Journal of Alloys and Compounds 509 (2011) 490–493

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Dielectric response of carbon coated TiC nanocubes at 2–18 GHz frequencies

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ARTICLE INFO

Article history:
Received 4 August 2010
Received in revised form 8 September 2010
Accepted 9 September 2010
Available online 22 September 2010

Keywords:
Dielectric response
Nanostructures

ABSTRACT

Microwave frequency (2–18 GHz) dielectric response has been investigated in the carbon-coated cubic TiC nanoparticles embedded in paraffin matrix with different weight fractions. DC conductivity measurements showed that the TiC nanocubes/paraffin composites have a percolation threshold of about 30 wt%. Absorption property was found to be improved with increasing mass ratio in the present system, up to a mass ratio of 50 wt%. Reflection loss exceeding −20 dB in the frequency range of 6–16 GHz, with layer thicknesses from 2 to 4 mm, was found in the 50 wt% loaded sample. TiC nanocube/paraffin composite with a proper mass ratio can be very good prospective microwave absorption agent.

1. Introduction

Anti-reflective coatings for microwave range were extensively investigated at least from the middle of 1940s in conjunction with stealth technology, and are now still under world-wide investigations, with the goal of broadening frequency range and strengthening absorption peaks [1–5]. The basic idea of anti-reflective/absorbing coatings is based on a coating with certain absorption, and the waves reflected from the front and the back of the coating will compensate each other due to interference [6]. Reflection loss (RL, in unit of decibel) of a single layer coating on metal is expressed by the well known transmission line theory [7],

$$\mathrm{RL} = 20\log_{10}\left|\frac{jZ\tanh(kd)-1}{jZ\tanh(kd)+1}\right|, \quad \text{with} \quad Z=\sqrt{\frac{\mu_r}{\varepsilon_r}} \quad \text{and}$$

$$k=\frac{2\pi f}{c}\sqrt{\mu_r\varepsilon_r}, \tag{1}$$

Here $\mu_r = \mu' - j\mu''$ and $\varepsilon_r = \varepsilon' - j\varepsilon''$ are materials constants: the complex permeability and complex permittivity, respectively, d is the absorption layer thickness, and f is the frequency of incident wave. The value of RL can be taken as a criterion of absorption properties, for example, an RL exceeding −20 dB corresponds to 99% attenuation, which means very good absorption.

Traditional technological approach of microwave absorption materials (MAM) was based on addition of micron size lossy powders (such as carbon black) in polymeric host [8]. However, drawbacks of micron size powders, such as high density and large thickness, have suppressed their practical applications. Also, as in micron size powders, the eddy current effects will prevent the microwaves from penetrating them and thus will decrease relative complex permeability of the absorbing materials at high frequencies [5]. On the desire of a new generation of MAM, nanocomposites have come out into physicists' sights in recent years, overcoming those shortcomings of traditional MAMs with broad absorption band, low density and good coupling of dielectric and ferromagnetic losses. Among these nanocomposites, dielectric-shell/magnetic-core structured nanocomposites (such as carbon coated 3d metal nanocapsules) are of particular interest in their dielectric multi-polarizations, because of their heterogeneous interface and the special core–shell structure [3,4,9].

In our previous work, non-magnetic carbon coated Sn nanorods are found to exhibit good RL due to their proper material constants [2], which has inspired us to explore new nano-absorbents with a non-magnetic nature. It is known that in heterogeneous material, charge accumulation at the interfaces between phases will take place when the product of dielectric constant and conductivity in each phase are different, namely, $\varepsilon_1\sigma_1 \neq \varepsilon_2\sigma_2$ [10]. This polarization, or more exactly, accumulation, may occur within a very short time if one phase has a high conductivity, and it is possible to anticipate this kind of interfacial relaxation at the microwave frequency region [11]. TiC and carbon are seldom combined into nanocomposites, but are both good conductors due to their band structures [12], and this, together with the interfacial structure between TiC and C, make it of great interest to investigate carbon coated TiC nanoparticles. In this paper, we report the microwave frequency dielectric permittivity of carbon coated cubic TiC nanoparticles embedded in paraffin matrix with different mass ratios. A percolation threshold of about 30 wt% was found in the present system by DC conductivity measurements, and the nanomixtures with a

