

Preparation and characterization of carbon nanotube reinforced silicon nitride composites

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Abstract

Multiwall carbon nanotube (MWNT) reinforced silicon nitride ceramics matrix composites have been prepared. The hot isostatic press (HIP)-sintering method was used for composite processing. Bending strength and elastic modulus of MWNT-silicon nitride composites showed a considerable improvement compared to matrices with added carbon fiber, carbon black or graphite. However, the silicon nitride samples without any carbon addition, because of higher densities present an even higher value. In the case of carbon fibers addition, a deterioration during sintering has been observed. The increasing pressure and sintering time resulted in carbon nanotube free structures.

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1. Introduction

As carbon nanotubes present exceptional mechanical, superior thermal and electrical properties in general, there are high expectations for improvement of quality of carbon nanotube nano- and microcomposites [1–5]. Despite of this, only modest improvements were reported related to electrical or mechanical properties of carbon nanotube silicon carbide-, polymer-, metal oxide matrix composites [6–10]. One of the possible approaches is to modify the shape factor of CNTs [11]. It was shown that an optimization of the stress distribution and the reinforcement of mechanical bonding can be achieved by using noncircular or hollow shape carbon fibers in an epoxy matrix [12]. In a recent study, high temperature extrusion has been used to align the CNTs in bulk metal oxide nanocomposites, which could lead to an increase of electrical conductivity [13].

In the use of nanotubes to form advanced composites, a crucial question was identified, namely the interfacial

bonding of the nanotubes to different matrices. Using an acidic treatment in a cc. H₂SO₄/cc. HNO₃ mixture results in nanotubes covered by carboxyl groups at their ends and/or their shell. These groups can easily be converted into carbonyl chloride groups simply by reacting them with SOCl₂. The resulting material is very reactive towards amines so choosing the appropriate reactant any kind of functional groups can be generated [14]. Many efforts have been done to modify the surface properties of carbon nanotubes. A simple mechanochemical functionalization of the CNT surface [15] or application of different coatings [16] may be prospective choices to enhance nanotube–matrix bonding. The manufacture of a ceramic composite generally requires high temperatures. A destruction of carbon nanotubes using hot-press technique was reported by Flahaut et al. Therefore, the high temperature degradation process of CNTs has to be further clarified to achieve a proper protection of CNTs at high temperature processes.

In this study, CVD grown multiwall carbon nanotubes (MWNTs) have been introduced into silicon nitride matrices. To evaluate the effectiveness of carbon nanotubes, carbon black, graphite and carbon fiber containing composites were used as comparison samples.

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2. Experimental method

2.1. Materials

Details about sample preparation can be followed in Table 1. The compositions of the starting powder mixtures of the eight materials were the same: 90 wt.% Si_3N_4 (Ube, SN-ESP), 4 wt.% Al_2O_3 (Alcoa, A16) and 6 wt.% Y_2O_3 (H.C. Starck, grade C). In addition to batches MWNTs (produced as described elsewhere [15]), carbon black (Taurus Carbon black, N330, average particle size between ~ 50 and 100 nm), graphite (Aldrich, synthetic, average particle size $1\text{--}2$ μm) and carbon fibers (Zoltek, PX30FBSWO8) were added [19]. The powder mixtures were milled in ethanol in a planetary type alumina ball mill for several hours. Each batch contained approximately 1 g alumina as contamination from balls and jars. The batches were sieved with 150 μm mesh. Powder samples were passed to FTIR examinations. After milling, the powder mixtures and carbon nanotubes (samples 684 and 689) were introduced in an ethanol bath and sonicated together. Samples were compacted by dry pressing at 220 MPa. Carbon fibers (629 sample from Table 1) were added to mixtures only before dry pressing.

2.2. Sintering method

The materials were sintered at 1700 $^\circ\text{C}$ in high purity nitrogen by a two-step sinter-hot isostatic press (HIP) method using BN embedding powder. In the case of samples 642r (carbon free reference sample), 644, 645, 629 and samples 672r (carbon nanotube free reference sample) and 684, a pressure of 2 MPa was applied for 1 h. For samples 670r (carbon nanotube free reference sample) and 689, a pressure of 20 MPa was applied for 3 h. The dimensions of the as-sintered specimens were approximately $3.5 \times 5 \times 50$ mm.

