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Reinforcement of mullite matrix with multi-walled carbon nanotubes

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Abstract

Dense multi-walled carbon nanotubes (MWNTs)-mullite ceramic matrix composites were firstly prepared by hot pressure sintering with MWNTs, Al_2O_3 and SiO_2 powders as starting materials. It was found that when the sample was sintered at 1600 °C, the addition of 5 volume percent MWNTs led to 10% increase in bending strength and 78% increase in fracture toughness, respectively, compared with the monolithic mullite. 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 mullite matrix to the nanotubes, leading to the improvement of the mechanical properties.

Keywords: B. Composites; C. Mechanical properties; D. Mullite; MWNTs

1. Introduction

The inherent brittleness of ceramics hampers its wide application as structural parts. Many strategies have been developed to improve the fracture toughness of the ceramics. For example, it was reported that ZrO_2 particles, SiC whiskers and other micro- or nanoparticles were dispersed in the mullite ($3Al_2O_3\cdot 2SiO_2$) ceramic matrix as reinforcing phases and the strength and toughness of the corresponding composites were satisfactorily improved [1–3]. Recently, carbon nanotubes (CNTs) emerged as an attractive material for the reinforcement of ceramics [4]. Numerous researchers have reported remarkable physical and mechanical properties of this new form of carbon. Due to its unique electronic properties, higher thermal conductivity than that of diamond, and prominent mechanical properties compared with any existing materials, CNTs offer tremendous opportunities for developing fundamental new material systems [5–7]. In particular, the outstanding mechanical properties of CNTs ($E \approx 1.8$ TPa), [7] and low density (about 2.0 g cm^{-3}), [8] together with their chemical stability offer the space for the development of CNTs reinforced composites. Many applications of CNTs used as reinforcing additive fibers in polymers and metals have been proposed [9,10]. Several recent experiments on the preparation and mechanical characterization of CNT-ceramic composites have been reported [11–16].

Mullite has excellent mechanical properties, and is becoming increasingly important in electronic, optical, and high-temperature structural applications. However, the lower toughness limits its application in severe conditions. The early study of C fiber reinforced mullite composite indicated that there are good chemical compatibility between C and mullite [17]. Since mullite ceramic has complicated structure and is poorly sinterable, many reports so far have only concerned the preparation of CNTs composites with matrixs including SiC, [11] Si_3N_4, [12] SiO_2, [13] Al_2O_3, [14,15] and cermets [16], while few concerned the preparation and properties of CNT/mullite ceramics.

In the present work, MWNTs-mullite composites containing 5 vol.% multiwalled carbon nanotubes (MWNTs) were fabricated by hot pressing, and both the fracture toughness and the bending strength were preliminarily reported and compared with those of the monolithic mullite matrix.

2. Experimental procedure

The multi-walled carbon nanotubes (95% purity, diameter of 20–40 nm) fabricated by catalytic pyrolysis of hydrocarbon were kindly provided by Shenzhen NANO Tech. Port. Co. Ltd

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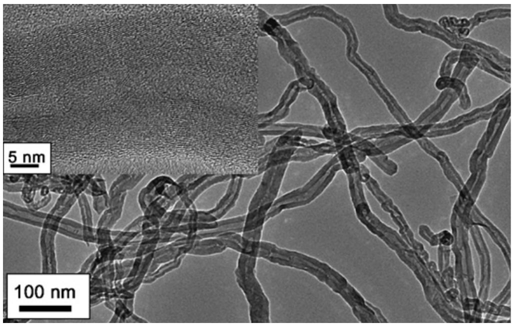

Fig. 1. TEM and HRTEM images of MWNTs.

(China). Fig. 1 shows the transmission electron microscopy (TEM) of the MWNTs. The MWNTs have diameters ranging from 20 to 40 nm, lengths about tens of microns (μm), and the inner diameter is around 5 nm. The inserted HRTEM image clearly shows that nantotube is multi-walled, with approximately 15–25 walls of graphitized carbon layer.

The highly pure alumina (99.9% purity, average particle size of 0.4 μm) and silica powders (99.8% purity, average particle size of 0.5 μm) were purchased from Shanghai Tianfeng Ceramics Factory (China) and used without any treatment. In a typical experimental procedure, firstly, the powders of MWNTs, alumina and silica were respectively dispersed into ethanol by magnetic stirring and ultrasonic treating. Secondly, the obtained suspensions were mixed together and further ultrasonic stirring for 10 min. Then the mixed suspension was dried and sieved through 200-mesh sieve. From Fig. 2 it can be seen that the MWNTs are distributed homogeneously among the Al_2O_3 and SiO_2 powders.

