NOVEL SILICON NITRIDE – CARBON NANOTUBE COMPOSITES

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Abstract

Multiwall carbon nanotube reinforced silicon nitride composites have been prepared by hot isostatic pressing. A manufacturing process has been worked out to avoid the damage of nanotubes during sintering. This method provides their preservation even in severe circumstances at temperature of 1700°C and gas pressure of 20 MPa. As shown by scanning and transmission electron microscopy after low and high pressure processing, carbon nanotubes have good adherence to the silicon nitride grains. Moreover, carbon nanotubes have been found to be located not only at grain surfaces, but in several cases they are well integrated with the silicon nitride grains. Composites with higher strengths can be obtained by increasing the nitrogen gas pressure.

Keywords: carbon nanotube, silicon nitride, composites

INTRODUCTION

Carbon nanotubes (CNTs) discovered by Ijima, have shown to possess remarkable mechanical, electrical and thermal properties [1]. Therefore, carbon nanotubes are intensively studied to effectively apply as reinforcing agents in ceramic matrix composites [2-5]. One of the key problems of composite processing that still persist is the homogeneous dispersion of CNTs throughout the matrix. For this reason, to increase the dispersion grade of CNTs in ceramic matrix we performed high efficient ultrasonic homogenisation and milling processes, or functionalisation of carbon nanotubes has been applied [6,7]. Another interesting dispersion method is given by An *et al.* [8]. In this case, the CNT-reinforced ceramic composites are realised by using polymer derived ceramics (PDCs), which assures the desired dispersion grades in liquid–phase precursors just prior to pyrolysis. A colloidal processing as an efficient dispersing tool has been also proposed by Sun *et al.* [9]. In order to effectively utilise the CNTs it is crucial to retain CNTs un-attacked in the composites and to optimise the interconnection between CNTs and the matrix to achieve load and current transition. Using conventional sintering techniques (hot pressing, hot isostatic pressing), which are characterised by the requirement of extended holding times at very high temperatures and pressures, the destruction of CNTs has been reported [3,6,10]. Earlier studies have demonstrated the suitability of the spark plasma sintering (SPS) method to fast densification at low temperatures [11-15]. In our former work the validity of SPS technique in

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consolidating and tailoring the microstructure of multiwall carbon nanotube reinforced silicon nitride based composites has been studied and has been successfully applied [16]. Electrically conductive silicon nitride ceramics have been realized by carbon nanotube, and carbon black and graphite additions in comparison [17].We have found that the carbon addition may drastically change the electric properties of composites. Insulator and conductor silicon nitrides with low resistance were developed depending on the type and concentration of carbon addition. In a recent study carbon nanotube-dispersed silicon nitride ceramics with electrical conductivity were developed based on a lower temperature densification technique by using novel sintering aids [10]. This novel ceramic with a small amount of CNTs exhibits very high electrical conductivity in addition to high strength and toughness. This new type of electrically conductive silicon nitrides are proposed to be applied in aerospace as high performance static-electricity-free bearings.

In this work the optimisation of hot isostatic pressing together with a study about the interconnection phenomena of CNTs and silicon nitride grains have been performed. Morphological, structural and mechanical investigations will be presented.

EXPERIMENTAL PROCEDURE

Composition of the starting powder mixtures and some details about preparation methods are presented in Table 1. Starting powders used in experiments were as follows: Si_3N_4 (Ube, SN-ESP); whereas as sintering aids we used the following powders: Al_2O_3 (Alcoa, A16) and Y_2O_3 (H. C. Starck, grade C). The powder mixtures together with MWNTs (multiwall carbon nanotubes, produced by CCVD method described in details in [7]) were milled in ethanol in a planetary type alumina ball mill. After milling the powder mixtures and MWNTs were introduced in an ethanol bath and sonicated together for one hour. After sonication, polyethylenglycol (PEG) was added to the powder mixtures. The batches were sieved with 150 μm mesh. Green samples were obtained by dry pressing at 220 MPa. Samples prepared for HIP were oxidised at 400°C to eliminate the PEG. Hot isostatic pressing (ABRA type) was performed at 1700°C in high purity nitrogen using BN embedding powder. The heating rate did not exceed 25°C/min. The dimensions of the as-sintered specimens were 3.5 x 5 x 50 mm.

Tab.1. Starting compositions and preparation conditions of sintered samples.

