



Processing, mechanical and thermophysical properties of silicon nitride based composites with carbon nanotubes and graphene

O. Koszor¹, F. Wéber¹, P. Arató¹, A. Lindemann², L. P. Biró³, Z. E. Horváth³, Z. Kónya⁴, I. Kiricsi⁴, Cs. Balázs¹

¹*Ceramics and Composites Laboratory, Research Institute for Technical Physics and Materials Science, Hungarian Academy of Science, P.O. Box 49, Budapest XII, Konkoly-Thege út 29–33, H-1121 Budapest, Hungary*

²*Netzsch-Geratebau GmbH, Applications laboratory*

³*Nanotechnology Department, Research Institute for Technical Physics and Materials Science, Hungarian Academy of Science, P.O. Box 49, Budapest XII, Konkoly-Thege út 29–33, H-1121 Budapest, Hungary*

⁴*Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1., H-6720 Szeged, Hungary*

Received 11 August 2007; received in revised form 7 November 2007; accepted 12 November 2007

Abstract

Silicon nitride based composites with different amount (1, 2 and 3 wt%) of multi-wall and single-wall carbon nanotubes, and graphene have been prepared. Optimisation of the manufacturing processes has been conducted to preserve the carbon nanotubes in composites and to avoid damaging during high temperature processing. The first results show that carbon nanotubes have a good contact to the surface of silicon nitride grains. In the case of increase of sintering pressure an increase of bending strength was achieved. It was found that microstructure features achieved by properly designed sintering parameters are the main responsible factors for the strength improvements.

Keywords: carbon nanotubes, graphene, silicon nitride, mechanical properties

I. Introduction

Carbon nanotubes (CNTs) have been reported to possess exceptional mechanical and electrical properties [1–5]. Therefore, it is expected that the addition of CNTs will radically improve the quality of different matrices, such as polymer, metal and ceramic. So far, only modest improvements of properties were reported in CNTs reinforced silicon carbide [6] and silicon nitride matrix composites [7], whereas a noticeable increase of the fracture toughness and of electrical conductivity has been achieved in CNTs reinforced alumina matrix composites [8,9]. Another research group have found for these composites rather low increments in toughness in the classical sense, but the material shows resistance to indentation (contact) damage [10,11]. The CNTs positioned to the grain boundaries in alumina which can

provided shear weakness under indentation could explain this phenomenon. In order to get the full benefits provide by CNTs, it is crucial to achieve a good dispersion of CNTs in the ceramic matrix. Retaining the CNTs un-attacked in the composites and to optimising the interfacial bonding between CNTs and matrix are the further requirements. In this way the toughening effects characteristic to nano-scale fiber composites could be explored: crack bridging by CNTs, CNT pullout on the fracture surfaces and crack deflection at the CNT/matrix interface [12]. This study is focusing on the preparation processes that allow the tailoring of the microstructure of carbon nanotube reinforced silicon nitride-based ceramic composites. Experimental procedure has been conducted to effectively disperse the CNTs in the matrix. Importance was given to temperature-pressure-holding time relation to preserve the carbon nanotubes in composites and to avoid damaging during high temperature processing. The existence of a strong enough bonding between the carbon nanotube

* Corresponding author: tel: +36 1 703 7571, fax: +36 1 392 2226, e-mail: koszor@mfa.kfki.hu

and the silicon nitride matrix has been monitored, too. Morphological, structural observations, as well as characterisation of mechanical and thermophysical properties will be presented.

Table 1. Starting compositions of sintered samples

Samples	Carbon additions			
	MWCNT [wt%]	SWCNT [wt%]	Graphene [wt%]	Carbon black [wt%]
A	–	3	–	–
B	3	–	–	–
C	–	–	1	–
D	–	–	3	–
E	–	–	–	3
F	–	–	–	1
G	2	–	–	1
H	3	–	–	–

II. Experimental Details

The details concerning the composition of the starting powder mixtures and preparation can be seen in Table 1. Si_3N_4 (Ube, SN-ESP), Al_2O_3 (Alcoa, A16) and Y_2O_3 (H. C. Starck, grade C) were used as starting powders in 90 wt%, 4 wt% and 6 wt% mixing ratios. Different amount of CNTs (multi-wall carbon nanotubes MWCNTs, produced as described elsewhere [13]; single-wall carbon nanotubes, SWCNTs, Nanocyl Co; graphene from Russia; and carbon black, Taurus Carbonpack, Hungary) were added to batches (1, 2 and 3 wt%).

