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A novel processing route to develop alumina matrix nanocompositesreinforced with multi-walled carbon nanotubes

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ABSTRACT

In the present work, we have reported a novel approach to fabricate carbon nanotubes (CNTs)/alumina nanocomposites with improved fracture toughness using a simple heterogeneous nucleation through the incorporation of functionalized multi-walled carbon nanotubes (MWCNTs). For this approach, homogeneous distribution of CNTs in ceramic matrix has been achieved up to 5.7 vol.% CNTs content, revealed by SEM observations of both composite powders and fracture surfaces of sintered specimens. Excellent comprehensive mechanical properties as high as 6.03 ± 0.45 MPa $m^{1/2}$ fracture toughness and 19.18 ± 0.33 GPa hardness are obtained in alumina nanocomposite with 5.7 vol.% MWCNTs fabricated via spark plasma sintering (SPS) with subsection pressure method, increasing 53% and 30% over that of pure alumina sintered under the same sintering condition, respectively. Furthermore, the fracture mode transition and the activated toughening mechanisms during crack propagation are taken into account to explain the improvement in fracture toughness.

1. Introduction

Due to its high Young's modulus of ~1.5 TPa and tensile strength of well above 100 GPa [1], carbon nanotubes, either single-wall (SWCNT) or multi-wall (MWCNT), have attracted significant interest worldwide as ideal reinforcing or toughening fibers for alumina ceramic matrix composites [2,3]. However, the significant properties of CNTs are only achieved in fully dispersed conditions. Hence, the importance of CNT agglomeration prevention in initial powder mixture and having a general balanced distribution is unquestionable [4].

Heterogeneous nucleation is an effective method to bridge the scale from molecular ion clusters to nanoparticles, and often adopted to introduce charged particles into ceramics matrix [5,6]. Due to the characteristics of heterogeneous nucleation technology, charged particles are required during precipitation. Thus, CNTs must be firstly functionalized with carboxyl group before non-agglomerated fully introduced into ceramics matrix by heterogeneous nucleation technology. Similar process has been successfully applied to the uniform dispersion of other nanoparticles [7–9]. On the other hand, charged particles can improve the interfacial compatibility among different particles during composite powders preparation, which is also helpful for the preparation of composites and the improvement of interface strength between different phases in composites [9].

Spark plasma sintering (SPS) technique allows specimens to heat rapidly because of the pulsed direct current used in the technique. Consequently, grain growth can be retarded with shorter time of sintering process [10]. Moreover, low-sinterable materials can be densified easily at a moderate temperature [11]. In order to avoid CNTs damage during high temperature sintering process, SPS is often used to prepare dense CNTs/alumina nanocomposites at low sintering temperature [12,13].

Fan et al. [4] successfully prepared Al_2O_3 powders with non-agglomerated fully dispersed CNTs by mixing CNTs and Al_2O_3 powders in aqueous dispersion medium. The fabricated MWNTs/Al_2O_3 composites had a fracture toughness of 5.55 MPa $m^{1/2}$ measured by Single Edge Notched Beam (SENB) method, increasing 80% over pure Al_2O_3. Basing on Fan's research, by means of a novel processing route—heterogeneous nucleation, we had [14] successfully fabricated CNTs/ZrO_2 composites with fracture toughness of 6.24 MPa $m^{1/2}$, increasing 31% over pure ZrO_2 sintered at the same condition.

In an effort to address the above issue, the objective of the present investigation was to improve the dispersion of CNTs in the alumina matrix by functionalized MWCNTs and thus fracture toughness. To obtain fully dense composites and avoid damaging CNTs during sintering, SPS technique is used due to rapidly consolidating powders to near-theoretical density under vacuum.

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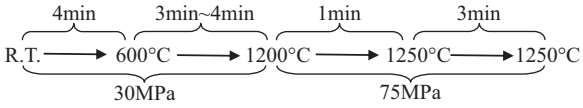
2. Experimental

2.1. Composite powders and specimens fabrication

About 0.3 μm α-Al_2O_3 powder (Zichuan Phoenix Precision Ceramics Co., Ltd., China) have been used for the raw materials. The MWCNTs were functionalized by treating MWCNTs with H_2SO_4 and HNO_3 mixed solution (volume ratio: 3:1). Y_2O_3 was used as the dopant (sintering aids) and the content was about 0.05 wt.%. Alumina particles and functionalized MWCNTs, mixed with dispersant of polyethylene glycol (PEG2000), were first dispersed in a bath under ultrasound for 60 min to limit their agglomeration. The precursor solution was prepared by dissolution of metal nitrates in aqueous solution. Afterwards, the dopant (in the form of nitrate) was introduced into the alumina powder and MWCNTs suspension under magnetic stirring at room temperature. Then $NH_3{\cdot}H_2O$ was dropped into the suspension slowly under strong magnetic stirring to tailor the pH value of the suspension. It is important to control pH value to realize the deflocculation of the alumina particles. We have found that the dispersibility and stability of the slip could achieve the best effect when the pH value was adjusted in the range of 8.5–9. In addition, it is vital to control the dropping rate of $NH_3{\cdot}H_2O$ to ensure the reaction of precipitation onto the surface of alumina powder. The resultant suspension was continuously stirred for 2 h. Consequently, the CNTs-Al_2O_3 slurries were dried in an oven at 40 °C for 12 h. After drying, composite powders were sieved using a 100 mesh. The content of MWCNTs in composites was about 5.7 vol.%.