Batch	Starting powders	MWNT	Ball milling (in ethanol)	Ultrasonic homogenisation (in ethanol)	Sintering conditions		
	[wt.%]	[wt.%]			T [°C]	Holding time	Pressure [MPa]
	Si_3N_4 Al_2O_3 Y_2O_3						
SN	90 4 6	-	3h (mixture)	-	1700	-	2
C1	90 4 6	1	3h (mixture)	1h (mixture+MWNT)	1700	-	2
C2	90 4 6	1	3h (mixture)	1h (mixture+MWNT)	1700	1 h	2
C3	90 4 6	1	3h (mixture)	1h (mixture+MWNT)	1700	3 h	20

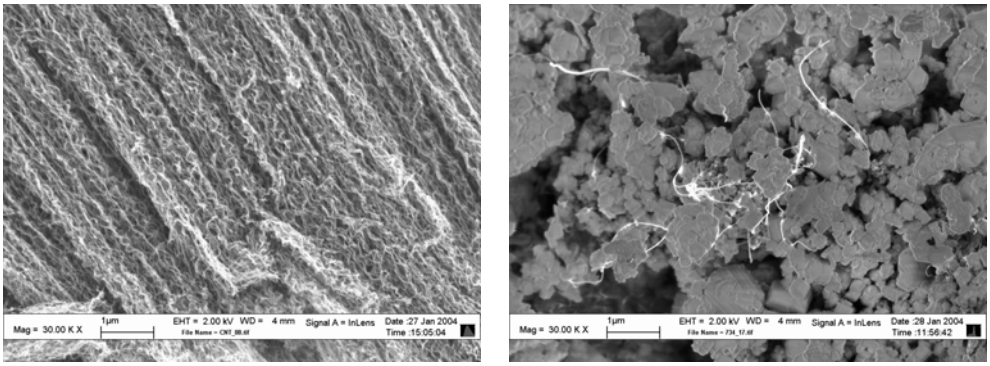
The density of the sintered materials was measured by the Archimedes method. Phase compositions were determined by Philips PW 1050 diffractometer. Morphology of the solid products was studied by field emission scanning electron microscope, LEO 1540 XB. For HIP samples the three-point bending strength was determined by a bending test with spans of 20 mm.

Transmission electron microscopy (TEM) study

Cross-sectional specimen was made by mounting and gluing a 1.5 x 1.5 x 0.5 mm^3 piece of the composite into a Ti grid [18] followed by mechanical thinning, polishing and thinned to electron transparency by ion beam milling with 10 keV Ar+ impinging at 4° with respect to the surface. The ion milling was finished at 3 kV to avoid the damage. The sample was examined in JEOL 3010 and Philips CM20 transmission electron microscopes operated at 300 kV and 200 kV with a point resolution of 1.7 and 2.8 Å, respectively.

RESULTS AND DISCUSSION

The characteristics of starting MWNTs are presented in Fig.1a. The nanotubes have the diameter around 10-20 nanometer and can reach 8-10 micrometer length. In Figure 1b the scanning electron micrographs of MWNTs dispersed in starting powder mixture consisting of α-Si_3N_4, Al_2O_3, Y_2O_3 and PEG can be seen. To assure a good homogeneity the ball milling and ultrasonic homogenisation of MWNT containing powder mixtures have also been performed.



a b

Fig.1. Scanning electron micrographs of MWNTs as prepared by CCVD (a), and MWNTs dispersed in starting powder mixture α-Si_3N_4, Al_2O_3, Y_2O_3 and PEG (b).

The fracture surface of a sample from batch C2 prepared at low gas pressure (2 MPa) and short holding time (1h) at 1700°C is presented in Fig.2. First, a general view about the characteristic fracture surface is shown (Fig.2-left). As can be observed well developed β-Si_3N_4 grains (with length 1-2 μm) evolved during sintering. A more detailed view about the characteristics of CNTs and silicon nitride contacts are shown in Fig.2-right. In some parts web-like connected MWNTs can be found in the structure, but individual MWNTs, properly attached to β-Si_3N_4 surfaces can also be observed (Fig.2-left). It was shown in an earlier study that MWNTs can serve as ideal crystallisation sites for β-Si_3N_4 grains during the complex liquid phase sintering process [19]. X-ray observations for composite samples are presented in Fig.3.

