

Carbon nanotube-ceramic composites

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Abstract The effective utilization of CNTs in composite application depends strongly on the ability to disperse CNTs homogeneously throughout the matrix and the interfacial combination is necessary for improving the CNT-based composite properties. In our work, we used surfactant and acid treatment to modify the CNTs surface and then incorporated the functionalized CNTs into various ceramic matrices including oxide and nitride ceramics. The fabrication of ceramic nanoparticle-immobilized CNTs not only improves the homogeneous distribution of CNTs in the ceramic matrices, but also makes the combination between two phases more tight. Mechanical property measurements clearly reveal obvious enhancement confirming the fabrication of true CNT-based composite materials with improved toughness properties. The addition of 0.1 wt% CNTs in the alumina increased the fracture toughness by about 1.6 times from 3.7 to 4.9 MPa·m^{1/2}. For 1 wt% CNTs/BaTiO₃ composite, the toughness value (1.65 MPa·m^{1/2}) is about 2.4 times than that of pure BaTiO₃ (0.68 MPa·m^{1/2}). For 5 wt% CNTs/TiN composite, the fracture toughness is 3.81 MPa·m^{1/2}, which is about 1.6 times than that of pure TiN ceramic whose toughness is 2.45 MPa · m^{1/2}.

Keywords Carbon nanotubes · Ceramic · Composites

Introduction

Carbon nanotubes (CNTs) are new one-dimensional carbon materials with excellent mechanical, electrical, thermal and

chemical stability properties. Incorporation of CNTs into ceramics has attracted more and more interests in recent years [1–3]. However, the study is still far from exploited due to the strong aggregation of CNTs in the matrix. Unlike carbon fibers, the as-prepared CNTs tend to form bundles due to van der Waals forces, and it is difficult to separate them individually. The effective utilization of nanotubes in composite applications depends strongly on the ability to disperse CNTs homogeneously throughout the matrix. Furthermore, good interfacial bonding is required to achieve load transfer across the CNT-matrix interface, a condition necessary for improving the mechanical properties of ceramic composites.

From the viewpoint of colloidal processing, multicomponents could be distributed evenly when they possess similar surface properties. Successful modification of CNTs by using dispersants or acid treatment proves more homogeneity in the matrix compared with that of simple mixed samples using pristine CNTs [4, 5]. Hwang et al. [6] synthesized silicon glass rods by using surfactant-carbon nanotube co-micelles as templates. These glass rods were used as additives to reinforce inorganic ceramics. They showed ~100% enhancement on hardness in the presence of ~6 wt% of CNTs. Gong et al. [7] reported the use of a surfactant as a processing aid to improve the dispersion of single-wall carbon nanotubes (SWNTs) in epoxy resin, leading to a significant improvement of mechanical properties. In our work, the dispersants and acid treatment were used to modify the CNTs and then the functionalized nanotubes were incorporated into various ceramic matrices including Al₂O₃ [8], BaTiO₃ and TiN. The mechanical properties of these composites have been investigated.

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Experimental section

CNTs prepared by the catalytic decomposition of CH_4 were kindly provided by Shenzhen Nanoport company, and purity of about 95% was claimed by the producer. The impurities may contain some catalyst metal particles and amorphous carbon. The CNTs have lengths ranging from several to tens of micrometers with an inner diameter around 10 nm. The nanotubes are multiwalled, with about 25–30 graphene layers [9].

For the CNTs/ Al_2O_3 composite [8], the nanotubes were treated in NH_3 at 600°C for 3 h and then were put into a solution containing a dispersant of 300 mg/L polyethyleneamine (PEI, M_w 50000, BDH Laboratory Supplies). Commercially available α - Al_2O_3 consisting of particles with diameter of 30 nm was obtained from Taimei Chemical Co., Ltd., Japan. Alumina (0.04 g) was dispersed into 100 mL of deionized water, and then 300 mg/L poly (acrylic acid) (PAA, from Polymer Sciences, PA) with polymer weight of 50000 was added into this very dilute alumina suspension. The prepared dilute alumina suspension with PAA was added dropwise into the vigorously stirred as-prepared carbon nanotube suspension with PEI, and before that both suspensions were ultrasonicated for 30 min. The coated CNTs collected from the mixed suspension were subsequently added into a concentrated alumina suspension of about 50 wt% in ethanol; finally the content of CNTs was only 0.1 wt% of alumina amount. Further drying and grinding obtained the CNTs/ Al_2O_3 composite powder. The single-phase alumina powder and 0.1 wt% CNTs/ Al_2O_3 composite powder were sintered by spark plasma sintering (SPS, Dr Sinter 1050, Sumitomo Coal Mining Co., Ltd.) in a graphite die at 1300°C , with a pressure of 50 Mpa for 5 min in an Ar atmosphere, respectively.