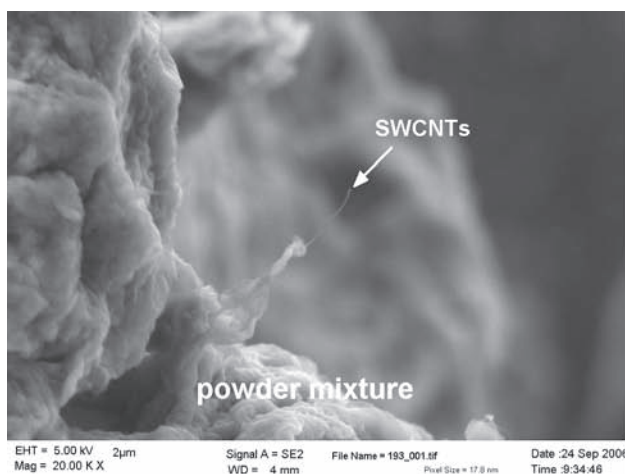
The powder mixtures together with the added CNTs were milled in distilled water in a highly efficient attritor mill (Union Process Inc.) for five hours. As resulted from weight measurements each batch contained approximately 1–3 wt% zirconia as contamination from

balls and discs. After milling surfactants (polyethyleneglycol, PEG) were added to the powder mixture. The batches were dried and sieved. Green samples were obtained by dry pressing at 220 MPa. Before sintering an oxidation was carried out at very low heating rates up to 400°C, to eliminate the PEG from samples. Hot isostatic pressing was performed at 1700°C in high purity nitrogen by a two-step sinter-HIP method using BN embedding powder. The heating rate was not exceeding 25°C/min. The gas pressure (2 and 20 MPa) and holding time (0 to 3 hours) were also varied. The dimensions of the as-sintered specimens were 3.5×5×50 mm. After sintering, the weight change of the samples was determined. All surfaces of the samples were finely ground on a diamond wheel, and the edges were chamfered.

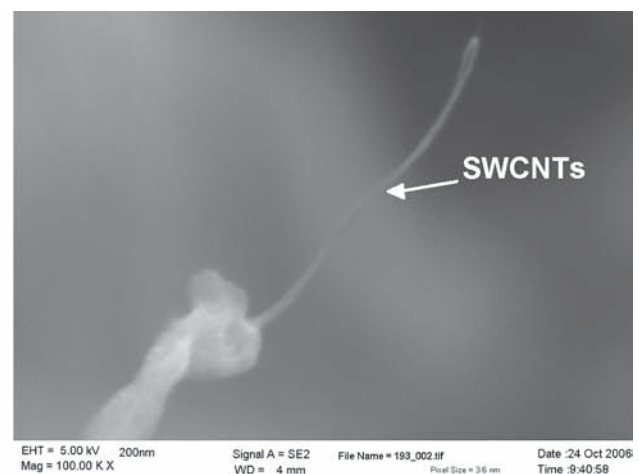
The density of the sintered materials was measured by the Archimedes method. Phase compositions were determined by Philips PW 1050 diffractometer. Morphology of the solid products was studied by field emission scanning electron microscope, LEO 1540 XB. For sintered samples the elastic modulus and four point bending strength were determined by a bending test with spans of 40 mm.

III. Thermophysical Properties of Composites

The samples were tested with the LFA 457 from room temperature to 900°C. The measured samples were disks with a diameter of approx. 10 mm and thickness between 1.3 and 2.0 mm. The samples were coated with graphite on the front and back surfaces in order to increase the absorption of flash light on the samples' front surface and to increase the emissivity on the samples' back surface. The samples were measured five times at each temperature. The specific heat was measured using the comparative method. For this the system was calibrated with a ceramic standard (Pyroceram).