In the case of sample SN (reference sample without CNT addition) we found more α-Si_3N_4 than β-Si_3N_4 in structure. As it can be observed from Fig.3, for the same preparation conditions, the CNT addition promotes the β-Si_3N_4 formation, more β-Si_3N_4 lines appeared in the case of sample C1 compared to sample SN. If the gas pressure was increased to 20 MPa and holding time to 3 hours (at 1700°C) only β-Si_3N_4 can be found in the structure of composites (sample C3). The similar microstructure was observed for sample C2 (not shown in Fig.3).

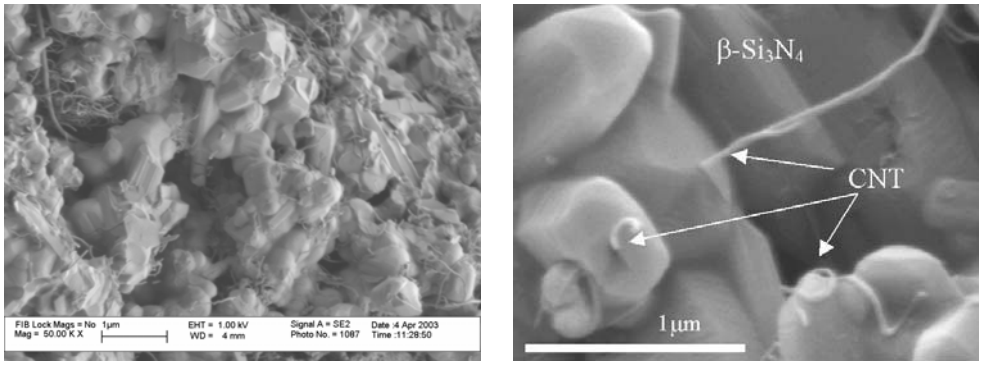


Fig.2. Fracture surface of composite C2. A general view (a); Details about MWNT/grain surface interaction (b).

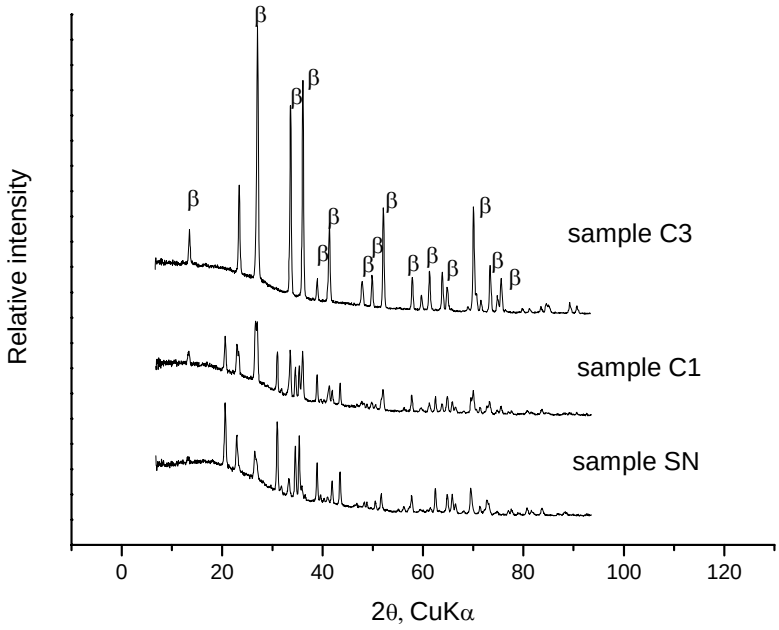
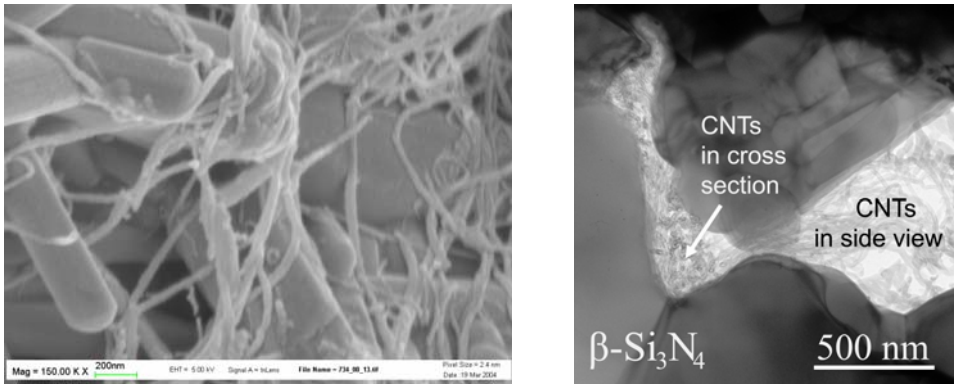


Fig.3. XRD results for reference SN, and composites C1 and C3 prepared as in Table 1.

