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Structural characterization of Si₃N₄-carbon nanotube interfaces by transmission electron microscopy

Csaba Balázsi^{*1}, Katarína Sedláčková², Zsolt Czigány²

¹ *Ceramics and Composites Laboratory, Research Institute for Technical Physics and Materials Science, Konkoly-Thege M. út 29-33, 1121 Budapest, Hungary*

² *Thin Film Physics Laboratory, Research Institute for Technical Physics and Materials Science, Konkoly-Thege M. út 29-33, 1121 Budapest, Hungary*

Corresponding author: Csaba Balázsi, Phone: +36-1-392-2249, Fax: +36-1-392-2226

E-mail: balazsi@mfa.kfki.hu

1. Introduction

In recent years, ceramic materials with combination of carbon nanotubes (CNTs) have been intensive studied for their general potential applications [1-3]. Composites prepared by combining CNTs with brittle ceramics can impart some of the attractive mechanical properties of the carbon nanotubes to the resulting matrices. Ma *et al.* incorporated 10 vol.% multiwall carbon nanotubes (MWCNTs) into SiC, however only a marginal increase in bend strength and toughness over SiC ceramics without MWCNTs was found [4]. 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 homogenization and milling processes, or functionalization of carbon

nanotubes has been applied [3,5]. Another interesting dispersion method is given by An *et al.* [6]. In this case, the CNT-reinforced ceramic composites are realized 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 also been proposed by Sun *et al.* [7]. In order to effectively utilize the CNTs it is crucial to retain CNTs intact in the composites and to optimize the interconnection between CNTs and the matrix to achieve load and current transition. In a recent study, Vasiliev *et al.* presented some new results on grain boundaries and nanotube orientation which resulted between 10 vol.% single wall carbon nanotubes (SWCNTs) in Al₂O₃ ceramic [8].

In this work the study and characterization of silicon nitride/CNTs interfaces by transmission and high resolution microscopy will be presented.

2. Experimental

2.1. Preparation of composites

The main starting powder used in experiments was α -Si₃N₄ (Ube, SN-ESP). We used the sintering aids in form of following powders 4 wt% Al₂O₃ (Alcoa, A16) and 6 wt% Y₂O₃ (H.C. Starck, grade C). The powder mixtures together with 1 wt% MWCNTs were milled in ethanol in a planetary type ball mill (Fritsch), whereas the powders with 3 wt% MWCNTs were processed using a water based mixing in attritor (Union Process). The MWCNTs were prepared by CCVD method described in [5]. After 3h ball milling the powder mixtures and MWCNTs were introduced in an ethanol bath and sonicated for 1h. In the case of attrition milling a high rotation speed (4000 rpm) was used for 5h. The powder mixtures were sieved, compacted and sintered by hot isostatic

pressing (HIP, ABRA type). Sintering was performed at 1700°C, in high purity nitrogen at 20 MPa, with 3h holding time. The heating rate did not exceed 25°C/min.

2.2. Characterization techniques

The structure of ceramic composites was investigated by conventional transmission electron microscopy (TEM) using a Philips CM-20 (200 kV) microscope and by high resolution electron microscopy (HREM) using a JEOL 3010 (300 kV) microscope. The elemental compositions were measured by Ge detector NORAN EDS (Energy Dispersive Spectrometer), attached to the CM-20 microscope.

3. Results and Discussion

3.1. Silicon nitride ceramics with CNTs prepared by ball milling

The starting powder mixtures consisted of 90 wt% α -Si₃N₄, 4 wt% Al₂O₃, 6 wt% Y₂O₃ and 1wt% MWCNTs. Ball milling and ultrasonic agitation of powder mixtures assured a decent homogeneity. In our previous work [3], we characterized the starting powder mixtures by SEM. That study showed that the nanotubes have the diameter ~ 20 nm and can reach 8 ÷ 10 μ m in length.

The HREM characterization of sintered silicon nitride with CNTs showed that there is a good contact between nanotubes and the surface of silicon nitride grains (Fig. 1). Nanotubes located in porosity enclosed within β -Si₃N₄ grains are shown by the cross section TEM image (Fig. 1a). Selection area electron diffraction (SAED) with 3.5 Å reflection maximum (typically for (002) graphite) confirmed the presence of CNTs between silicon nitride grains (Fig. 1).

3.2. Silicon nitride ceramics with CNTs prepared by attrition milling

In this case, starting powder mixtures consisted of 90 wt% α -Si₃N₄, 4 wt% Al₂O₃, 6 wt% Y₂O₃ grains and 3 wt% MWCNTs addition.

As revealed by TEM analysis, after milling by high efficient attritor, the ceramic powder comprised of ~ 200 nm crystallites and dispersed CNTs (Fig. 2a). In Fig. 2b the dispersed nanotubes in ceramic powder mixture may be observed. The nanotube radius is ~ 25 nm. This observation is in correlation with our previous SEM study [3].

