Journal of the European Ceramic Society 38 (2018) 1639–1646

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Electrical conductivity, dielectric and microwave absorption properties of graphene nanosheets/magnesia composites

Cheng Chen[a,b,1], Limei Pan[a,b,1], Senchuan Jiang[a,b], Shuang Yin[a,b], Xiaoyun Li[a,b], Jingxian Zhang[c], Yongbao Feng[a,b], Jian Yang[a,b,*]

[a] Jiangsu Collaborative Innovation Center For Advanced Inorganic Function Composites, China
[b] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China
[c] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

ARTICLE INFO

Keywords:
GNSs/MgO composite
Electrical conductivity
Dielectric property
Microwave absorption property

ABSTRACT

Herein, a novel microwave absorbing material with Graphene nanosheets (GNSs) as microwave absorbing filler and magnesia (MgO) as matrix were prepared by hot-pressing sintering. The composites were highly dense with a homogeneous distribution of GNSs. Electrical conductivity, dielectric and microwave absorption properties in X-band were investigated. The results revealed that the electrical conductivity of the GNSs/MgO composites showed a typical percolation-type behavior with a percolation threshold of 3.34 vol%. With GNSs content increased to 3 vol%, the real permittivity, imaginary permittivity and dielectric loss tangent of the composites increased from ~9, ~0 and ~0 to 26–43, 23–28 and 0.55–0.96, respectively. By adjusting the GNSs content, thickness and frequency, the 2.5 vol% GNSs/MgO composite shows the minimum reflection loss of −36.5 dB at 10.7 GHz and the reflection loss below −10 dB (90% absorption) ranges from 9.4 to 11.4 GHz with 1.5 mm thickness, exhibiting excellent microwave absorption properties.

1. Introduction

With the fast development of microwave communication technology, microwave absorbing materials are playing an increasing important role in the field of anti-electromagnetic interference, wireless communication and military equipments [1–5]. At present, most microwave absorbing materials consist of polymer matrix and various microwave absorbing fillers [6]. In comparison, microwave absorbing materials with ceramics as matrix exhibit unique superiority of good durability at room and high temperature. For example, AlN [7], Al_2O_3 [8] and SiBCN [9] based microwave absorbing materials have been developed to satisfy the requirements of application in some special fields. Magnesia (MgO), an environment-friendly material with high melting point (~2800 °C), high thermal conductivity (about 60 W/(m K) at 25 °C and 13 W/(m K) at 1000 °C), insulation performance, good chemical stability, high thermal shock resistance, jointly with superior dielectric property ($\varepsilon \sim 9$, $\tan\delta \sim 10^{-4}$ at 25 °C, 10^6 Hz) [10–13], is expected to be an ideal candidate for ceramic matrix of microwave absorbing materials. Jia et al. [13] reported the dielectric and microwave attenuation property of SiC/MgO composite ceramics with SiC as the attenuation phase in X-band. With the increase of SiC content, the dielectric constant, dielectric loss and effective attenuation bandwidth increase, and the resonance peak shifts to the lower frequency.

Owing to the high electrical conductivity, the carbon materials, including graphite, carbon black, activated carbon, pyrolytic carbon (PyC), carbon nanotubes (CNTs) and carbon fiber (CF) [14–19], show good microwave absorption properties as absorbing fillers of various polymer and ceramic matrix microwave absorbing materials. Wen et al. [16] has reported the excellent microwave absorption property of CNTs/SiO_2 composites in X-band. The minimum reflection loss (RL) value of the composites filled with 5 wt% CNTs is −74.8 dB at 8.6 GHz. Huang et al. [14] investigated the effect of CF on the dielectric and microwave absorption properties of Al_2O_3 ceramics with MgO additive, and found that both the real permittivity (ε') and imaginary permittivity (ε'') of the composites increase with increasing CF content in X-band, the minimum RL value reached −44 dB at 9.8 GHz when the CF content is 0.3 wt%. Graphene, the new member of carbon materials family, has shown extraordinary properties including outstanding electronic transport with a room-temperature electron mobility of 2.5×10^5 $cm^2/(V\,s)$ [20], unique mechanical properties with a Young's modulus of 1 TPa, an intrinsic flexural strength of 130 GPa and a