The fracture surface of a sample from batch C3 prepared at high gas pressure (20 MPa) and long holding time (3h) at 1700°C is presented in Fig.4. The long β-Si_3N_4 grains

together with attaching carbon nanotubes can be observed in the fracture surface (Fig.4a) and in the TEM micrograph as well (Fig.4b).



a b

Fig.4. Scanning electron micrograph and transmission electron micrograph of composite C3.

Selected Area Electron Diffraction (SAED) study

The diameters of these rings provide information about the plane spacing to identify the structure of the present phase(s), while the brightness and width of the diffraction rings can be used to deduce information on the degree of short range ordering (Fig.5). According to the HRTEM image the structure of the multiwall nanotubes is well preserved after the applied sintering process (case of sample D). Based on the analysis of the distribution of the diffraction pattern the diameters of the first five rings correspond to the plane spacings of approximately 3.5Å, 2.13Å, 1.75Å, 1.24Å and 1.07Å.

Similar diffraction patterns were reported for the fullerene-like allotropes of carbon or CNx where four easily distinguishable rings with diameters of ≈1.15, 1.75, 1.95 and 3.5 Å [24]. The two rings at ≈1.15 Å and ≈1.95 Å coincide with those observed for the amorphous allotropes of carbon and CNx films. However, the innermost ring matches a plane spacing of approximately ≈3.5 Å and ≈1.75 Å corresponding to the plane separation of hexagonal basal planes of graphite (0002) and (0004), respectively, indicating the short/medium range graphitic order.

The plane spacing of 3.5Å, and 1.75Å, can be indexed as graphite (0002) and (0004) respectively. Due to the broad nature of the rings (102) and (103) reflections may be involved in the case of 1.75Å ring. For similar reasons the peaks at 2.13Å, are sums of (100) and (101) reflections. The peaks at 1.24Å and 1.07Å coincide with graphite (110) and (201) reflections and the broad feature between them may involve (112) and (006) reflections.

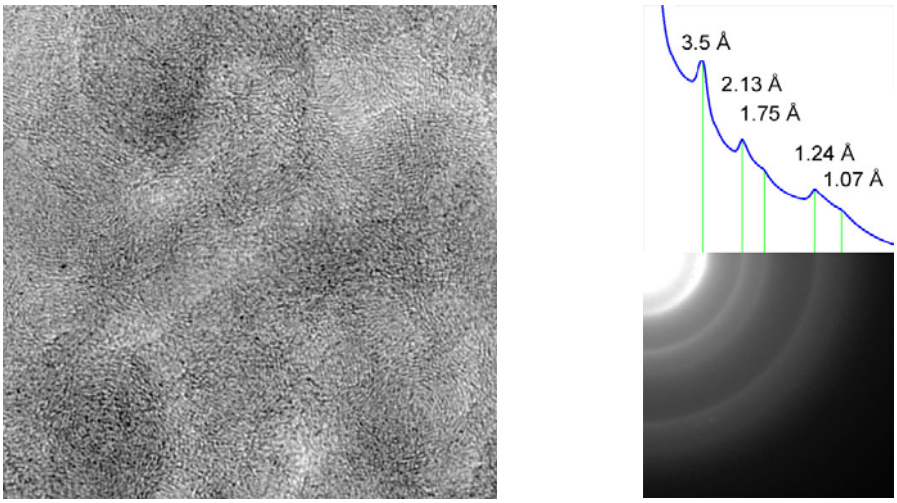


Fig.5. TEM micrograph and SAED pattern of CNTs in the composite C3 after sintering process, revealing the preservation of CNTs after high gas pressure sintering (20 MPa, 1700°C, 3 h)