The structure of $\text{Si}_3\text{N}_4/\text{CNT}$ composite is shown in Fig. 3a and 4. The sample consisted of $\sim 300 \div 400$ nm nanocrystalline grains. The CNTs were distributed into porosities and in the intergranular places (Fig. 3). The HREM investigation of $\beta\text{-Si}_3\text{N}_4/\text{CNTs}$ interface revealed the good ceramic-nanotube contact (Fig. 3b). Cross section TEM analysis showed, that the CNTs between $\beta\text{-Si}_3\text{N}_4$ grains had similar orientation as in the case of ball milling; cross section and side view of CNTs are evidenced (Fig. 4). Similar observation was founded in Al_2O_3 ceramics with single-wall CNTs [8].

4. Conclusions

Silicon nitrides with (1 and 3 wt%) CNTs were prepared by two milling techniques. The structure of composites and the interface between $\beta\text{-Si}_3\text{N}_4$ crystallites and nanotubes were investigated by TEM and HREM. In the case of ball milling the average size of $\beta\text{-Si}_3\text{N}_4$ crystallite grains $\sim 1 \mu\text{m}$ and the pore size ~ 500 nm were obtained after sintering. In comparison, in the case of attritor milling smaller grain size ~ 300 nm and pore size ~ 250 nm resulted after sintering. In both cases, the nanotubes were located mainly into porosities and in intergranular places. The CNTs had similar orientations, cross section and side view of CNTs have been observed.

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Fig.1

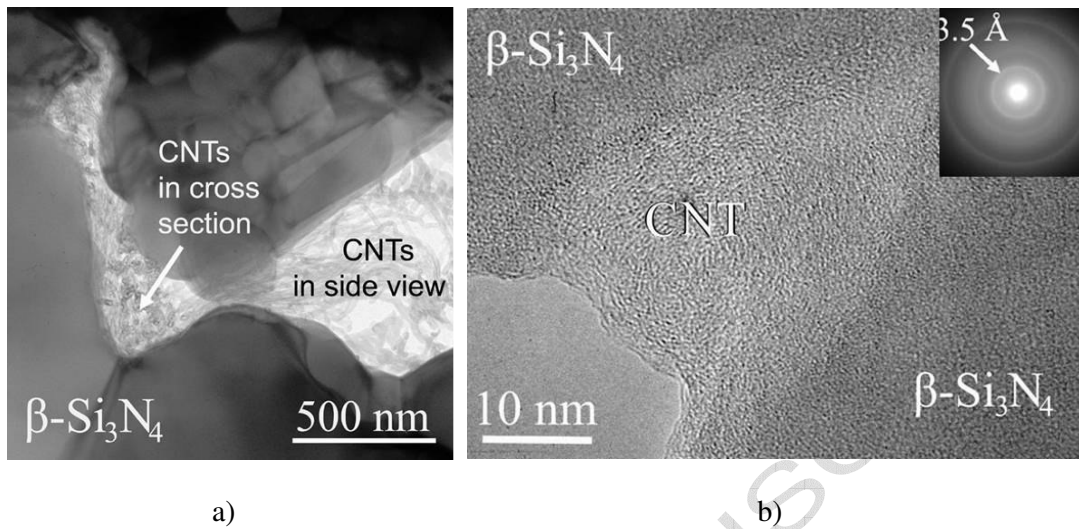


Fig. 1 TEM images of sintered silicon nitride with 1 wt% CNTs prepared by ball milling. a) TEM image of CNTs located in porosity reveals two different orientations. b) HREM image of sintered Si_3N_4 shows CNTs embedded between two β - Si_3N_4 grains. The electron diffraction confirmed the presence of CNT.

