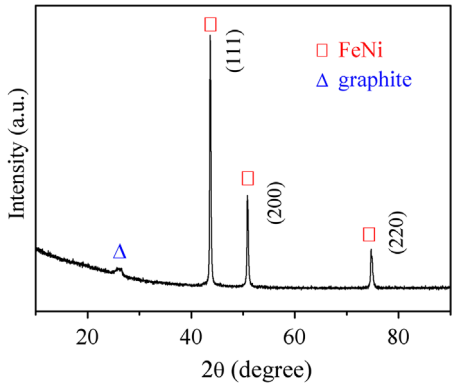

Fig. 1. XRD patterns of MWCNT/FeNi nanopowders.

Fig. 2 shows the SEM image of MWCNTs (a) and MWCNT/FeNi nanopowders (b). It is obvious that the average diameter of MWCNTs is 20 nm, and the presence of impurity cannot be detected, as shown in Fig. 2(a). Fig. 2(b) shows that the FeNi nanopowders are spherical in diameter about 70 nm. Moreover, the FeNi nanopowders were well dispersed in the MWCNTs matrix. More morphology information can be seen from the TEM images of MWCNT/FeNi nanopowders, as presented in Fig. 3(a)–(d). Fig. 3(a)–(c) shows that FeNi nanopowders are uniformly dispersed in MWCNTs, and that FeNi nanopowders have been wrapped by MWCNTs. HRTEM image of the individual FeNi nanopowder is shown in Fig. 3(d), revealing a single-crystalline structure. The interplanar spacing is measured to be 1.80 Å, consistent with the (200) crystallographic orientation of γ-FeNi alloy. Due to the intermolecular van der Waals force between the MWCNTs, the MWCNTs exhibit a strong tendency to form entanglement around FeNi nanopowders. The uniformity of mixed samples is better than that of ultrasonic mixture of MWCNTs and carbonyl iron [22]. The good state of dispersion will be beneficial for impedence matching to achieve excellent microwave absorption properties.

Fig. 4 shows the Raman spectra of randomly oriented MWCNTs and MWCNT/FeNi nanopowders in the 1200–1800 cm^{-1} range at room temperature. MWCNTs and MWCNT/FeNi nanopowders all exhibit two broad peaks around 1346 cm^{-1}, labeled as D peak for 'disorder carbon' and 1573 cm^{-1}, labeled as G peak for 'graphite carbon' [23,24]. For I_D/I_G, comparing with 0.72 of MWCNTs, that of MWCNTs/FeNi is 0.97. The increase in intensity of the D peak indicates the increase of disorders for MWCNT/FeNi. On the other hand, this may be mainly attributed to a symmetry-lowering effect due to defects during the sintering of MWCNT/FeNi [25]. The high disorders and defects are beneficial for producing high resistivity and to prevent formation of a conducting network, which will profit the impedence matching for microwave absorbers [26].

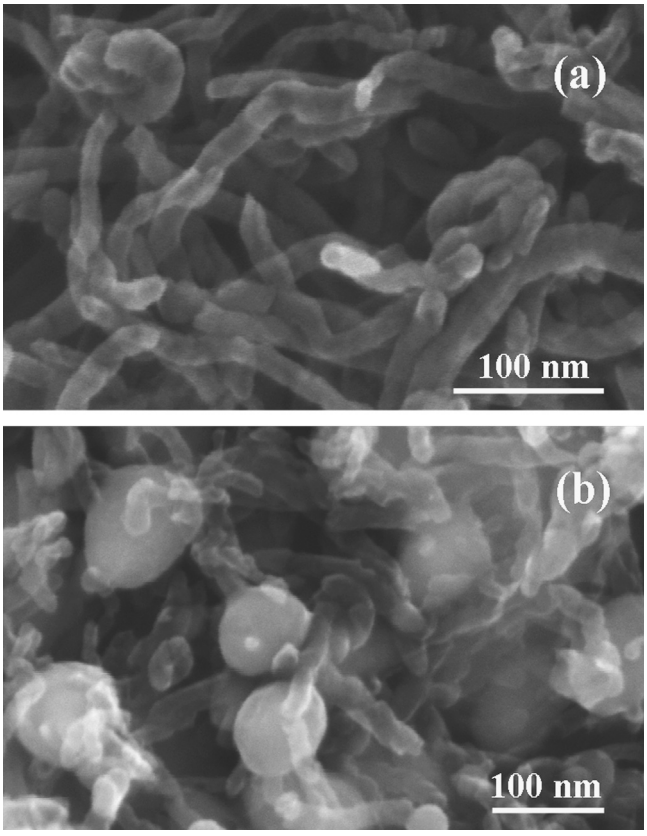

Fig. 2. SEM image of MWCNTs (a) and MWCNT/FeNi nanopowders (b).