For CNTs/ BaTiO_3 composite [10], the TiO_2 -immobilized CNTs were firstly synthesized. 1.2 g CNTs were suspended in 35 mL of 15 M nitric acid and refluxed for 2 h in a silicon oil bath maintained at 140°C to modify the CNTs surface. When this solution was cooled to the designed reaction temperature, 10 mL 3 M titanium tetrachloride solution was rapidly injected into the vigorously stirred CNTs solution while maintaining the temperature at 90°C . After 6 h reaction, the final products were filtered out, washed with distilled water and ethanol in sequence, and later dried at 100°C for 12 h. 0.27 g of as-synthesized TiO_2 /CNTs, 3.68 g $\text{Ba}(\text{Ac})_2$, and 0.8 g NaOH were loaded into 30 mL distilled water. After vigorous stirring and ultrasonic irradiation for 10 min, the mixture solution was transferred into a 35 mL Teflon-lined stainless-steel autoclave and underwent hydrothermal treatment at 160°C for 8 h. The final products were filtered out, washed with distilled water and ethanol in subsequence, and later dried at 100°C for 12 h. The resultant CNTs/ BaTiO_3 hybrid material has a Ti/C mol ratio of 3:10.

To synthesize a large amount of CNTs/ BaTiO_3 composite powders, the as-prepared CNTs/ BaTiO_3 hybrid material was mixed with nanosized tetragonal phase BaTiO_3 powders by highly-efficient ball-milling for 24 h in ethanol solution using agate ball media. The obtained CNTs/ BaTiO_3 composite powder slurry was dried at a constant temperature of 100°C for 12 h and further dehydrated in a vacuum oven at 60°C for 12 h. Dry composite powders were finally sieved using 200 mesh. Pure BaTiO_3 and CNTs/ BaTiO_3 composite powders were sintered by SPS. The annealing time, sintering temperatures and heating rate were set to 5 min, 950°C and $300^\circ\text{C}/\text{min}$, respectively.

For CNTs/TiN composite [11], CNTs were firstly oxidized by refluxing at 140°C in 15 M nitric acid for 24 h. $\text{Ti}(\text{OC}_4\text{H}_9)_4$, used as a starting material, was dissolved in anhydrous ethanol to form a 10 vol% solution. The mixed solution was added dropwise into the acidic CNTs solution with vigorous stirring until the final Ti: H_2O molar ratio reached 1:150. The hydrolyzate was filtered and rinsed twice with anhydrous ethanol, then dried at 120°C for 2 h. The precipitate was subsequently calcinated at 450°C for 2 h in an N_2 atmosphere. The TiO_2 /CNTs powder was loaded into a quartz boat and heated in flowing NH_3 (0.5 L min^{-1}) at 800°C for 5 h in a tube furnace to obtain TiN/CNTs composite powder. SPS was used to sinter the composite powders in a graphite die at 1280°C , with a pressure of 60 MPa for 2 min in N_2 atmosphere.

Zeta potential measurements were employed to characterize the modified CNTs by using acid treatment and dispersants. Transmission electron microscopy (TEM, JEM 2010, JEOL, Japan) was performed to observe the morphology of the composite powders. Scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) was used to observe the microstructure of the sintered samples. Indentation tests were done on a Wilson-Wolpert Tukon 2100B (Instron) hardness tester with a diamond vickers indenter, and used to measure the toughness of products.

Results and discussion

Zeta potentials of the pristine CNTs and modified CNTs by acid treatment or dispersants are shown in Fig. 1. After acid treatment, the isoelectric point (pH_{iep}) of the CNTs moves to a more acidic value, with the zeta potential values being more negative. The result must be due to the existence of acidic groups on the surface of the CNTs [12]. After NH_3 treatment, the pH_{iep} moves from 3.3 to 9.8 in Fig. 1(c). Our trial [8] on the treatment at an optimum temperature in NH_3 results in a so-called H carbon surface, which has a high isoelectric point. The treated CNTs have positive surface charge in wide pH range. Addition of a small amount of PEI not only moves pH_{iep} to a little higher pH value, but also promotes a good