Table 1

The preparation conditions and carbon contain of starting powder mixtures

Batch	Added carbon species				Milling (in ethanol)	Ultrasonic agitation (in ethanol)
	Carbon black (wt.%)	Graphite (wt.%)	Carbon fiber (wt.%)	MWCNT (wt.%)		
642r					3 h	
644	23				150 h	
645		23			150 h	
629			1		3 h	
672r					3 h	
684				1	3 h (mixture)	1 h (mixture + CNT)
670r					3h	
689				1	3 h (mixture)	1 h (mixture + CNT)

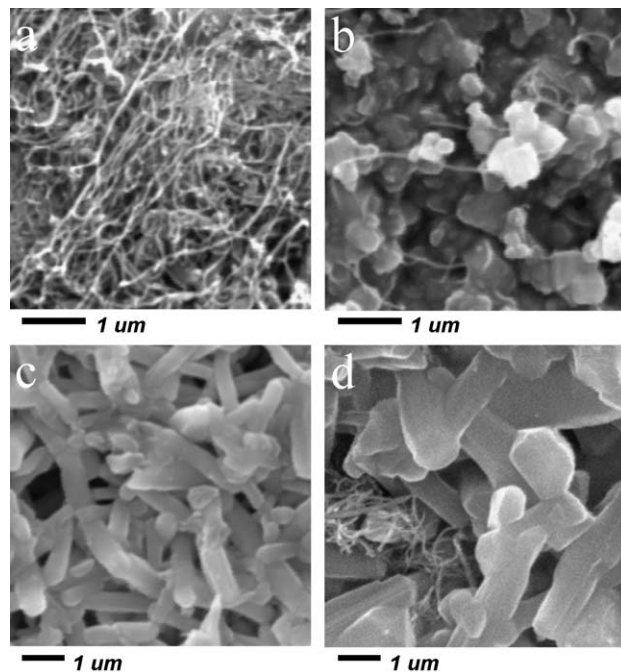


Fig. 1. Scanning electron micrographs of bundles of MWNTs (a), MWNTs introduced in powder mixture and polyethylene glycol (b), sintered reference sample (642) (c) and sintered MWNT composite at 2 MPa, 1700 $^\circ\text{C}$ for 1 h (sample 684).

2.3. Microstructural observations and mechanical tests

After sintering, the weight of the samples were determined. All surfaces of the test bars were finely ground on a diamond wheel, and the edges were chamfered. The density of the as-sintered materials was measured by the Archimedes method. Phase compositions were determined by Philips PW 1050 diffractometer. Infrared absorption

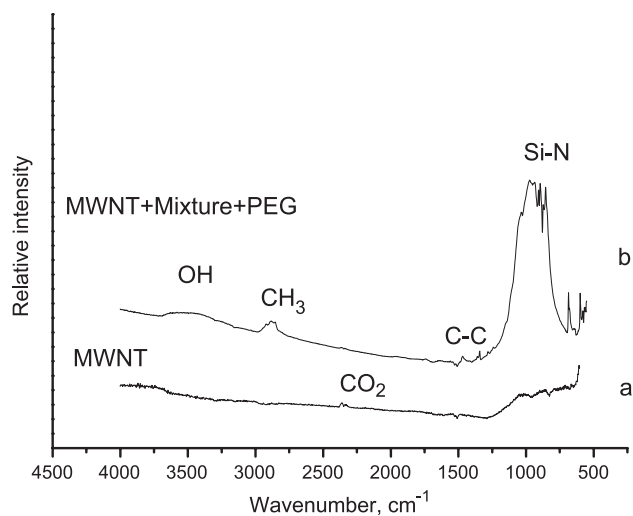


Fig. 2. Infrared spectra of MWNT (a) and MWNT composite (684) before sintering (b).