* Corresponding author at: College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China.
E-mail address: yangjian1976@163.com (J. Yang).
[1] These two authors contributed equally to this work.

https://doi.org/10.1016/j.jeurceramsoc.2017.11.052
Received 3 August 2017; Received in revised form 16 November 2017; Accepted 23 November 2017
Available online 24 November 2017
0955-2219/

stiffness of 1060 GPa [21], jointly with an ultrahigh thermal conductivity of 5300 W/(m K) [22]. Compared with the monolayer graphene, graphene nanosheets (GNSs) consist of several layers of graphene and have a thickness up to 100 nm. As a potential reinforcing and conductive nanofiller, GNSs have been incorporated into many oxide and non-oxide ceramics, e.g., Al_2O_3 [23–25], SiO_2 [26], ZrO_2 [27], SiC [28–31], B_4C [32], TaC [33], TiC [34], Si_3N_4 [35–37], AlN [38–40], TiN [41], ZrB_2 [42] and SiBCN [43], which significantly improved the mechanical and electrical properties of these ceramic materials. The alumina composites containing 0.5 wt% GNSs showed a 72% increase in fracture toughness [23]. Belmonte et al. [29] reported a 70% increase in flexural strength for 5 vol% GNSs/SiC composite. The electrical conductivity of the GNSs/AlN composite increased by eight orders of magnitude with 10 vol% GNSs addition, which showed a typical percolation phenomenon with a threshold of 2.5 vol% [40]. Recently, the dielectric properties and microwave absorption properties of GNSs-containing composite have been paid much attention [44–48], showing the great potential of GNSs as microwave absorbing fillers. Luo et al. [48] found that superior dielectric property can be obtained in graphene/barium titanate nanocomposites, the dielectric constant and dielectric loss tangent of the composites increase from about 2400 and 0.02 to 3600 and 0.05 with the graphene content increasing from 0 to 3 wt%, respectively, in the frequency of 40–10,000 Hz. Li et al. [44] reported the excellent microwave absorption property of reduced graphene oxide (RGO)/barium aluminosilicate composites in X-band, the minimum reflection loss (RL) reached −43 dB at 11.7 GHz with 1.5 wt % RGO addition. Qing et al. [8] reported the minimum RL of −24 dB at 9.8 GHz for 1 vol% GNSs/Al_2O_3 composites. Therefore, it is reasonable to predict that the hybrid composite of GNSs and MgO will show excellent microwave absorption properties, which has not been reported so far.

In our previous work [49], highly dense GNSs/MgO composite ceramics with GNSs content up to 7 vol% were prepared by hot-pressing at 1700 °C for the first time, which showed an increase of 37.3% and 32% in flexural strength and fracture toughness, respectively. In addition, the thermal physical properties, including thermal conductivity at elevated temperature up to 1000 °C were also investigated. Owing to the relatively high thermal conductivity of MgO (about 60 W/(m K) at 25 °C and 13 W/(m K) at 1000 °C), the GNSs/MgO composite ceramics show relatively high thermal conductivity. Taking the 7 vol% GNSs/MgO sample as example, its room-temperature thermal conductivity is 33.9 W/(m K), which is higher than that of 7 vol % GNSs/Al_2O_3 composite ceramic (27 W/(m K)) [50]. In this work, focusing on the microwave absorption properties, the electrical conductivity and complex permittivity (8.2–12.4 GHz, X-band) as a function of GNSs content were investigated. Based on this, the reflection loss depending on the electromagnetic parameters, thickness and frequency was calculated and optimized, which renders GNSs/MgO composites a promising prospect as microwave absorption or attenuation materials.