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.09.074

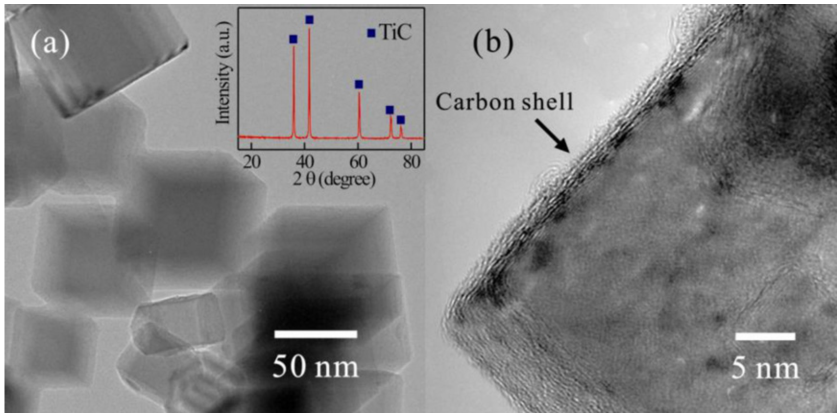

Fig. 1. (a) and (b) TEM images of the TiC nanocubes, inset of (a) shows the XRD pattern of the nanocubes.

proper mass ratio are found to exhibit good microwave absorption properties.

2. Experimental

The TiC nanocubes were synthesized by arc-discharging a Ti (99.9% in purity) target ingot in an atmosphere of ethanol (99.7% in purity). Details of the synthesis procedure can be found elsewhere [4]. The core–shell nanocubes were investigated by a transmission electron microscope (TEM, TECNAI F20) with an emission voltage of 200 kV. X-ray diffraction (XRD) data were recorded by a D/max 2500PC diffractometer with Cu Kα radiation at 50 kV and 300 mA. The specimens for the measurements of the complex permittivity and permeability were prepared by uniformly mixing the nanocubes and paraffin with an ultrasonic agitation while heating, and then mould these mixtures into toroidal shape with outer and inner diameters and a thickness of 7.00, 3.04, and 2 mm, respectively. Coaxial method was used to determine the EM parameters of the toroidal samples in a frequency range of 2–18 GHz using an Agilent 8722ES vector network analyzer (VNA) with a transverse electromagnetic mode. The complex permittivity and complex permeability were extracted from the two-port S-parameters tested by the calibrated VNA, using a simulation program for the Reflection/Transmission Nicolson–Ross model [13]. The TiC nanocube-paraffin mass ratio was initiated at 10 wt%, and increased with an interval of 10 percent up to a limit of 50 wt%, due to the viscous limit of the nano-inclusions in the paraffin matrix. DC conductivity measurements (by cutting the toroidal samples into rectangular cylinders) are performed with a standard four-point method using the Keithley 2400 SourceMeter.

3. Results and discussions

TEM images in Fig. 1(a) show that the nanoparticles are of cubic shape, having a size distribution ranging from 5 to 20 nm. It is seen from a magnified detail of a corner of the cube in Fig. 1(b) that the TiC nanocube is covered by a 2 nm thick carbon shell on its surface. Nanocapsules are commonly reported to have spherical forms, and very few investigations have been done on the cubic core–shell structured nanocomposite. XRD pattern in the inset of Fig. 1(a) shows that the as-prepared nanoparticles are indexed as a single phase of TiC. Fig. 2 shows the real and imaginary parts of the relative complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) of the TiC nanocube/paraffin samples with different mass ratios. It can be seen, for every mass ratios, that both ε' and ε'' show a general decreasing tendency in the 2–18 GHz, while their absolute values increase with increasing mass ratios. The shape of the present permittivity spectra is quite similar to, but with the value of ε' lower than the 50 wt% loaded Co/C nanocapsules in paraffin [9].