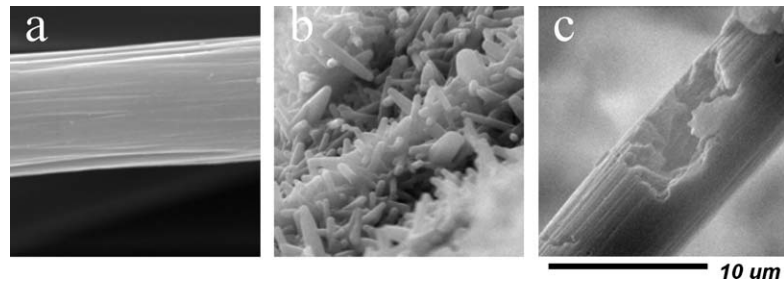


Fig. 3. Scanning electron micrographs showing the deterioration process of carbon fibers during sintering. (a) Intact carbon fiber as received. (b) Carbon fiber covered by β - Si_3N_4 crystals. (c) Cavity on the carbon fiber surface.

spectra were taken by BOMEM MB-102 FTIR spectrophotometer equipped with deuterio-triglycine-sulfate detector, at a resolution of 4 cm^{-1} , in the range of $400\text{--}4000\text{ cm}^{-1}$; 2 mg/g KBr pellets were used. Morphology of the solid products was studied by scanning electron microscopy. The elastic modulus and the four-point bend strength were determined by a bending test with spans of 40 and 20 mm. Three-point strength was measured on broken pieces with span 20 mm.

3. Results and discussion

A morphological study has been performed to follow the structural changes during the preparation of MWNT-silicon nitride composites. On Fig. 1a the MWNT bundles are presented. MWNTs are characterized by 10–20 nm thickness and can reach 1–2 μm length. MWNTs introduced in the powder mixture are shown in Fig. 1b. Note that sonication resulted in a successful dispersion of MWNTs in the powder mixtures. Fig. 1c shows the typical microstructure of a reference sample (672) after sintering at 1700 $^\circ\text{C}$, 2 MPa for 1 h. The growth of grains (mainly β - Si_3N_4 as defined by X-ray diffraction, not shown in this paper) can

be seen in the reference sample. The $\alpha \rightarrow \beta$ - Si_3N_4 conversion was completed in the case of MWNT composites as well (samples 684). Moreover, larger size β - Si_3N_4 grains evolved in the presence of MWNTs, as presented in Fig. 1d.

On the MWNT's infrared spectra no characteristic peak can be observed (Fig. 2a). As it regards the spectra of pre-composite, peaks related to alpha silicon nitride (in the $500\text{--}1000\text{ cm}^{-1}$ region), characteristic PEG vibrations ($1000\text{--}1400\text{ cm}^{-1}$ region, C–C stretching), C=O and OH stretching vibrations (2900 respective 3500 cm^{-1}) can be recognized.

We have found a deterioration process in the case of sample 629 with carbon fiber addition (Fig. 3). The degradation of carbon fibers during sintering is manifested in two characteristic ways. The smooth surface of carbon fibers after sintering is covered by β - Si_3N_4 crystallites (as shown in Fig. 3b). Another finding is presented in Fig. 3c; cavities are developing on the fibers surface which can lead to a total disappearance of carbon fibers from the structure. We ascribe these degradations to chemical reactions taking place during sinter-HIP method [17,18]. The reaction gases may reduce the second phases present in structure, which are exhausted from composite (in the form of CO, CO_2) during the procedure.