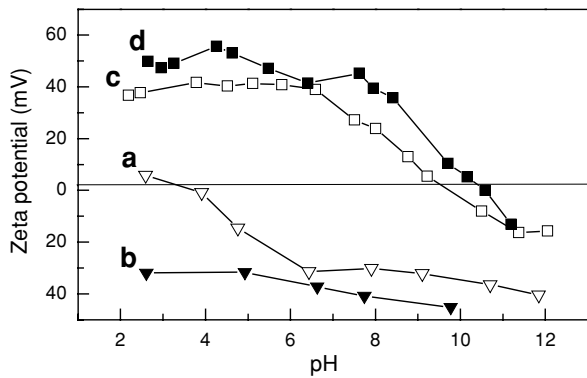


Fig. 1 Zeta potential values changed with pH of: (a) pristine CNTs, (b) acid-treated CNTs, (c) NH_3 -treated CNTs and (d) NH_3 -treated CNTs in the presence of PEI

dispersion after the ultrasonication. Another feature should be mentioned is that the zeta potential value of treated CNTs in the presence of PEI is about 20 mV higher than that without dispersant at pH 9, which means the surface of CNTs is more positive with PEI.

For the fabrication of $\text{CNTs}/\text{Al}_2\text{O}_3$ composite powders [8], a colloidal heterocoagulation method was adopted to coat the surface of CNTs with alumina powder. It is well known that when two sols of opposite charge are mixed, mutual coagulation may occur. If the proper pH range is selected, ceramic particles will be adsorbed onto the CNTs by electrostatic forces. Once the PAA-treated alumina suspension is mixed with the dilute solution of NH_3 -treated CNTs with PEI, particles of alumina will bind onto the CNTs because of the strong electrostatic attractive force between each other. The composite powders containing 0.1 wt% CNTs and the single-phase alumina were sintered fully by SPS at 1300°C for 5 min. Calculations of the fracture toughness were made from measurements of the lengths of cracks created by Vickers indentations. The addition of 0.1 wt% CNTs in the alumina

increased the fracture toughness by about 1.6 times from 3.7 to $4.9 \text{ MPa} \cdot \text{m}^{1/2}$. Compared to the results [13] of 10 vol% multi-walled carbon nanotube addition to the alumina which increased the fracture toughness by about 24% from 3.4 to $4.2 \text{ MPa} \cdot \text{m}^{1/2}$, our results showed a more effective and obvious improvement on the mechanical properties by this simple colloidal processing method. In our previous study from SEM microstructure [8], a significant crack-bridging effect and pullout of CNTs at interface are possible mechanisms leading to the improvement of the fracture toughness.

A lot of the direct covalent functionalization methods have been based on the acid oxidation of CNTs [14]. Treating CNTs with nitric acid could create various functional groups at both tips and sidewalls, such as COOH , OH , and CO , which can act as nucleation sites for metal clusters. We used acid-treated CNTs to fabricate $\text{CNTs}/\text{BaTiO}_3$ and CNTs/TiN composites [10, 11]. The CNTs/TiO_2 hybrid material was firstly fabricated in order to prepare $\text{CNTs}/\text{BaTiO}_3$ composite through simple hydrothermal treatment and CNTs/TiN composite through nitridation technique. Two different methods was used to fabricate CNTs/TiO_2 hybrid materials, whose microstructure images are shown in Fig. 2. One method is the *in situ* acid refluxing of CNTs and TiCl_4 , which results the functional groups on CNTs and realize the attachment of TiO_2 on CNTs. From Fig. 2(a), the rod-like TiO_2 nanoparticles are decorated on the surface of CNTs. The diameter and length of TiO_2 is ca. 4–6 and 10–30 nm, respectively. Through the hydrothermal treatment, the $\text{CNTs}/\text{BaTiO}_3$ composite powders were synthesized. The other method is the heterocoagulation of acid-treated CNTs and $\text{Ti}(\text{OC}_4\text{H}_9)_4$, which combines the Ti precursor with the acidic groups generated on the nanotubes and produces the tiny TiO_2 nanoparticles on CNTs. In Fig. 2(b), the tiny TiO_2 nanoparticles are well attached to the CNTs, with a diameter of ca. 5–10 nm. Further treating the CNTs/TiO_2 powders in NH_3 at 800°C for 5 h, the CNTs/TiN composite was fabricated.

