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Controlled fabrication of TiC nanocrystal clusters on surface of Ti particles for application in electromagnetic wave absorption

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ABSTRACT

TiC nanoclusters densely grew on surface of metal Ti particles and were successfully prepared by a thermo-chemical reaction in acetone. The optimal synthesized conditions were 800 °C and 2.0 h under flowing acetone/Ar of 50 ml min^{-1}. The morphology, microstructure and constituent of as-prepared composites were characterized by complementary analytical techniques. The TiC nanoparticles/Ti-paraffin hybrids had distinct electromagnetic (EM) loss abilities in X-band. Theoretic analysis showed that the EM wave absorption behaviors obeyed impedance match and quarter-wave law. This work confirmed the as-prepared composites were promising candidates as EM wave absorbers.

1. Introduction

Due to the extensive application of electromagnetic (EM) waves, EM interference and radiation pollution problems are becoming more and more serious. Thus, researchers put a lot of attention on EM wave absorbing/shielding materials, which are widely used in equipment electromagnetic shielding, civil and military applications [1–3]. EM wave absorbing materials are generally consisted of EM wave transparent matrixes and absorbents to ensure a good impedance matching. The absorbents are usually classified, according to loss characteristics, into two kinds: dielectric and magnetic fillers. In recent years, the fillers with heterogeneous structure have come out into the researchers' eyes, because of their heterogeneous interface and multi-polarizations. Plenty of articles have been reported about magnetic/dielectric heterogeneous structured nanocomposites, such as metal (Fe or Ni)/oxide (SiO_2, Al_2O_3, B_2O_3, MnO_2, Y_2O_3) [4], $Fe_3O_4/CuSiO_3$ [5], Fe_3O_4/SiO_2 [6], NiO/SiC [1], FeCo/C/$BaTiO_3$ [7], etc, for application on EM wave absorption. Nevertheless, the applications of the magnetic materials are restricted in high-temperature environments due to their low Curie temperature [8]. Nonmagnetic/dielectric particles with heterogeneous structure, e.g. TiC/C nanocubes [9], Multi-walled carbon nanotubes (MWCNTs)/TiC [10], MWCNTs grafted Ag nanoparticles [11] and ZnO coated CNT [12], can offset the shortages of the magnetic materials and show good EM wave absorbing abilities, because of their dielectric multi-polarizations in heterogeneous interfaces. But little work in relation to TiC/Ti particles has been reported in detail on the synthesis, microstructure and properties.

As one of the representative dielectric materials, TiC is a kind of important EM wave absorbing material, due to its high melting point, low mass density, good electrical conductivity, and excellent environmental stability [9,13,14]. Lately, Huo et al. have reported that TiC nanomaterials on Ti foil were prepared by thermo-chemical reaction at 800 °C, in which used acetone as carbon source and Ti foil as Ti source and substrate [15]. On the basis of the above analysis, the TiC nanoparticles/Ti composites will be a possible candidate for EM wave absorption, due to the more interfaces and multi-polarization in heterogeneous interfaces that can be beneficial to attenuate of EM wave power.

In this paper, the TiC nanocrystals grown on surface of Ti particles were successfully fabricated by a simple one-step thermo-chemical reaction in acetone. The optimal synthesized conditions were determined and their morphology and microstructure were investigated in detail. The dielectric and EM absorption properties of the TiC nanocrystals/Ti-paraffin hybrids were investigated. The quarter-wavelength law and impedance matching map were constructed to obtain the matching absorbing thickness and the optimal reflection loss (RL). Meanwhile, the relevant loss mechanisms were also proposed herein.

2. Experiment section

The TiC nanocrystals grown on surface of Ti powders (99% in purity, −325 mesh, Alfa Aesar) were synthesized by a thermo-chemical reaction in acetone (99.7% in purity). A schematic illustration of the synthesized procedure is shown in Fig. 1. In a typical process, 2.0 g Ti powders full-flatted on graphite sheets were put into

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a horizontal tube furnace. The furnace was then heated to the target temperature x °C (x = 700, 800 and 900) with a rate of 3 °C min^{-1} under high-purity Ar (99.99%) atmosphere with a flow rate of 50 ml min^{-1}. When the setting temperature was reached, the Ar changed its route and acted as carrier gas to go through the acetone bottle placed in the ice water (0 °C) for carrying the acetone into the chamber by bubbling. The reaction proceeded for y h (y = 1.0, 2.0 and 3.0) and then Ar returned to its original route to protect the sample. Finally, TiC nanocrystals grown on surface of Ti particles were generated by a thermo-chemical reaction in acetone and denoted as TiC/Tip-x-y.

The surface morphologies were investigated by a field-emission scanning electron microscope (SEM, S4700). Transmission electron microscopy (TEM) measurements were conducted on a FEI Tecnai G2 F30 microscope operated at 300 kV. The samples were dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. The X-ray diffraction (XRD) patterns were achieved using a Philips X'Pert PRO X-ray diffraction system (Cu Kα radiation, 0.15406 nm). Raman spectrum was performed on a micro-Raman spectroscopy (Renishaw, Gloucestershire, UK) with the excitation wavelength of 514 nm. Wave-guide method was used to determine the EM parameters of the cuboid (22.86 mm × 10.16 mm × 2.0 mm) hybrids by a vector network analyzer (VNA, MS4644A, Anritsu, Atsugi, Japan) in a frequency range of 8.2–12.4 GHz (X-band). The specimens for obtaining the EM parameters were prepared by uniformly mixing the as-prepared powder and paraffin in n-hexane solution under an ultrasonic agitation. While the n-hexane volatilize, the mixture was pressed with dimensions of 22.86 mm × 10.16 mm × 2.0 mm using cuboid mould. The mass ratio of as-prepared powder in paraffin hybrid was initiated at 50 wt%, and increased with an interval of 10 percent up to a limit of 70 wt%.