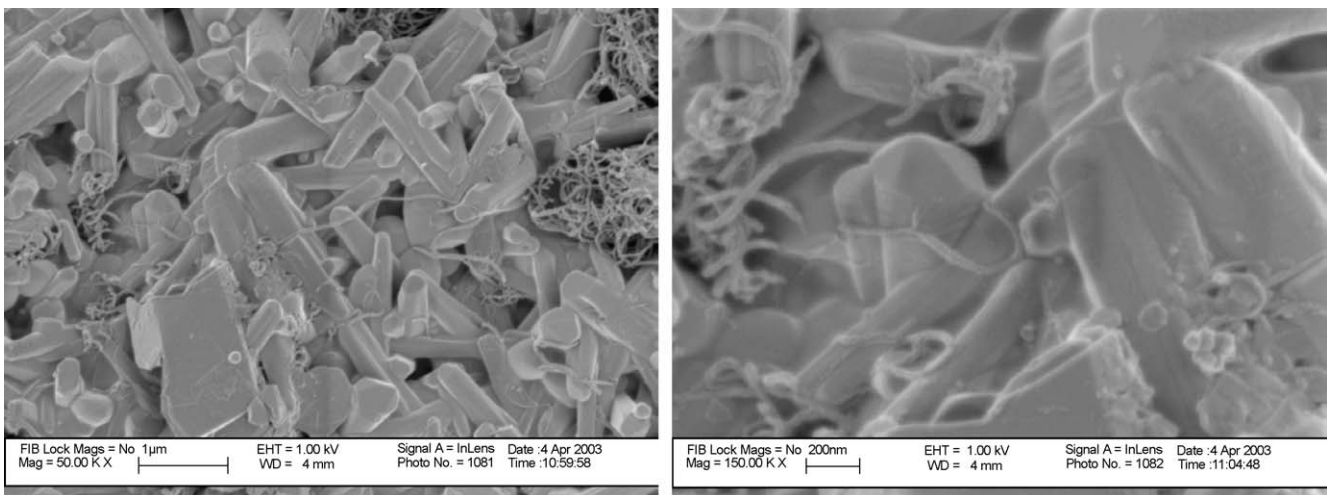


Fig. 4. Scanning electron micrograph of composite 684, with MWNT bundles and lonely MWNTs connecting β - Si_3N_4 crystals, in the center (left) and higher magnification of interconnected β - Si_3N_4 grains by MWNTs, in the center (right).

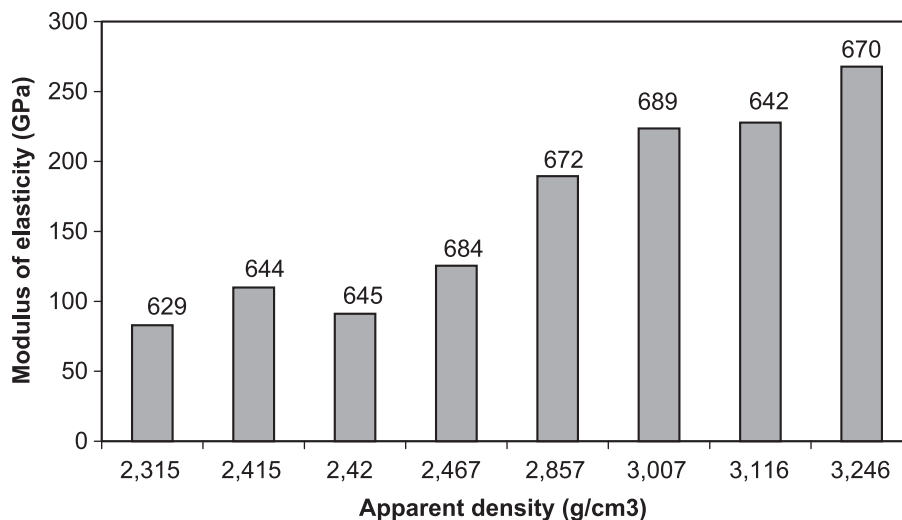


Fig. 5. Modulus of elasticity of composites as a function of apparent density. In each column, the average value of three samples is presented.

The fracture surfaces of MWNT composite after sintering (684) are presented in Fig. 4. At lower magnification (on the left side) it is shown that after sintering at 1700 °C, 2 MPa for 1 h the composite contains MWNT bundles, but MWNTs separated are also shown. These separated nanotubes can connect up to two or five β -Si₃N₄ grains as it is shown in the center of the micrograph. At higher magnification (right side) interconnected β -Si₃N₄ grains by separated MWNTs can be seen.

