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Processing and properties of carbon nanotubes–nano-SiC ceramic

R. Z. MA, J. WU, B. Q. WEI, J. LIANG, D. H. WU
Department of Mechanical Engineering, Tsinghua University, Beijing, 100084, People's Republic of China
E-mail: mrzdlc@263.net

Carbon nanotubes–nano-SiC ceramic has been fabricated by the hot-press method. The preparation steps involved the use of dispersing nano-SiC powders and carbon nanotubes in butylalcohol using an ultrasonic shaker. The reasonable relative density of about 95% has been achieved by hot-pressing at 2273 K (at 25 MPa in Ar for 1 h). The three-point bending strength and fracture toughness of the composite has about 10% increment over monolithic SiC ceramic which was fabricated under the same process. The reasons for the increment are the strengthening and toughening role of carbon nanotubes occuring in the matrix. © *1998 Kluwer Academic Publishers*

1. Introduction

Carbon nanotubes (CNTs) probably offer a kind of nanosize reinforcement that is lightweight, has a hollow core, has immense aspect ratio and exceptional high axial strength [1–3]. Moreover, CNTs have been proven to be stable under temperatures as high as 2700 K in an argon atmosphere or under vacuum [4, 5]. So, they are considered to be the utmost type of fibre-like reinforcements. The excellent toughness of carbon nanotubes should be helpful in solving the inherent brittleness of ceramics, which has troubled researchers in this field for a long time [6].

Based on the facts mentioned above, we consider it reasonable to process ceramic matrix CNTs composite materials, where the tubes serve as potential reinforcement. We believe it may be a new way of improving the brittleness of ceramics. The present work presents the preliminary findings of a programme designed to investigate the processing and properties of CNTs–SiC ceramic.

2. Experimental procedure

The starting material was a silicon carbide powder (β-SiC) with an average size of 80 nm, which is commercially available from the Institute of Chemical Metallurgy Engineering, the Academy of Science of China. The chemical analysis is given in Table I and the morphology is shown in Fig. 1a. Carbon nanotubes with a diameter of 30–40 nm were produced by catalytic pyrolytic C_2H_4/H_2 [7] in our own laboratory. The transmission electron microscope (TEM) image, after nitric acid treatment, is shown in Fig. 1b. The sintering additive used in this experiment was B_4C, which had a mean particle size of 3.5 μm. The powders were dispersed in butylalcohol, respectively, and then mixed in an ultrasonic shaker for 15 min. The mixed powders were dried at 353 K and broken up using a pestle and mortar so as to pass through a 50-μm sieve and subsequently uniaxially pressed at about 40 MPa to form cylindrical pellets. The pellets were then broken up again and passed through a 355-μm sieve. Finally the powders were hot-pressed in a graphite die with a diameter of 50 mm at 2273 K (at 25 MPa under Ar for 1 h). In this experiment, pure tubes were hot-pressed under the same condition to investigate the thermostability of carbon nanotubes.

The bulk density was measured using a conventional water-displacement method. The microstructure of the fracture surfaces was observed by means of a scanning electron microscope (SEM). The specimens were cut using a diamond saw and polished into $3 \times 4 \times 36$ and $4 \times 6 \times 30$ mm pieces for the purpose of testing three-point bending strength and fracture toughness (at room temperature). Measurements of the fracture toughness were made using a single edge nicked beam (SENB) specimen containing precracks, which was about 3 mm in depth and 0.2 mm in width. The bridging distance was 24 mm and the loading velocity was about 0.05 mm min^{-1} for the measurements of toughness, and 30 mm, 0.5 mm min^{-1} for the measurements of strength.

3. Results and discussion

3.1. The mixture of CNTs and SiC powders

As shown in Fig. 1b, the self-made CNTs are tangled together. This is the main feature of catalytic pyrolytic CNTs. When mixed with SiC powders by the method of butylalcohol solution and ultrasonic shaking, the tubes are dispersed throughout the nano-SiC powders, as can be seen clearly from Fig. 1c.

