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Short communication

Reinforcement of alumina matrix with multi-walled carbon nanotubes

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Abstract

A colloidal processing route was adopted to disperse multi-walled carbon nanotubes (MWNTs) into alumina powders homogenously. One weight percent MWNTs–alumina composites were prepared by hot pressing. It was found that when the sample was sintered at 1450 °C, the addition of carbon nanotubes (CNTs) led to 10% increase in bending strength compared with monolithic alumina. The reinforcement mechanism was discussed based on the microstructure investigation. The broken nanotubes and pullout of MWNTs at interfaces are efficient in transferring the load from the alumina matrix to the nanotubes, leading to the improvement of the mechanical properties.

Keywords: B. Nanocomposites; C. Mechanical properties; D. Alumina

1. Introduction

Carbon nanotubes (CNTs) have exceptional mechanical properties, with elastic moduli of the order of 1 TPa or slightly more [1] and fracture strains are estimated to be 10–30% [2]. These properties together with their chemical stability suggest that nanotubes might be suitable as a novel fiber material for nanocomposites. Many applications of CNTs used as reinforcing additive fibers in polymers and metals [3–5] have been proposed. Several recent experiments on the preparation and mechanical characterization of CNT–ceramic composites have been reported [6–13]. The mechanical properties, mainly fracture toughness measured by Vickers indentation, suggest modest enhancements of CNT-embedded matrices compared to the unreinforced ceramic matrices. However, these fracture toughness data [8,12] varied much from 4.2 to 9.7 MPa $m^{1/2}$ for an alumina matrix, which is unusual for typical ceramic materials. The following might be the possible reasons. First, the mechanical properties are closely related to the quantity and quality of CNTs, but also depend on the processing which determines the dispersion/orientation and the interfacial bonding states. Second, the fracture toughness is calculated from the length of the cracks and the measurement varied depending on the measurer. Third, for the composites that contained a high amount or an inhomogeneous distribution of CNTs, fracture toughness would be difficult to measure because of the irregular shape of the cracks and very short or even no cracks around regions of aggregated nanotubes. The first issue can be solved by strict control of the quality and dispersion state of CNTs, which is not the concern of this paper. For the second and third problems, if the bending strength of the CNT–ceramic composites could be measured, it would be more objective to evaluate the mechanical properties of materials. In this paper, CNT–alumina composites containing 1 wt% multi-walled carbon nanotubes (MWNTs) were fabricated by hot pressing, and both the fracture toughness and the bending strength were measured and compared with those of the monolithic alumina matrix.

2. Experimental procedure

Multi-walled carbon nanotubes prepared from catalytic decomposition of CH_4 were kindly provided by Chengdu

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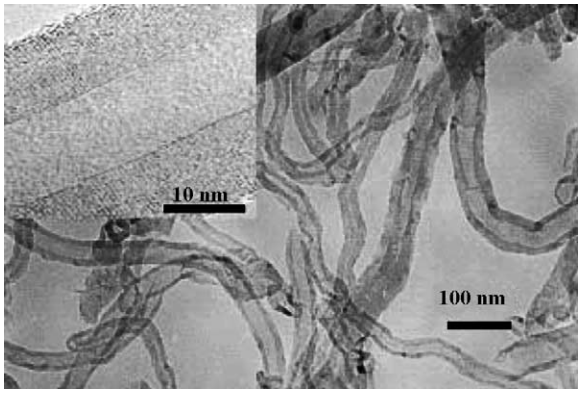

Fig. 1. TEM and HRTEM images of MWNTs.

Institute of Organic Chemistry, China. Fig. 1 shows the transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images of MWNTs. The MWNTs have lengths ranging from several 100 nm and the inner diameter is around 10 nm. The inserted HRTEM image clearly shows that nanotube is multi-walled, with approximately 25–30 walls of graphitized carbon layer.