However, in the case of MWNT composite 689, sintered at 1700 °C, 20 MPa for 3 h the carbon nanotubes are missing from microstructure. To justify this microstructural observation a compositional analysis was performed, as presented elsewhere [20]. The compositional analysis of sintered samples were done by prompt-gamma activation analysis (PGAA) which is based on the detection of

prompt gamma rays originating from (n, γ) reaction, and gives average elemental composition of the total volume of the sample [21]. The MWNT composites of batch 689 showed no carbon content in the structure. In Figs. 5 and 6, the results of mechanical testing are shown. We choose two density range 2.3–2.4 and 2.8–3.3 g/cm³, respectively, to separate the effects of structure and density. In each column, the average values of three samples are presented. For the composites having the apparent density in the range of 2.3–2.4 g/cm³ the carbon nanotube addition yields the highest modulus (Fig. 5). A relative improvement of 15% can be achieved by nanotube addition (composite 684) in comparison to carbon black addition (644). On the other hand, the carbon black containing composites have higher modulus than graphite (645) and carbon fiber (629) added composites. However, as it can

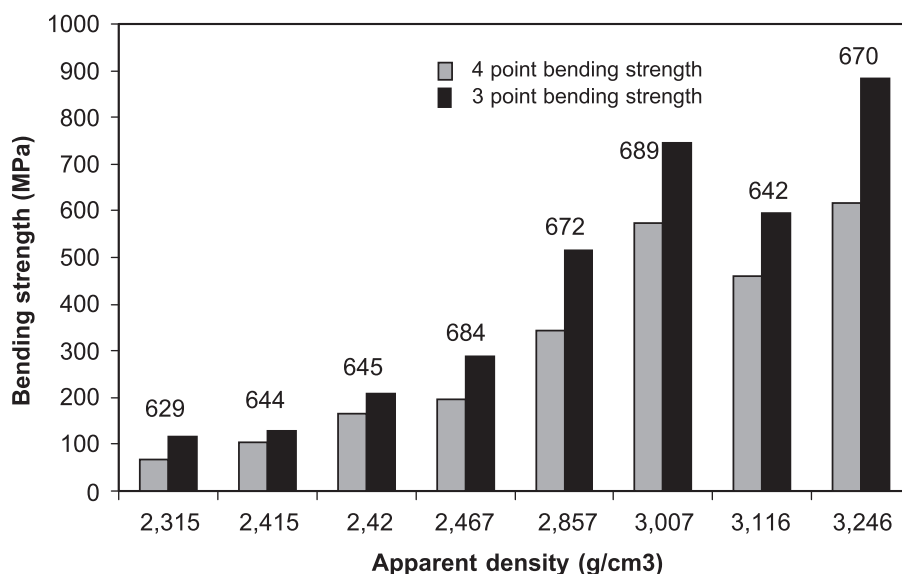


Fig. 6. Bending strength (three and four point) of composites as a function of apparent density. In each column, the average value of three samples is presented.

be observed, the compacted reference samples present higher modulus values than carbon added samples, because of their higher apparent densities.

Three- and four-point bending strengths of composites as a function of apparent density are shown in Fig. 6. A relative increase of four-point bending strength of about 18% in comparison to graphite added composites (645) can be noticed in favour of carbon nanotube added samples. A relative high increase of 37% is shown in the case of three-point bending strength comparing the same samples (684 and 645). The graphite containing composites have higher strengths than carbon black (645) and carbon fiber (629) added composites. Compacted samples (2.8–3.3 g/cm³) have higher strengths than carbon-added samples.

4. Conclusions

MWNT-silicon nitride composites were manufactured by sinter-HIP method. For comparison, carbon fiber, carbon black and graphite added composites have been also prepared. The microstructure of sintered MWNT composite consisted mainly of β -Si₃N₄ and nanotubes. Two characteristic ways of deterioration of carbon fibers were detected. Either the surface of carbon fibers was covered by crystallites, or cavities developed due to chemical reactions. The CNTs after sintering at 2 MPa survived; they connect the β -Si₃N₄ grains and produce a 15–37% improvement of the mechanical properties as compared with other carbon filled samples. Pressure and sintering time increase resulted in disappearance of MWNTs from composite structure. Further studies are needed to optimize the relation of preparation conditions and the improvement of mechanical properties.

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