3. Results and discussion

3.1. Morphology and microstructure

Fig. 2 shows SEM images of the TiC nanocrystals/Ti composites at different reaction parameters. It can be seen that the TiC grains growth started at 700 °C, when the reaction time was 2.0 h. TiC grain liked a small burr about 25 nm and grew on the surface of the Ti particles uniformly but sparsely (shown in Fig. 2a). When the reaction temperature increased to 800 °C, the pyrolysis of acetone and the reactivity of Ti all intensified. In this case, abundant TiC nanoparticles with the size of around 320 nm were on surface of metal Ti particles (shown in Fig. 2b). In Fig. 2c, the size of TiC nanoparticles obviously grew up and was about 900 nm at 900 °C. Thus, the optimal reaction temperature was 800 °C under flowing acetone/Ar of 50 ml min^{-1}. Meanwhile, the roughish mass ratio values of the synthesized TiC in TiC/Tip composites at different reaction parameters were calculated by weight method:

$$\frac{m_{TiC/Ti} - m_0}{m_{TiC/Ti}} \times 100\%,$$

where m_0 is 2.0 g Ti powders and $m_{TiC/Ti}$ is the mass of TiC/Ti composites. The results were 1.4 wt% for TiC/Tip-700-2, 6.4 wt% for TiC/Tip-800-2 and 7.8 wt% for TiC/Tip-900-2.

The effect of reaction time on morphologies was discussed at 800 °C (shown in Fig. 2d–f). When the reaction time was 1.0 h, there were sparse TiC grains on surface of metal Ti particles. With gradually increasing the reaction time to 2.0 h, plenty of TiC nanoparticles uniformly grew up. However, excessively long reaction time (3.0 h) led to PyC coated on the surface of TiC nanoparticles, which was clearly observed from the high-magnification image (the inset in Fig. 2f). The average sizes of TiC nanoparticles were about 140 nm for TiC/Tip-800-1 and 430 nm for TiC/Tip-800-3, respectively. Finally, the typical parameters for TiC nanoparticles densely grown on surface of metal Ti composites were 800 °C and 2.0 h under flowing acetone/Ar of 50 ml min^{-1}.

To detail analysis, SEM and TEM images of the TiC/Tip-800-2 composite at different magnifications are shown in Fig. 3. SEM and TEM images with low magnification (shown in Fig. 3a and c) represented the overall morphology of the TiC/Tip-800-2 composite. TiC nanoparticles uniformly and densely grew on the surface of metal Ti particles. From the high magnification image (indicated in Fig. 3b), it was clear to see that the combination of TiC nanoparticles and Ti matrix was tight. Their microstructures were obvious from HR-TEM images and fast Fourier transforms (FFT) results: TiC nanocrystals with clearly-defined lattice fringe edges shown in Fig. 3d and clear electron diffraction spots in the FFT pattern indicated in Fig. 3e. From the inset in Fig. 3d, the spacing between two adjacent lattice fringes was 0.243 nm, as (1 1 1) planes of TiC. The corresponding FFT pattern exhibited electron diffraction spots and rings and all of them are indexed to the diffraction planes of TiC nanocrystals, which were in good agreement with the result of XRD pattern discussed below.

The crystal structure of TiC/Tip-800-2 was characterized by XRD. The diffraction peaks were indexed to the face-centered cubic (fcc) TiC phase according to the JCPDS 65-8805 (shown in Fig. 4a) except the metal Ti phase diffraction peaks. Using the Scherrer formula $D = 0.89\lambda/(\beta \cos\theta)$ [16], the mean grain size of TiC estimated from the XRD patterns was about 7.8 nm. This result was in good agreement with that of HR-TEM. As Raman is more sensitive to the composition on the surface, the peaks at around 258, 407 and 609 cm^{-1} (shown in Fig. 4b) were the characteristic TiC Raman features [13,15]. Meanwhile, two small peaks which were the typical features of amorphous carbon, namely the D-peak located at around 1350 cm^{-1} and the G-peak centered around 1578 cm^{-1}. This result indicated that a handful of carbon were in the as-synthesized TiC/Tip materials.

3.2. Dielectric and electromagnetic wave absorbing properties

As is known to all, the real part (ε') and imaginary part (ε'') of relative complex permittivity represent the energy storage ability and loss ability, respectively. Fig. 5a and b show the ε' and ε'' of the TiC/Tip-800-2 dispersed in paraffin hybrids with different mass ratios at X-band. The values of ε' and ε'' had a remarkable increase with the increasing mass ratios: the average values of ε' and ε''

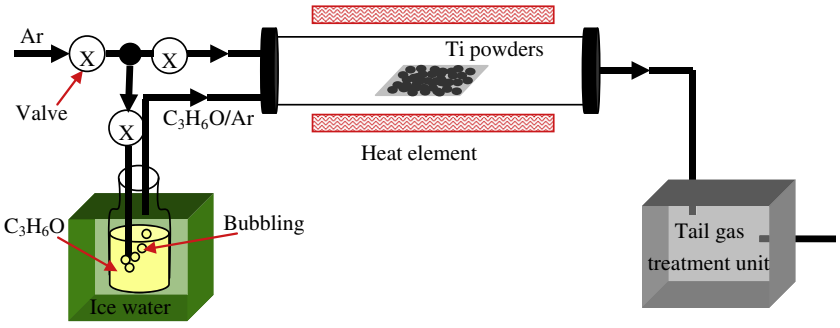

Fig. 1. Schematic illustration of the experimental apparatus.