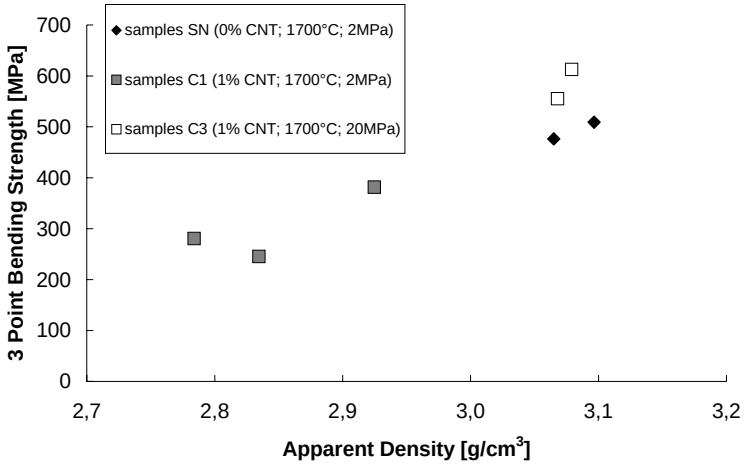


Fig.6. Three point bending strength of reference samples SN and composites C1 and C3 as a function of the apparent density.

On the basis of the width of the rings the diffraction pattern is more similar to that of nanocrystalline graphite than to the fullerene-like allotropes of C or CNx. This is due to higher degree of short/medium range graphitic ordering, i.e. in the direction of tube axes (parallel with the basal planes) indicating the preservation of the multiwall nanotubes.

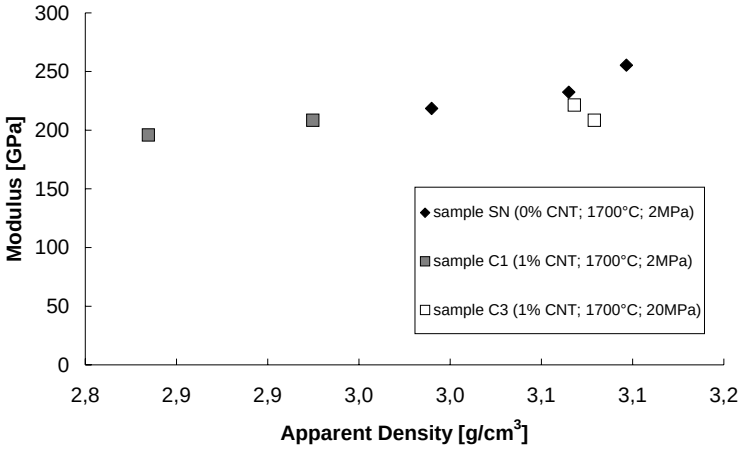


Fig.7. Modulus of elasticity of reference sample A and composites B and D in function of the apparent density.

The relationship between apparent density and three point bending strength of composites and reference sample SN can be seen on the Fig.6. By applying a higher pressure (20 MPa) a higher densification level, and a strength increase by 100% from an average level of 300 MPa to 600 MPa can be realised in the case of 1% CNT addition (composite C1 and C3). The sample C3 was found to have the highest degree of densification connected to highest strength. The strength of composite C3 was even higher than for reference sample SN (prepared at low pressure (2 MPa) without any nanotube addition).

A linear relation between the apparent density and the modulus of the composites has been observed as presented in Fig.7. The reference samples from batch A, without any nanotube addition have the highest degree of densification connected to highest modulus value. As can be observed in the case of composites prepared at lower pressure (2 MPa, samples from batch B), with CNT addition the porosity has been increased which had a detrimental role to modulus. By increasing the gas pressure (and holding time) the same level of densification can be achieved for composites with 1% CNT (samples from batch D) as for reference sample A, realised at low pressures. A higher densification level, but similar modulus values could be realised with increasing the pressure by one order of magnitude (from 2 to 20 MPa) in the case of 1% CNT addition.

CONCLUSIONS

Silicon nitride composites reinforced with CNTs have been manufactured by hot isostatic pressing. Appropriate parameters of technology were chosen which provided the maintenance of carbon nanotubes in composites and hindered their degradation during sintering even at high temperature (1700°C) and high pressure (20 MPa). As shown by scanning and transmission electron microscopy carbon nanotubes have good adherence to the silicon nitride grains, as observed for low and high pressure processing as well. Moreover, carbon nanotubes have been found to be located not only at the surface of silicon nitride grains but in several cases well integrated with them. The increase of the nitrogen gas pressure during HIP treatment resulted in an increase of bending strength.

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