The mixed powders were hot pressedunder Ar atmosphere at 30 MPa in a graphite die with a diameter of 50 mm at 1500, 1550, 1600 and 1650 °C for 1 h. Pure mullite 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 bending strength of samples (3 mm × 4 mm × 30 mm) was measured with a universal tester (Instron-1195) using a three-point test method with a span length of 20 mm and a crosshead speed of 0.5 mm min^{-1}. The fracture toughness, K_{1C}, was evaluated by the single-edge notch beam method (Instron-1195, notch width: 0.25 mm, the notch depth: 2.5 mm, samples size 5 mm × 2.5 mm × 25 mm) with

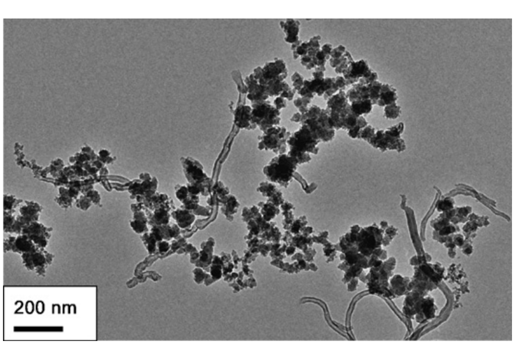

Fig. 2. TEM image of MWNTs–alumina–silica mixed powders.

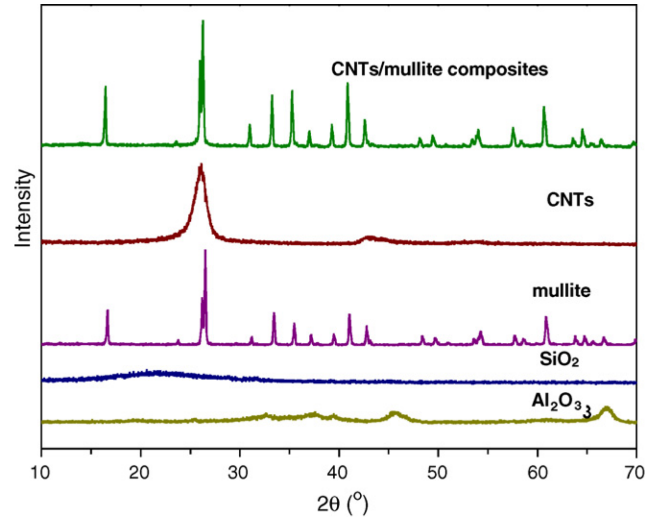

Fig. 3. XRD patterns of CNTs, Al_2O_3, SiO_2 powders, mullite and CNTs/mullite composites.

six samples each data. The crystalline phases of the raw material powders and sintered specimen were analyzed by XRD (Rigaku D/max 2200PC, Japan). The micrographs of the CNTs and the mixed powders were observed by the transmission electron microscope (TEM) (Model JEM-2010). Microstructures were observed by field emission scanning electron microscopy (FESEM) (Model JSM-6700, Japan).

3. Results and discussion

Fig. 3 shows the XRD patterns of MWNTs, Al_2O_3, SiO_2 powders, mullite ceramics and MWNTs-mullite composites, respectively. Maybe due to their similar position and the small quantity of MWNTs (5 vol.% means only 3 wt.%), it is difficult to discern the MWNTs from the MWNT-mullite composites by XRD pattern. However, the CNTs in the mullite matrix composites could be clearly observed in the following SEM images.

Table 1 shows the fracture toughness and bending strength of 5 vol.% MWNTs-mullite and monolithic mullite ceramics. It can be seen that both the fracture toughness and bending

Table 1
The room temperature fracture toughness and bending strength of 5 vol.% MWNTs-mullite composites and mullite ceramics

Sinter temperature (°C)	Fracture toughness K_{1c} (MPa $m^{1/2}$)	Bending strength σ_f (MPa)
Mullite + 5 vol.% MWNT		
1500	2.91 ± 0.30	432 ± 38
1550	3.27 ± 0.42	501 ± 29
1600	3.60 ± 0.45	512 ± 36
1650	2.60 ± 0.36	302 ± 45
Mullite		
1500	1.72 ± 0.33	384 ± 37
1550	2.00 ± 0.35	429 ± 25
1600	2.02 ± 0.23	466 ± 16
1650	1.97 ± 0.26	443 ± 12