Composite powders were placed in a graphite die and sintered using a SPS apparatus (Dr. Sinter SPS-1050 T, Japan) under vacuum. According to Inam [13] and Guillard [15], composite ceramics were sintered by the following rapid densification technology. Temperature was automatically raised to 600 °C within 4 min, and a heating rate of 180 °C/min between 600 and 1200 °C was applied under a pressure of 30 MPa, then a heating rate of 50 °C/min up to 1250 °C was used under a pressure of 75 MPa. The dwell time at 1250 °C was 3 min. In all cases, the consolidated specimens were cooled to room temperature by turning off the power. The sintering process can be seen as following:



2.2. Microstructure and mechanical properties evaluation

Sintered specimens were ground flat using a diamond grinding wheel and then polished carefully with successively finer diamond pastes. The final density of the sintered compact was determined by the Archimedes method with deionized water as the immersion medium, and the theoretical density (TD) of the specimen was calculated according to the rule of mixture. The morphology of composite powders, fracture surfaces was observed by SEM (JSM-6460LV, Shimadzu, Japan).

Hardness and fracture toughness were measured by Vickers indentation on polished surface using Vickers Hardness Tester (HV-50; Shanghai Material Testing Machine Factory, China) with a load of 49 N, 98 N and 196 N, respectively. More than 10 perfect indentations were made on each sample. Hardness (H_V) and fracture toughness (K_R) were calculated according to the following formulae given by Niihara [16] for Palmqvist cracks:

$$H_V = 1.8544{\cdot}P{\cdot}d^{-2} \quad (1)$$

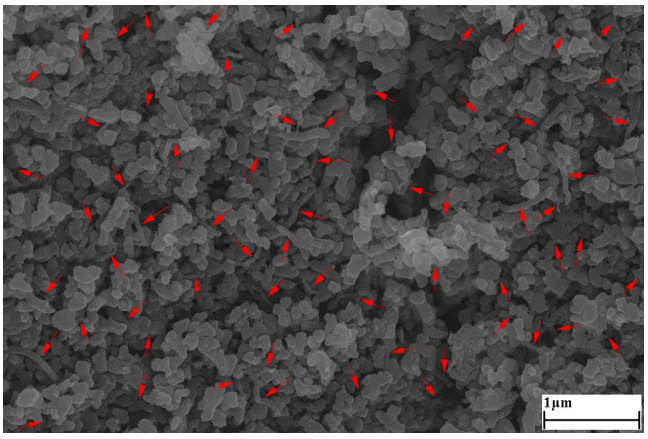


Fig. 1. A representative SEM image of obtained composite powders.

$$K_R = 9.052{\cdot}10^{-3}{\cdot}H^{3/5}{\cdot}E^{2/5}{\cdot}d{\cdot}c^{-1/2} \quad (2)$$

where H_V: Vickers hardness (Pa); P: applied load (N); d: average diagonal length of indentation (m); c: average crack length (m); and E: Young's modulus (Pa) obtained by ultrasonic velocity measurements.

3. Results and discussion

3.1. Morphology of composite powders

A representative SEM image of obtained composite powders is shown in Fig. 1, indicating the clear presence of CNTs (shown by red arrows) and individual Al_2O_3 particles with a size of about 0.3 μm. Such fine powders highly tend to agglomerate due to its high-surface area. Therefore, it is very difficult to homogeneously disperse CNTs in such ceramic matrix. However, according to the fabrication process, it is observed that CNTs are homogeneously distributed in composite powders without formation of ropes and bundles up to the content of CNTs of 5.7 vol.% (shown in Fig. 1). However, according to Sarkar [17], the presence of CNTs bundles/agglomeration can be observed when its content is only 2.4 vol.%, indicating that functionalized CNTs induced in this research indeed facilitate their uniformity of dispersion in alumina matrix.

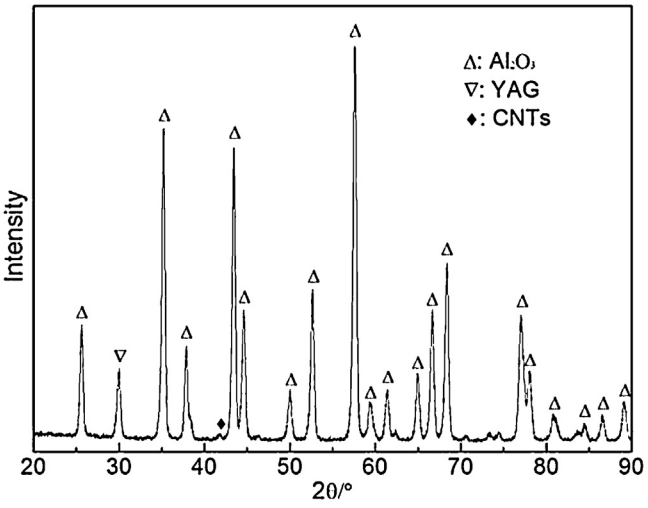


Fig. 2. XRD pattern of the sintered composite specimen.