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Microstructure and fracture toughness of graphene nanosheets/alumina composites

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Abstract

Graphene nanosheets (GNS)/alumina composites were fabricated by hot pressing. The microstructure and mechanical properties are apparently influenced by the addition of GNS. In particular, the fracture toughness of the composites improves notably. The maximum value is 6.6 MPa $m^{1/2}$ for the 0.2 wt% GNS/alumina composite, which is about 43.5% higher than that of the monolithic. The main toughening mechanisms are crack deflection, crack bridging, crack branching and the pullout of GNS.

Keywords: B. Composites; Alumina; Graphene nanosheets; Toughening

1. Introduction

Since 2004, when Novoselov et al. successfully exfoliated graphene by the Scotch tape method [1], graphene has drawn considerable attention due to its impressive mechanical, electrical and thermal properties [2–4]. Graphene nanosheets (GNS) [5] consist of several layers of graphene, which are also named graphene platelets (GPLs) [6], graphene nanoplatelets (GNPs) [7,8], multilayer graphene nanosheets (MGN) [9] or few-layer graphene (FG) [10,11] in the literature. Just as graphene, GNS possesses a large specific surface area and exceptional mechanical properties; therefore they have been taken as good fillers in polymers and ceramics.

Similar to their allotropes, i.e. carbon nanotubes, GNS were added into polymers to increase their mechanical properties and electrical conductivity at first. Zhao et al. reported an improvement of 150% in the tensile strength of poly(vinyl alcohol) composite with 1.8 vol% graphene nanosheets as fillers [12]. Ramanathan et al. employed solution-based procedures to fabricate GNS/PMMA, which had a 133% increase in room temperature modulus with the addition of 5 wt% GNS [13]. Polystyrene/GNS composites were prepared by a solution blending method, and the electrical conductivity was sharply increased, from approximately 10^{-14} S m^{-1} for the pure to 5.77 S m^{-1} for the composite with 0.38 vol% GNS [14].

Recently, researchers paid more attention to ceramics with incorporating GNS and mainly focused on the electrical properties. GNS/Si_3N_4 fabricated by Ramirez et al. [15] possessed the highest electrical conductivity (about 40 S cm^{-1} by dispersing 25 vol% of GNS) hitherto for Si_3N_4-based ceramics. And the conductivity ratios showed a visible anisotropy, more than one order between the directions perpendicular and parallel to the SPS pressing axis. Then the group synthesized graphene/Si_3N_4 composites by in situ reduction of graphene oxide (GO) during SPS [16]. The composite with 7 vol% reduced-GO exhibited large electrical conductivity value, reaching 7 S cm^{-1}. Fan et al. prepared GNS/Al_2O_3 composites with ball-milling expanded graphite and the electrical conductivity outperforms most of CNT/Al_2O_3 composites, up to 5709 S m^{-1} when incorporating 15 vol% GNS [17]. They also produced well dispersed GNS/Al_2O_3 composites using a colloidal processing route, with GO

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colloid and alumina colloid added dropwise to each other [10]. The electrical conductivity achieved 10^3 S m^{-1} when GNS content was only 2.35 vol%. GNS/Al_2O_3 presenting high electrical conductivity (up to 172 S m^{-1}) were also fabricated with introducing GO, reduced by hydrazine monohydrate, into Al_2O_3 matrix by Wang et al. [18].

In these three years, some reports began to focus on the use of GNS as fillers to improve the mechanical properties of ceramics. Walker et al. applied aqueous colloidal processing methods to prepare GNS/Si_3N_4 composites and the fracture toughness reached 6.6 MPa m$^{1/2}$ for the 1.5 vol% GNS/Si_3N_4, which is ~235% higher than the monolithic [19]. Dusza et al. and Kvetková et al. also demonstrated the toughening effect of GNS to the Si_3N_4 matrix [20–22]. In addition, some other researchers reported the improvement of other mechanical properties, such as bending strength [23], elastic modulus [24] and tribological properties [25].

Up to now, however, there have been only few reports about the toughening of GNS to the Al_2O_3 ceramics. Porwal et al. prepared Al_2O_3–graphene composites using liquid phase exfoliation graphenes and dispersed them into alumina matrix using an ultrasonication and powder processing route [26]. The fracture toughness increased by 40% with the content of graphene as low as 0.8 vol%. Liu et al. found 30.75% improvement of flexural strength and 27.20% increase of fracture toughness for the GNS/Al_2O_3 composites than the monolithic [27].