A colloidal processing route [10] was adopted to make the distribution of MWNTs more homogenous. MWNTs were dispersed in dilute solutions with 300 ppm polyethylene amine (PEI; Mw 50,000; BDH Laboratory) as dispersant. 0.04 g alumina with particle size of 200–300 nm (Taimei Chemical Co. Ltd., Japan) was dispersed in 100 mL deionized water with polyacrylic acid (PAA; Polymer Sciences, PA) as dispersant. The prepared dilute alumina suspension was added dropwise into the vigorously stirred carbon nanotubes suspension. The coated carbon nanotubes collected from this suspension were subsequently added to a concentrated alumina suspension of about 50 wt% in ethanol so that the final content of MWNTs was 1 wt% of the amount of alumina. Further drying and grinding produced the CNT–alumina composite powder. From Fig. 2, it can be seen that the surface of MWNTs was coated by alumina particles due to the heterogeneous reaction and the two components are distributed homogenously. The composite powders were hot pressed to 30 MPa under an Ar atmosphere in a graphite die with a diameter of 50 mm at 1350, 1400, 1450 and 1500 °C for 1 h. Pure alumina was hot pressed under the same conditions to compare the mechanical properties. The bulk densities of the sintered samples were measured by the Archimedes method and all the samples reached full density. The hardness of the composites was measured using a Vickers hardness tester (AVK-A) with a load of 98 N applied on the surface for 10 s. The fracture toughness was calculated by the Antis equation [14]. Four or five testing bars were adopted to measure the bending strength by the three-point bend test.

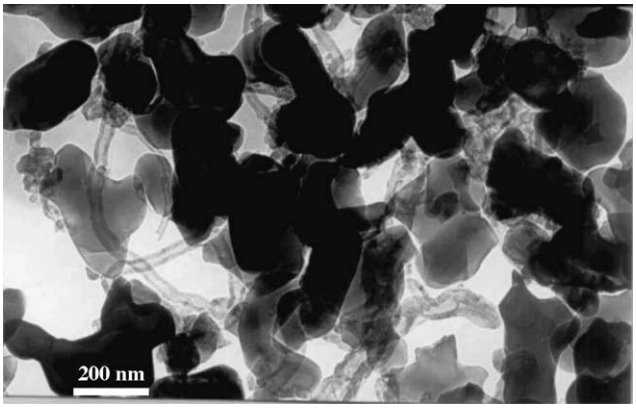

Fig. 2. TEM image of the MWNTs–alumina composite powders.

3. Results and discussion

Table 1 shows the fracture toughness and bending strength of 1 wt% MWNTs–alumina and monolithic alumina ceramics. It can be seen that both the fracture toughness and bending strength varied with the sintering temperature. The highest fracture toughness value of the 1 wt% MWNT–alumina composite is 4.0 MPa $m^{1/2}$, and that of monolithic alumina is 3.9 MPa $m^{1/2}$, almost the same within experimental error range. The maximum bending strength obtained from the composite is 554 MPa after sintering at 1450 °C, while it was 496 MPa for alumina matrix sintered at 1300 °C. This is about a 10% increase in strength for the composite compared with the alumina. A similar improvement on hot pressed SiC was reported previously [6]. Though the increase is lower than expected, we believe that the bending strength data are more representative for the mechanical characterization of CNT–ceramic composites.

Fracture surfaces of the composite sintered at 1450 °C were examined by scanning electron microscopy (SEM). MWNTs were reasonably well distributed in the alumina matrix as shown in Fig. 3A. The particle size of alumina is about 0.5–1 μm; both intergranular and intragranular fracture modes existed. Buckling was first observed in bent

Table 1
The room temperature fracture toughness and bending strength of 1 wt% MWCNTs–alumina composites and alumina ceramics