It is noticed that small fluctuations at certain frequencies can be found, as indicated by a magnified detailed fluctuation in the ε' curve of the 10 wt% sample in the inset of Fig. 2(a), in the permittivity spectra of TiC nanocubes/paraffin composite. Such oscillation-like behavior of measured material parameters may appear from improper calibration of the VNA [14]. Dielectric function $\varepsilon = \varepsilon' - j\varepsilon''$ in microwave frequency range is often described by a typical relation $g(\omega) = a + (b/1 + j\omega\tau)$, known as Debye relaxation [15], where a and b are material-dependent constants, τ the relaxation time, and $\omega = 2\pi f$ the angular frequency of the driven field. Here, the function $g(\omega)$ can represent for conductivity σ, or permittivity ε, etc. One may notice that the function can be written into a complex form of $g' = a + g''/(2\pi f\tau)$. This means that if there is only one relaxation type in the frequency range, the plot of ε' against ε''/f will have a uniform slope. It can be seen that the ε'–ε''/f plots in Fig. 3 show some tiny oscillations. However, the improper calibration may be the most probable reason for the oscillations shown in Fig. 3; with neglecting these oscillations the slopes of the curves seem to be quite linear. It is well established that for a composite with tiny metal powders, the microwave frequency-dependent behavior may be of Debye-like type relaxation. The characteristic frequencies of the dielectric dispersion may be estimated based on

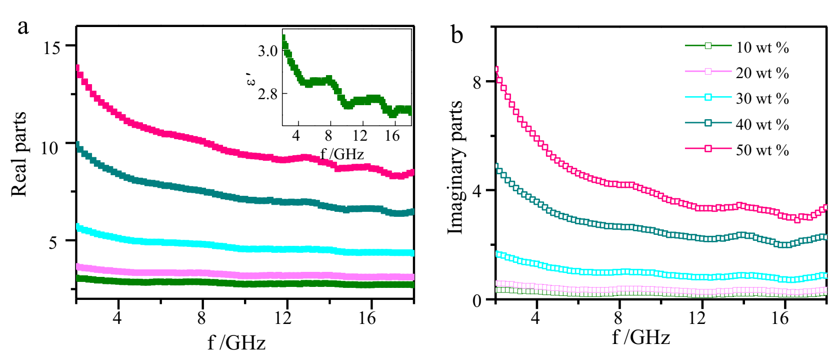

Fig. 2. Frequency dependence of the relative complex permittivity of carbon coated TiC nanocubes dispersed in paraffin with different mass ratios. Solid symbols and the open ones refer to the real and imaginary parts of ε_r, respectively. Inset in (a) shows a detailed fluctuation in the ε' curve of the 10 wt% sample (i.e. the lowest green line in (a)). (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)

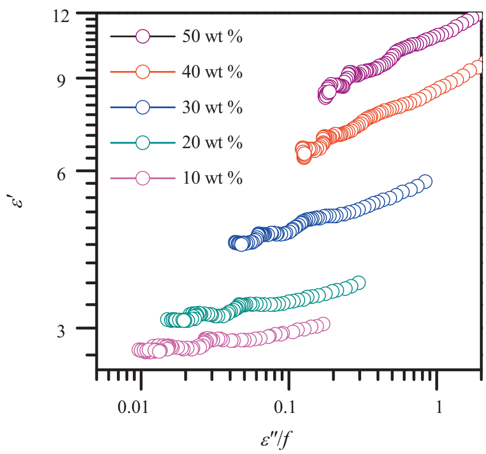

Fig. 3. $\varepsilon'-\varepsilon''/f$ plot of the 5 samples. To look into the details more clearly, the curves are plotted in log–log scale.