The aim of the present work is to investigate the influence of the addition of GNS on the microstructure development and fracture toughness of GNS/Al_2O_3 composites.

2. Material and methods

Commercial α-Al_2O_3 power (Hangzhou Wanjing New Material Co., Ltd., China) with a high purity of 99.99%, an average particle size of 500 nm and a surface area of 4–10 m^2 g^{-1} was selected as raw material. The fillers, GNS, were purchased from Nanjing XFNANO Materials Tech Co., Ltd. And the thickness of the GNS is about 1–5 nm.

The GNS were dispersed in the N-Methyl-2-pyrrolidone (NMP) through ultrasonication 2 h and dissolved at concentration of 5 mg/ml. After ball milling for 8 h, the α-Al_2O_3 powder was mixed with the GNS suspension, then continued to ball mill for another 4 h. The slurry was dried at 120 °C and screened in a 100-mesh sieve. The batches were hot pressed at 1500 °C in a multipurpose high-temperature furnace (Fujidenpa Kogyo Co., Ltd., Osaka, Japan) under a pressure of 25 MPa in argon atmosphere for 1 h. And different amounts of GNS were added into the batches (0, 0.1, 0.2, 0.5 and 1 wt%) and the corresponding composite was denoted as AG0, AG0.1, AG0.2, AG0.5 and AG1, respectively.

Three-point bending strength of the bar specimens (3.0 mm × 4.0 mm × 25 mm) was measured with a span of 20 mm at a crosshead displacement speed of 0.5 mm min^{-1}. Before the test, the edges of all the specimens were chamfered to reduce the influence of stress concentration due to machining defects. In addition, the fracture toughness (K_{IC}) of specimens (2.0 mm × 4.0 mm × 25 mm) was evaluated by the single-edge notched beam (SENB) method. Notches of 2.0 mm in depth were introduced by diamond blades of 0.3 mm in width. A minimum number of five specimens were tested for each group. The bending strength and fracture toughness tests were all conducted on a CMT5105 electromechanical universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, Guangdong, China). After polishing, the samples were prepared to be thermally etched at 1300 °C for 30 min dwell time in a muffle furnace for grain size study. The grain size was evaluated by the linear intercept method. The images used to calculate the grain size were magnified 5000 times by SEM. Ten lines in each SEM image were drawn and then count the number of grain boundaries in each line. Typically three image were chosen and more than 300 grains were covered for each sample to calculate the grain size.

Moreover, Archimedes' method was employed to measure the bulk density of the prepared samples in distilled water and the theoretical density was calculated by a rule of mixtures, where the theoretical densities for Al_2O_3 and GNS were 3.97 and 2.1 gcm^{-3} respectively.

The morphology of GNS in the matrix and the microstructure of the composites were examined via a SU-70 type thermal field emission scanning electron microscope (FESEM). A JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM) was employed to investigate the microstructure and bonding between GNS and Al_2O_3 matrix by grinding the composites into powders.

3. Results and discussion

3.1. Mechanical properties of sintered samples

As shown in Table 1, all the composites have density above 98% of the theoretical value, even though the density is a little decrease compared with the monolithic. With the addition of GNS, the densities of the composites reduce slightly, as Table 1 describes.

Fig. 1 are plots of the calculated bending strength and fracture toughness values for the GNS/Al_2O_3 composites, shown as a function of GNS content from 0, 0.1, 0.2, 0.5 to 1 wt%. In our composites, the bending strength and fracture toughness simultaneously increase with the addition of a small amount of GNS. The bending strength of the sample containing 0.1 wt% of GNS (Fig. 1a) reaches maximum value, about 542 MPa, which is about 30% higher than the monolith (416.5 MPa). The increment is mainly attributed to the grain refinement, since the large specific surface area of the GNS inhibits the growth of alumina grains.

Table 1
Relative density and grain size of AG0, AG0.1, AG0.2, AG0.5 and AG1.

GNS composition (wt%)	Relative density (%)	Average grain size (μm)
0	99.5	2.51 ± 0.54
0.1	99.2	1.98 ± 0.26
0.2	99.0	1.90 ± 0.18
0.5	98.6	2.13 ± 0.20
1	98.1	2.07 ± 0.33

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