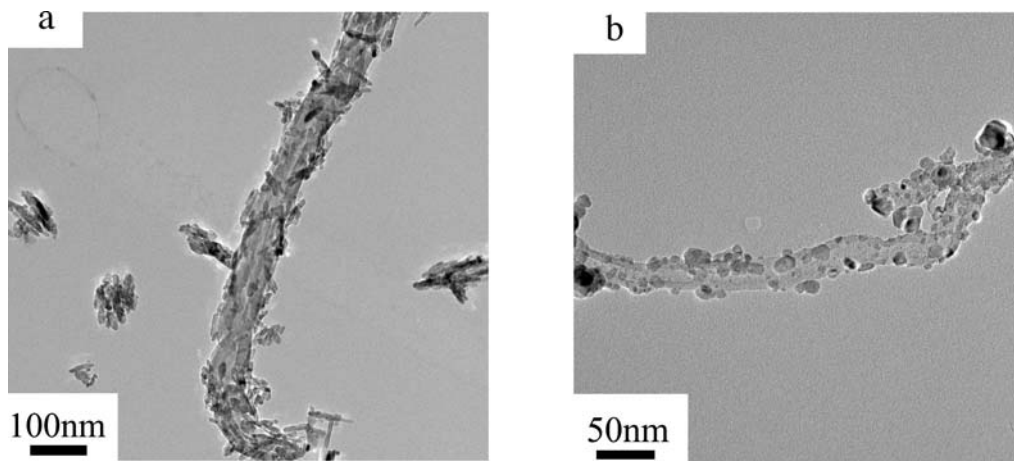
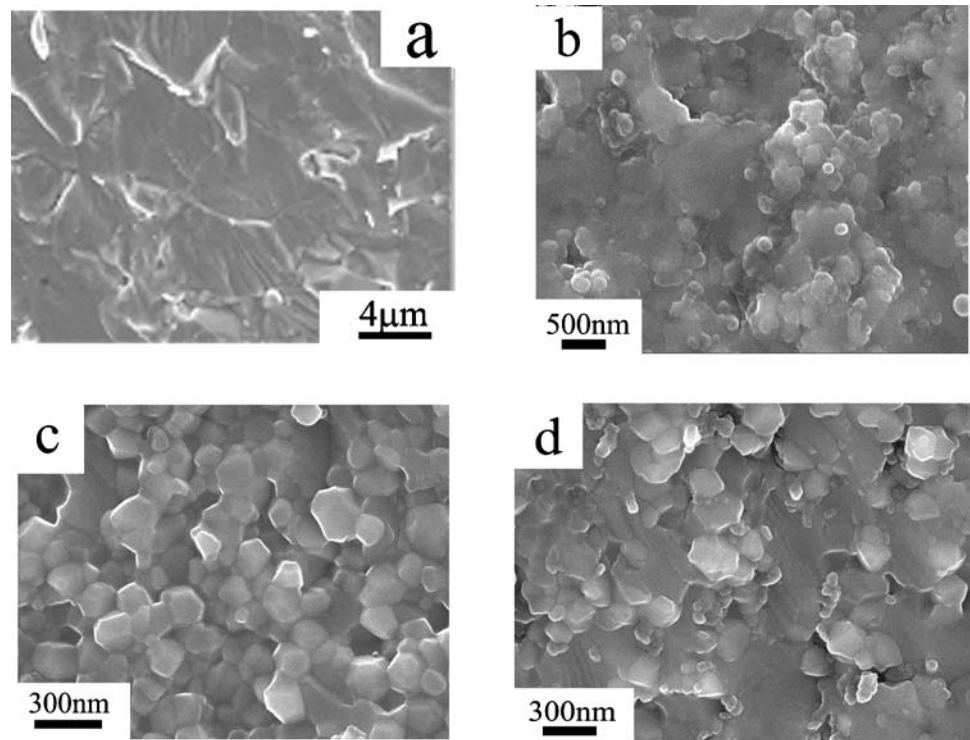


Fig. 2 TEM image of (a) rod-like TiO_2 nanoparticles on CNTs and (b) tiny TiO_2 nanoparticles on CNTs

Fig. 3 SEM image of the sintered (a) pure BaTiO₃ ceramic, (b) 1 wt% CNTs/BaTiO₃ ceramic, (c) pure TiN ceramic and (d) 5 wt% CNTs/TiN ceramic by SPS



SEM images well visualize the fracture microstructure of the CNTs/BaTiO₃ and CNTs/TiN composites, as shown in Fig. 3(b) and (d). These two composites are sintered densely and have few pores between grains. In the presence of CNTs, the fracture mode converts from intergranular fracture in pure BaTiO₃ or TiN ceramic to intragranular fracture in the composites containing CNTs. In the pure BaTiO₃ or TiN ceramics (Fig. 3(a) and (c)), the morphology of the cross section has clear edges and corners, which denotes the intergranular fracture mode. While in the presence of CNTs (Fig. 3(b) and (d)), the interface of grains become blurry and glaze-like morphology become dominant, indicative of the intragranular fracture mode. The CNTs are highly homogeneously distributed in the ceramic matrix. No hole surrounding the CNTs is formed after fracture. The CNTs protruding out of the ceramic matrix are also very short of merely like a hummock. These unique features indicate that tight binding between the CNTs and ceramic matrix is achieved. This result not only validates the rationalization of the preparation process, but also is very vital to take advantage of properties of CNTs in the composite materials.