2. Experiment

2.1. Preparation of GNSs/MgO composites

The detailed preparation process can be found in our previous work [49]. To be brief, GNSs (5 μm in lateral size and 20 nm in thickness, The Sixth Element Materials Technology Co., Ltd., China) was firstly dispersed in 1-Methyl-2-pyrrolidone (Sinopharm Chemical Reagent Co., Ltd, China) by ultrasonication for 1.5 h. Simultaneously, MgO powders (≥98.0% purity, AR, Xilong Chemical Co., Ltd, China) were ground by a planetary mill using ethanol (≥99.7% purity, AR, Wuxi City Yasheng Chemical Co., Ltd, China) as medium for 4 h at 230 rpm with ZrO_2 balls. Then the resulting MgO slurry was mixed with the GNSs suspension, which was followed by another grinding for 2 h at 200 rpm. After filtration, drying at 80 °C and sieving through a 60 mesh sieve, the resulted mixed powder was placed into a graphite mold pre-sprayed with a layer of BN and pre-compacted (pressure: 2 MPa). Then the compacted mixture was heated to 1700 °C with a rate of 20 °C/min and hot-pressing sintered for 1 h under the pressure of 30 MPa in a flowing Ar atmosphere, which was followed by furnace cooling down to room temperature. The sample without GNSs was prepared following the same process without using GNSs suspension.

2.2. Tests and characterization

The phase composition of the sintered bodies was identified by X-ray diffraction (XRD; ARL X'TRA, Thermo Electron SA, Switzerland) using Cu-Kα radiation with the step of 0.02° and scanning rate of 10°/min over the 2θ range from 20° to 80° at 40 kV and 30 mA. The microstructure of the polished and thermally etched surface of the samples was observed by scanning electron microscope (SEM, JSM-5900, JEOL, Japan). A high-resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL, Japan) was used to characterize the microstructure of the 5 vol% GNSs/MgO composite at an operation voltage of 200 kV.

The sintered samples were cut by precision cutting saw (SYJ-200, Shenyang Kejing Co., Ltd, China) and polished by sandpapers with the mesh order of 800, 1500, 3500 and 5000 by precision lapping machine (UNIPOL-830, Shenyang Kejing Co., Ltd, China) for electrical conductivity and dielectric property test. Two methods were applied for the room temperature electrical conductivity measurements of the as-prepared samples because of the large variation in electrical conductivity of the samples as a function of the content of GNSs. High resistance meter (ZC-90E, Guangzhou 4 Probes Tech, China) was used for the almost insulated samples with a GNSs content of 0, 1, 1.5, 2 and 2.5 vol %, whereas four-probe tester (RTS-9; Guangzhou 4 Probes Tech, China) was used for the samples with a GNSs content of 3, 4, 5 and 7 vol%. The complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) in X-band with the sample dimensions of 22.86 × 10.16 × 2.5 mm^3 was measured by a vector network analyzer (PNA-N5244A, Agilent, USA) using the wave-guide method.

3. Results and discussion

3.1. Sintering properties and microstructure

Fig. 1 shows the XRD patterns of monolithic MgO ceramic and GNSs/MgO composites. It can be seen that all the diffraction peaks of MgO were well indexed to the cubic phase with the space group *Fm*-3m (PDF#89-7746, a = b = c = 4.22 Å), and the narrow sharp peaks suggest a high crystallinity of MgO grains. The diffraction peak located at 26.6° is attributed to graphene, which shows an increased intensity with the increase of GNSs content. From Fig. 1b, the diffraction peaks of GNSs can be observed clearly, whose intensity increases with the increasing addition of GNSs.

In our previous work, we have found that incorporating GNSs inhibited the sintering and grain growth of MgO and produced a significant strengthening and toughening effect [49]. Moreover, on the whole, the as-prepared 0–7 vol% GNSs/MgO composites show a quite high density with an apparent porosity lower than 0.24%. There is no obvious pores in monolithic MgO ceramic and GNSs/MgO composites. GNSs were homogeneously distributed along the grain boundaries of MgO. SEM micrographs of the polished and hot-etched surface of the samples were shown in Fig. 2, which indicate clearly again that all the samples are highly dense and the incorporated GNSs significantly inhibited the grain growth of MgO. It can be seen that, with the GNSs content increasing from 0 to 7 vol%, the average grain size of MgO decreases gradually from about 50 μm to 6 μm. The TEM and HRTEM images of 5 vol% GNSs/MgO composite are shown in Fig. 3. The images reveal that the GNSs semi-wrap around the MgO grains without any gap or interlayer and connect with each other to form a network structure. It can also be clearly seen that only a very small fraction of overlap exists in the MgO grain boundary, which indicates the effectiveness and