Fig.2

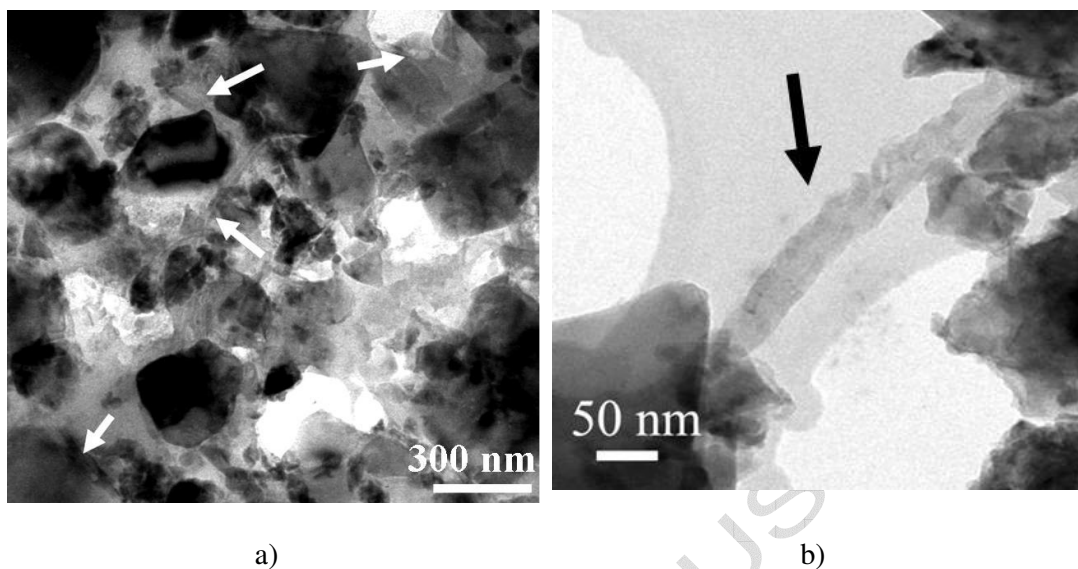


Fig. 2 Bright field TEM images of starting powder mixture with 3 wt% CNTs prepared by attrition milling. a) TEM image shows the CNTs (marked) between grains. b) The detail of CNT (marked) with ~ 25 nm radius.

Fig.3

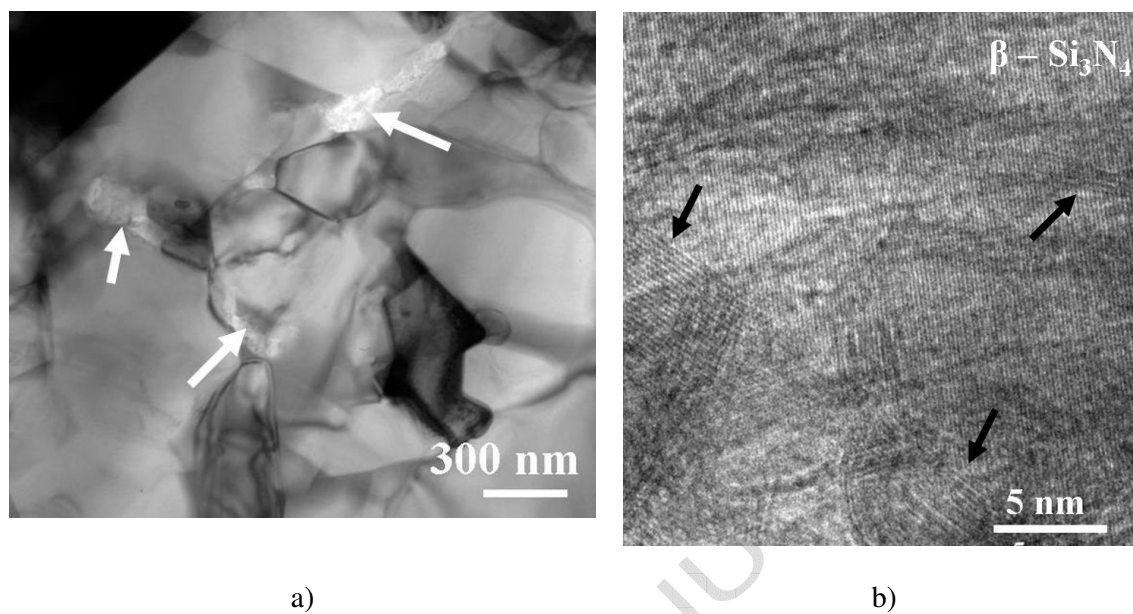


Fig. 3 TEM images of sintered $\text{Si}_3\text{N}_4/\text{CNT}$ composite prepared by attrition milling.

a) Cross-section bright field TEM image shows the CNTs located into porosities between β - Si_3N_4 grains. b) HREM image shows the silicon nitride-CNTs interfaces.

Fig.4

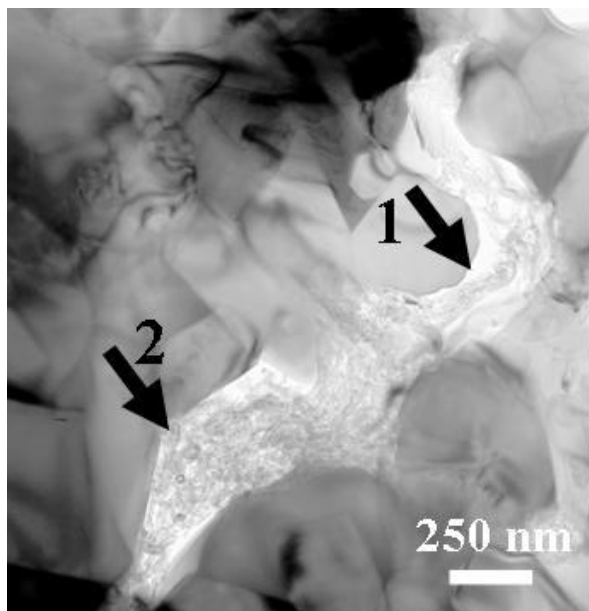


Fig. 4 Cross section TEM image of $\text{Si}_3\text{N}_4/\text{CNT}$ composite prepared by attrition milling. CNTs (marked) are located into porosity between Si_3N_4 grains. 1. CNTs in side view, 2. CNTs in cross section view.