Sintering temperature (°C)	Fracture toughness (MPa $m^{1/2}$)	Bending strength (MPa)
Al_2O_3 + 1 wt% MWNTs		
1350	4.0 ± 0.50	536 ± 44
1400	3.7 ± 0.41	550 ± 32
1450	3.9 ± 0.59	554 ± 64
1500	2.2 ± 0.15	200 ± 49
Al_2O_3		
1300	3.7 ± 0.93	496 ± 64
1350	3 ± 0.28	383 ± 97
1400	3.7 ± 0.45	460 ± 73
1450	3.9 ± 0.50	388 ± 29
1500	3.7 ± 0.34	371 ± 16

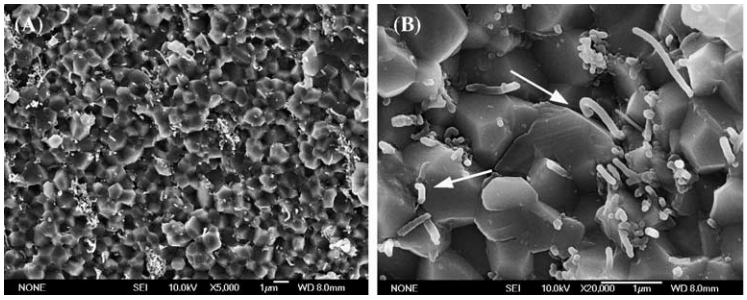

Fig. 3. The SEM images of the fracture surface of the composite sintered at 1450 °C.

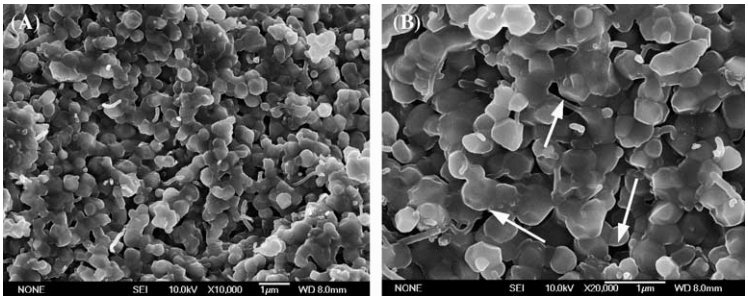

Fig. 4. The SEM images of the fracture surface of the composite sintered at 1500 °C.

nanotubes (indicated by arrows in Fig. 3B) with large curvatures. The bending and/or compressive forces were presumably caused by fracture during the three-point bend test process. A number of MWNTs were observed pulled out from the alumina matrix. The nanotubes clearly survived from the processing and sintering.

Here, it must be mentioned that both the fracture toughness and the bending strength data decreased sharply for the CNT composite sintered at 1500 °C. The fracture toughness value was 2.2 MPa $m^{1/2}$, only about 55% of the maximum value, while the bending strength decreased from 554 to 200 MPa when the temperature changed from 1450 to 1500 °C. Fig. 4 shows the scanning electron microscopy images of the fractured surface of composite sintered at 1500 °C.

Compared with Fig. 3, two features are prominent. One is that far fewer MWNTs existed after sintering at 1500 °C as shown in Fig. 4A. The alumina grains became more rounded and more pores (indicated by arrows) could be found in Fig. 4B. On the fracture surface, MWNTs were observed pulled out from the matrix, but their number was relatively less compared to the number of MWNTs in Fig. 3B. The relative density of composites is 98.9 and 97.9%, corresponding to the sintering temperature of 1450 and 1500 °C, respectively. We suspect the true density of the specimen sintered at 1500 °C was lower than the measured value, because the closed pores could not be detected by the Archimedes method. This lower density and fewer numbers of pulled-out MWNTs caused the catastrophic decrease in bending strength.

4. Conclusions

One weight percent addition of MWNTs to an alumina matrix can produce some improvement in bending strength about 10% over monolithic alumina. Microstructure examination indicates that the broken nanotubes and pullout of MWNTs at interfaces are efficient in transferring the load from the alumina matrix to the nanotubes, leading to the improvement of the mechanical properties.

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