3.2. Thermostability of the CNTs

Evidence shows that CNTs keep their fullerene features by changing into an onion-like structure under 2973 K in high vacuum [8]. But in order to ensure this texture

TABLE I Chemical analysis of silicon carbide powder (β-SiC)

Elements	Si (total)	Si (free)	C (total)	C (free)	O (total)	Cl^-
Content (wt%)	68.5	0.2	29.2	1.0	1.2	0.25

under our specific hot-press condition, pure tubes were hot-pressed to fabricate pure CNTs specimens. As shown in Fig. 2, the main characteristics of CNTs are distinguished after such treatment. The result of X-ray diffraction (XRD) is also in good agreement with the original tubes. There is no evidence that CNTs have changed into other types of carbon materials. Thus implying that CNTs can be used as reinforcement in this process.

3.3. Densification behaviour

Many researchers have pointed out that B_4C is the most effective additive for sintering of SiC ceramics. Our experimental results also support this conclusion. As shown in Table II, without B_4C, the relative density of the specimen is lower than 70% of theoretical density. So B_4C is necessary for the fabrication of CNTs–SiC ceramic. The size of B_4C used in this experiment was much greater than that of the SiC particles. But we found that the size difference did not prohibit the distribution of boron apparently. It is practical to use B_4C particles of this size for additives. Perhaps finer B_4C particles are more effective, and further investigation is needed.

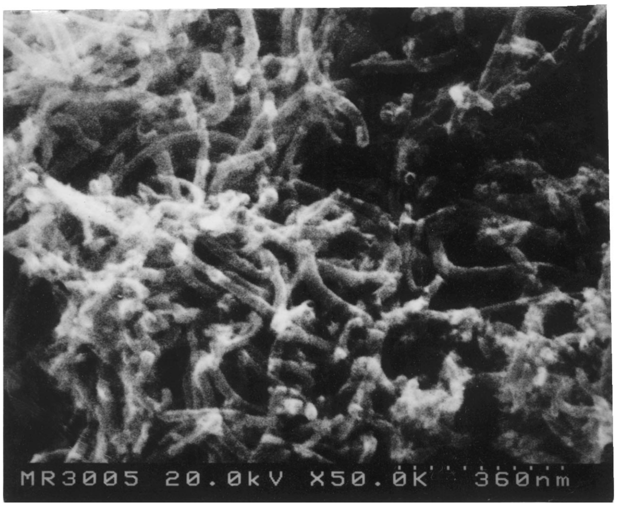


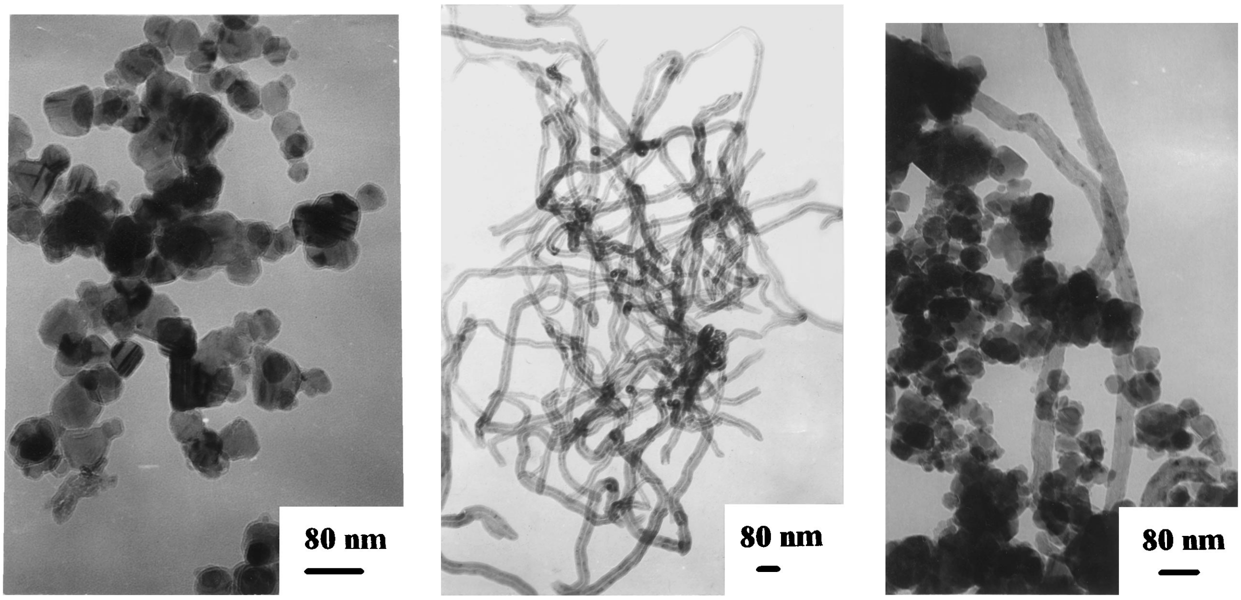
Figure 2 CNTs after hot-pressing.