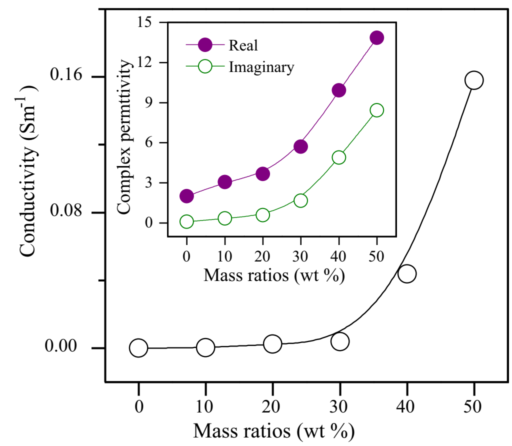

Fig. 4. DC conductivity of the TiC nanocubes/paraffin composites as a function of mass ratio. Inset shows the mass ratio dependence of the complex permittivity for the samples at 2 GHz. Solid lines are guides for eyes.

the RC model [16]. Taking carbon powders for example, the powder particles must have very elongated shape, in order to make the dispersion to fall into the microwave range [17]. The cubical TiC particles under consideration have the depolarization factor close to 1/3 and the Debye characteristic frequency must be located far beyond the microwave range. The microwave dielectric dispersion in composites can be explained by non-perfect electric contacts in large clusters or agglomerations of particles [18], which is very difficult to estimate.

An important fact is that the measured dielectric spectra in this study are of a sample which comprises of a huge number of TiC nanocubes embedded in paraffin matrix. Therefore, the measured data are collective behaviors or an integration of the intrinsic dielectric response of one single cube. With varying the mass ratios p (or volume fractions f), singularities of the real permittivity may be found near the percolation threshold p_C of heterogeneous materials, with the imaginary permittivity being continuous [19–21]. However, no singularity of the permeability has ever been observed near the percolation threshold. Liu et al. [6] reported the microwave absorption properties of CNTs/polyurethane composites with a layer thickness of 2 mm, which exhibited a maximum reflection loss (RL) value of −22 dB near its p_C. However, despite of a p_C at 5 vol%, a monotonic increase of the EM shielding effect with the volume fraction of the fillers up to 10 vol% was found in the mesoporous carbon/fused silica composites with a layer thickness of 5 mm [22]. Similar result was found in the Fe-catalyst contained carbon nanotube composites [23]. Actually, it is believed that absorption maximum may not be expected at percolation. The maximum loss appears only when an absorbing layer is perfectly matched (see, e.g., Refs. [24,25]). Fig. 4 shows the DC conductivity of the TiC nanocubes/paraffin composites as a function of mass ratios. It is observed that DC conductivity depends negligibly on p at concentrations below approximately 30 wt%, followed by an abrupt increase at p higher than 40 wt%. For the range of concentrations lower than 30 wt%, the resistivity is attributed to that of the host matrix, with negligible conducting path formed by TiC nanocubes. Hence, the percolation threshold of these composites is approximately 30 wt%. Inset of Fig. 4 shows the mass ratio dependence of the complex permittivity at a fixed frequency (taking 2 GHz for an example), which indicates an increasing tendency of the permittivity at a fixed frequency, starting from about 30 wt% (just around the p_C).

Due to the technological limit, the very small amount of nanopowders we have got is far less for carrying out direct measurement of the RL. However, it has been proved by many literatures that the directly-measured and calculated RL are in remarkable agreement [6,26], due to the same underlying physi-