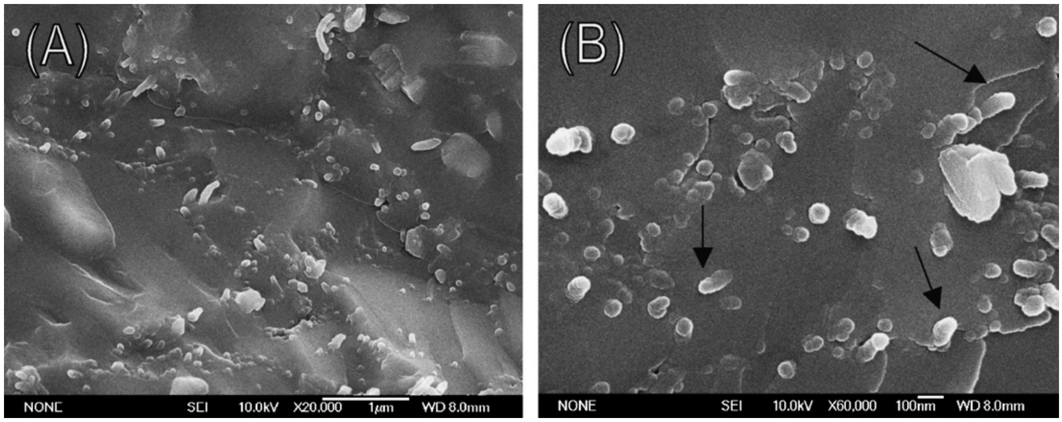

Fig. 4. The FESEM images of the fracture surface of the composite sintered at 1600 °C.

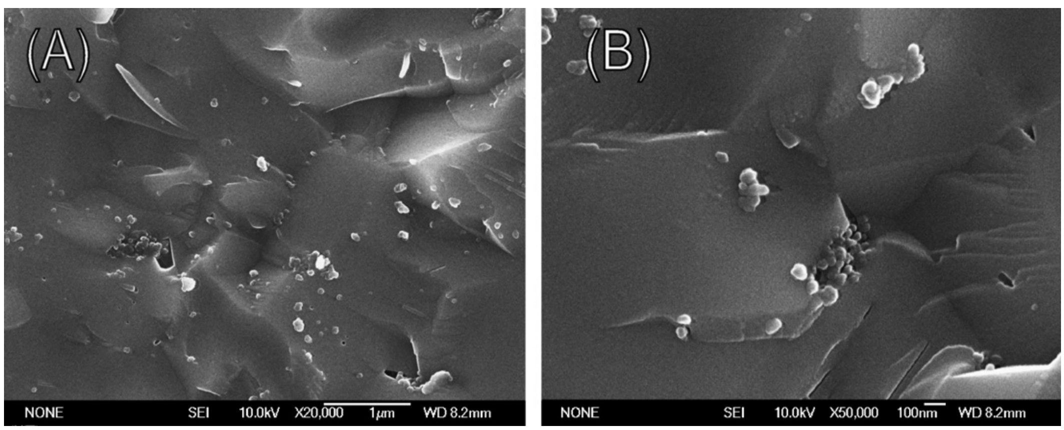

Fig. 5. The FESEM images of the fracture surface of the composite sintered at 1650 °C.

strength varied with the sintering temperature. The highest fracture toughness value of the 5 vol.% MWNTs-mullite composites is 3.6 MPa $m^{1/2}$,after sintering at 1600 °C, while it was 2.02 MPa $m^{1/2}$ for monolithic mullite. This is about 78% increase in fracture toughness for the composite compared with the mullite. The maximum bending strength obtained from the composite is 512 MPa sintering at 1600 °C, and that of monolithic mullite is 466 MPa. This is about 12% increase in bending strength for the composite compared with the mullite. A similar improvement on hot pressed SiO_2 was reported previously [13].

Fracture surfaces of the composite sintered at 1600 °C were examined by scanning electron microscopy (SEM). MWNTs were reasonably well distributed in the mullite matrix as shown in Fig. 4A. A number of MWNTs were observed pulled out (indicated by arrows in Fig. 4B) from the mullite 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 1650 °C. The fracture toughness was 2.6 MPa $m^{1/2}$, only about 72% of the maximum value, while the bending strength decreased from 512 to 302 MPa when the temperature changed from 1600 to 1650 °C.

Compared with Fig. 4, two features are prominent. One is that far fewer MWNTs existed after sintering at 1650 °C as shown in Fig. 5A. On the fracture surface, MWNTs were observed pulled out from the matrix, but there number was relatively less compared to the number of MWNTs in Fig. 4B. The density of composites is 96 and 94%, corresponding to the sintering temperature of 1600–1650 °C, respectively. We suspect the true density of the specimen sintered at 1650 °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 pullout MWNTs caused the catastrophic decrease in bending strength.

4. Conclusions

The introduction of 5 vol.% MWNTs to a mullite matrix can produce effective improvements about 10% in bending strength and 78% in fracture toughness over monolithic mullite. Microstructure observations indicate that the broken nanotubes and pullout of MWNTs at interfaces are efficient in transferring the load from the mullite matrix to nanotubes, leading to the improvement of the mechanical properties.

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