In order to improve the densification behaviour, increasing temperature is also proven to be effective. In

TABLE II Properties of several kinds of specimen sintered at 2273 K

Specimens	Relative density (%)	Mean bending strength (MPa)	Mean fracture toughness (MPa × $m^{1/2}$)
SiC + 10% CNTs	64.7	100.3	1.85
SiC + 10% CNTs + 1% B_4C[a]	98.1	227.8	
SiC + 1% B_4C	93.9	303.4	3.38
		331.5[b]	3.56[b]
SiC + 10% CNTs +1% B_4C	94.7	321.3	3.82
		375.8[b]	3.86[b]

[a] Sintering taken at 2473 K.
[b] Highest tested value.



(a) (b) (c)

Figure 1 TEM image of (a) nano-SiC powders, (b) catalytic pyrolytic (CNTs), and (c) mixture.

this experiment, the sintering process under was carried out at 2273 and 2473 K. The results indicate that increasing temperature is really helpful in achieving densities as high as 98%. But it must be noticed that in spite of higher density, the mechanical property decreases. It was founded by XRD analysis that the sinter mainly consists of α-SiC (6H). As discussed by other authors, when the sintering temperature is above 2373 K, β-SiC starts to turn into α-SiC. The action of boron promotes the transformation. So the sinter of SiC above 2473 K is mainly composed of α-SiC [9]. Considering both reasonable densification behaviour and expected microstructure, the most acceptable sintering temperature should be 2273 K.

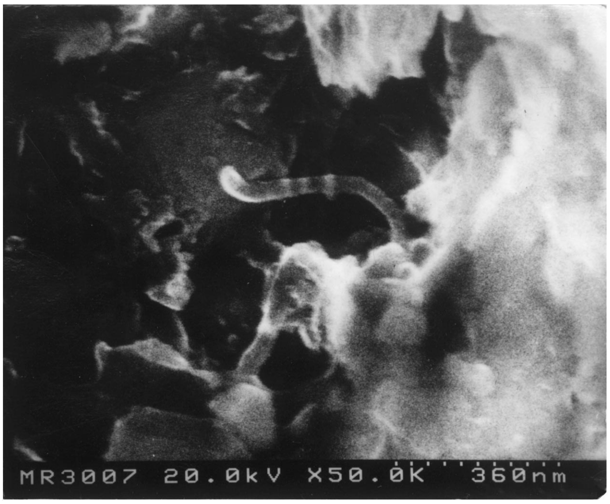


Figure 3 CNTs occurring in the composite.

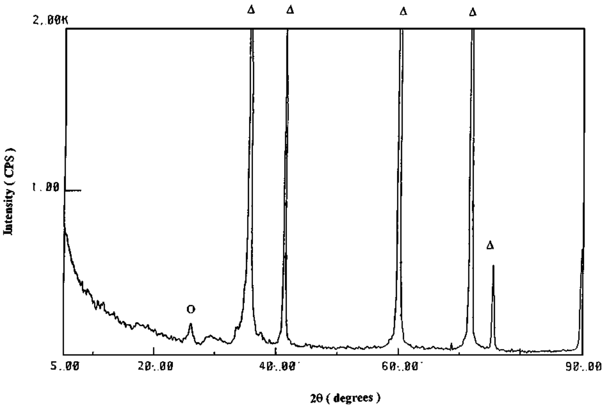


Figure 4 XRD of the composite: Δ (SiC), (O) CNTs.