The fracture toughness of the composites was measured compared with that of pure ceramics. For 1 wt% CNTs/BaTiO₃ composite, the toughness value is 1.65 MPa·m^{1/2}, which is about 2.4 times than that of pure BaTiO₃ ceramic whose toughness is only 0.68 MPa·m^{1/2}. For 5 wt% CNTs/TiN composite, the fracture toughness is 3.81 MPa·m^{1/2}, which is about 1.6 times than that of pure TiN

ceramic whose toughness is 2.45 MPa·m^{1/2}. A good dispersion of CNTs in the matrix and the tight interfacial bonding ensures a good stress transfer between the nanotube and ceramic matrix.

Conclusions

Modified CNTs by using dispersants and acid treatment have been proved as an effective way to improve the mechanical properties of CNTs/ceramic composites. By adjusting the surface properties of CNTs and that of ceramic powder, it is feasible to make them bind together with attractive electrostatic forces, which produces strong cohesion between two phases after sintering. The addition of CNTs effectively increases the fracture toughness of the CNTs/ceramic composites. For 0.1 wt% CNTs/Al₂O₃ composite, the fracture toughness increases by about 1.6 times from 3.7 to 4.9 MPa·m^{1/2}. For 1 wt% CNTs/BaTiO₃ composite, the toughness value increases by 2.4 times from 0.68 to 1.65 MPa·m^{1/2}. For 5 wt% CNTs/TiN composite, the fracture toughness is 3.81 MPa·m^{1/2}, which is about 1.6 times than that of pure TiN ceramic whose toughness is 2.45 MPa·m^{1/2}. The homogeneously distribution of CNTs in the matrix and tight binding between the nanotubes and the matrix are possible reasons to the improvement of mechanical properties of the composites. Future work, including a detailed investigation on the adhesion between CNTs and ceramic matrix, the optimization of

CNTs contents in composites for different applications and measurements of other important properties of the composites, is in progress.

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References

1. A. Peigney, C. Laurent, O. Dumortier, and A. Rousset, *J. Eur. Ceram. Soc.*, **18**, 1995 (1998).
2. G.D. Zhan, J.D. Kuntz, J.L. Wan, and A.K. Mukherjee, *Nature Mater.*, **2**, 38 (2003).
3. R.Z. Ma, J. Wu, B.Q. Wei, J. Liang, and D.H. Wu, *J. Mater. Sci.*, **33**, 5243 (1998).
4. K.R. Han, C.S. Lim, and M.J. Hong, *J. Am. Ceram. Soc.*, **79**, 574 (1996).
5. E.P. Luther, F.F. Lange, and D.S. Pearson, *J. Am. Ceram. Soc.*, **78**, 2009 (1995).
6. G.L. Hwang and K.C. Hwang, *J. Mater. Chem.*, **11**, 1722 (2001).
7. X. Gong, J. Liu, S. Baskaran, R.D. Voise, and J.S. Young, *Chem. Mater.*, **12**, 1049 (2000).
8. J. Sun, L. Gao, and W. Li, *Chem. Mater.*, **14**, 5169 (2002).
9. J. Sun and L. Gao, *Carbon*, **41**, 1063 (2003).
10. Q. Huang and L. Gao, *J. Mater. Chem.*, **14**, 2536 (2004).
11. L.Q. Jiang and L. Gao, *J. Mater. Chem.*, **15**, 260 (2005).
12. G.Z. Chen, M.S. Shaffer, D. Coleby, G. Dixon, W. Zhou, D.J. Fray, and A.H. Windle, *Adv. Mater.*, **12**, 522 (2000).
13. S. Chang, R.H. Doremus, P.M. Ajayan, and R.W. Siegel, *Ceram. Eng. Sci. Proc.*, **21**, 653 (2000).
14. S. Ravindran, S. Chaudhary, B. Colburn, M. Ozkan, and C.S. Ozkan, *Nano. Lett.*, **3**, 447 (2003).