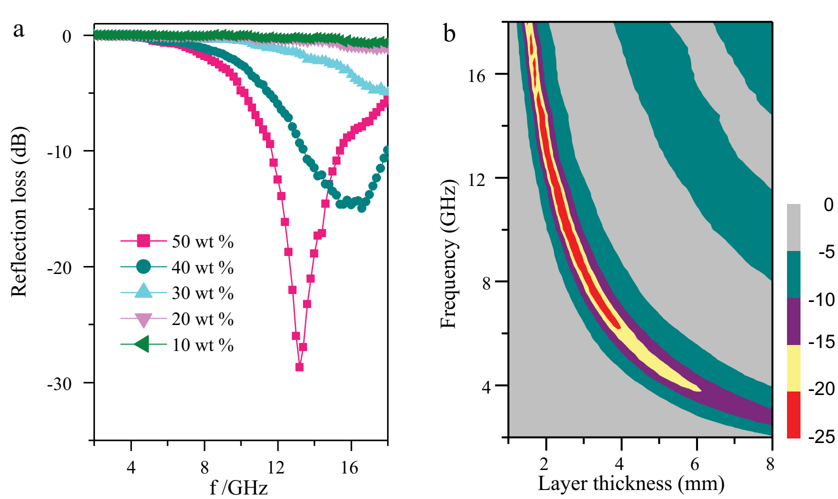

Fig. 5. (a) RL values for 2 mm thick layer of the TiC nanocube/paraffin composite with different mass ratios and (b) two-dimensional color map of the RL for 50 wt% loaded sample.

cal origin. According to Eq. (1), we have calculated the microwave absorption properties to investigate the application potential of the present nanocubes. Being a non-magnetic material, permeability of the TiC nanocubes is very close to 1 (not shown), which is almost the same as that of Sn/C-paraffin system [2]. It is interesting to notice that RL peak value of the present system is found to remarkably increase with increasing the mass ratios, beginning with nearly no absorption from 10 wt% to 30 wt%, and reaching RL values exceeding −10 dB in 40 and 50 wt% loaded samples. An illustration of RL for absorbent layer thickness of 2 mm with mass ratios from 10 to 50 wt% is given in Fig. 5(a). RL exceeding −20 dB (red region in Fig. 5(b)) can be found in the frequency range of 6–16 GHz, with layer thicknesses from 2 to 4 mm in the 50 wt% loaded sample. A detailed two-dimensional color map of RL for the 50 wt% loaded sample is shown in Fig. 5(b). Compared with other carbon-coated magnetic or non-magnetic nanoparticles or nanowires (e.g., Ni/C [27], FeCo/C [4], FeCoNi/carbon nanotubes [28], and Sn/C nanocapsules), the present carbon-coated TiC nanocubes exhibit quite different microwave absorption properties, which may be due to the special morphology of the cubic TiC nanocrystal encapsulated in a cubic carbon cage, the size of the TiC/C nanocapsules, and also the weight fraction of TiC nanocubes/paraffin composite. These above factors are possible to result in a good match of the absorbers, but we regret that a more detailed numerical model is too difficult to be handled at the current stage. Magnetic loss and dielectric loss are two main mechanisms of energy attenuation in materials. However, due to the non-magnetic nature, the present TiC/C system absorbs the microwave mainly by dielectric losses. The lossy behavior may become even more pronounced in the conducting-TiC and dielectric-carbon interfaces of the nanocubes [29]. As discussed above, TiC nanocubes embedded in paraffin with a proper mass ratio can be a good candidate for microwave absorption coatings.

4. Conclusion

In conclusion, complex dielectric permittivity in the 2–18 GHz range has been investigated in the TiC nanocube/paraffin composites with different mass ratios from 10 to 50 wt%. Percolation threshold of about 30 wt% was found in the present system by DC conductivity measurements. TiC nanocubes/paraffin composites are found to show increasing RL peak values with increasing mass ratios, up to 50 wt%. Reflection loss is calculated to be exceeding −20 dB in the frequency range of 6–16 GHz, with layer thicknesses from 2 to 4 mm, in the 50 wt% loaded sample. Carbon coated TiC nanocubes seems to be very good candidate for anti-reflective microwave absorption coating materials.

Acknowledgements

The authors are grateful to Prof. K.N. Rozanov for beneficial discussions. This work has been supported by the National Natural Science Foundation of China under Grant numbers 50831006 and 50701045, and by the National Basic Research Program (No. 2010CB934603) of China, Ministry of Science and Technology China.

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