3.4. Microstructure and mechanical properties of the composite

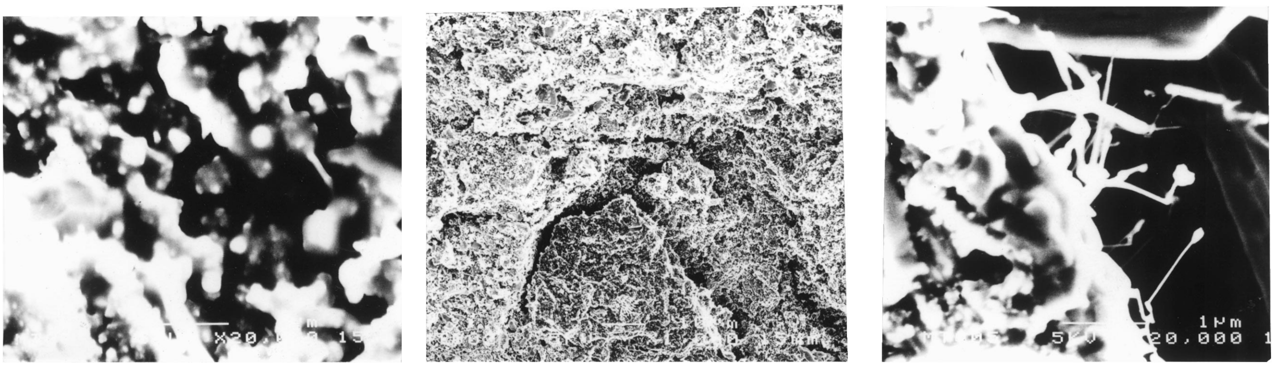
Fig. 3 shows the microstructure of the hot-pressed composite. CNTs bridging boundaries can be found, indicating that the tubes are retained in the composite when sintered with SiC powders under the condition of 2273 K and 25 MPa. As shown in Fig. 4, the XRD result also detects the occurrence of CNTs. Because of the small fraction of CNTs in the composite, only the most intensive peak ($2\theta = 25.94^\circ$) [10] can be noticed. This provides strong support that it is feasible to use CNTs as reinforcement in this process.

In order to contrast with the composite, pure SiC powders with B_4C additives alone were also hot-pressed under the same conditions. The properties of the two kinds of materials are also shown in Table II. As indicated, the composite shows an increase in both three-point bending strength and fracture toughness. These increases are believed to be due to the introduction of high module tubes into the SiC matrix. The fracture surface of the composite is revealed in Fig. 5. In Fig. 5b, the deflection of the crack path is substantial. Fig. 5c shows the image of debonding CNTs near the crack tip. This debonding could be attributed to the high strength of the CNTs and the weak interface between the CNTs and the matrix. The effect of whisker debonding and crack deflection is helpful in forming a new energy-absorption mechanism and leads to increases in strength and toughness [11].

Here it must be mentioned that there is only about a 10% increase in strength for the composite compared with the monolithic SiC ceramic. The extent of this increase depends on the processing technology. We believe that further investigation should focus on optimization of the processing technology and on improvement of the interface structure [12].

4. Conclusions

A carbon nanotube–nano-SiC composite has been fabricated. Processing involved dispersion in butylalcohol using an ultrasonic shaker and controlled drying.



(a) (b) (c)

Figure 5 (a) Fracture surface ×20 000, (b) deflection crack ×1000, and (c) debonding CNTs ×20 000.

Reasonable density has been achieved by hot-pressing at 2273 K and 25 MPa in an argon atmosphere.

The results prove that carbon nanotubes can be retained in SiC ceramic under the specific hot-press conditions employed. The mechanical properties of the SiC ceramic increased by the introduction of CNTs. For the present, there are improvements of about 10% over monolithic silicon carbide both in bending strength and fracture toughness. The increase can be explained by the effect of crack deflection and CNT debonding. So it is feasible to use CNTs as nano-size reinforcement in ceramics. Further improvements should be optimization of the processing procedure, so as to increase the strengthening and toughing role of CNTs.

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