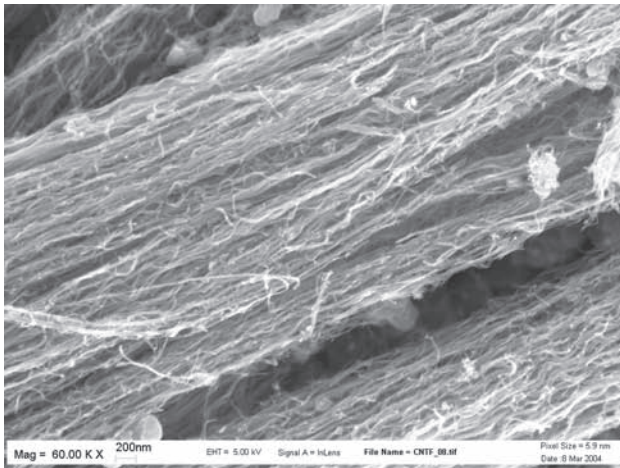


a)

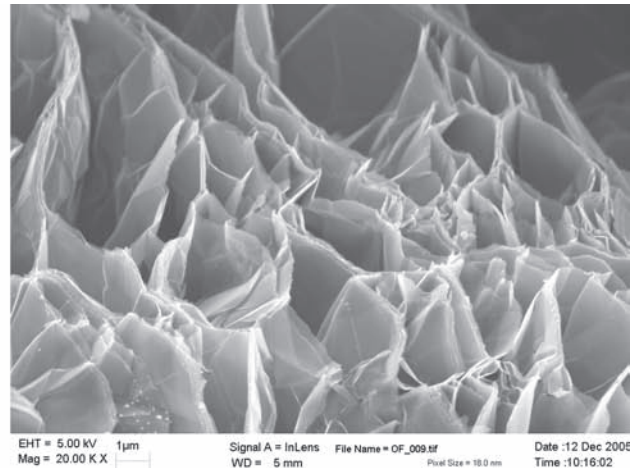


b)

Figure 1. Scanning electron micrograph of powder mixture consisting of $\alpha\text{-Si}_3\text{N}_4$, Al_2O_3 , Y_2O_3 and SWCNTs

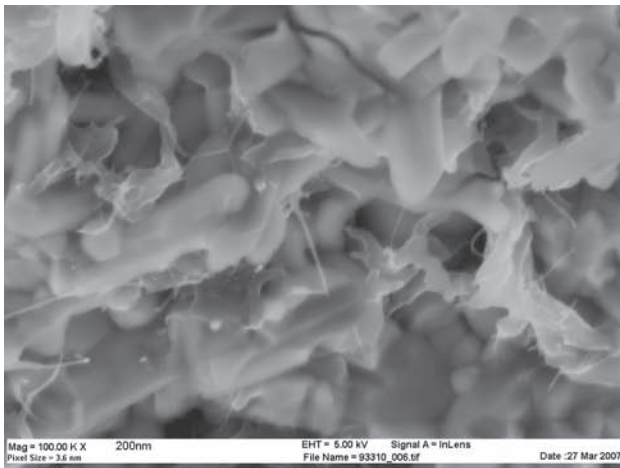


a)

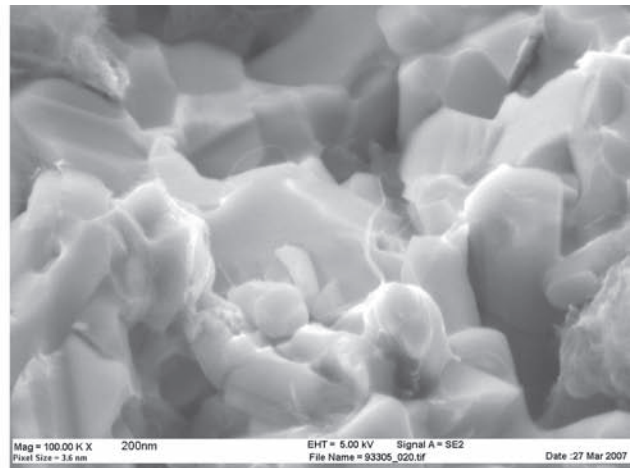


b)

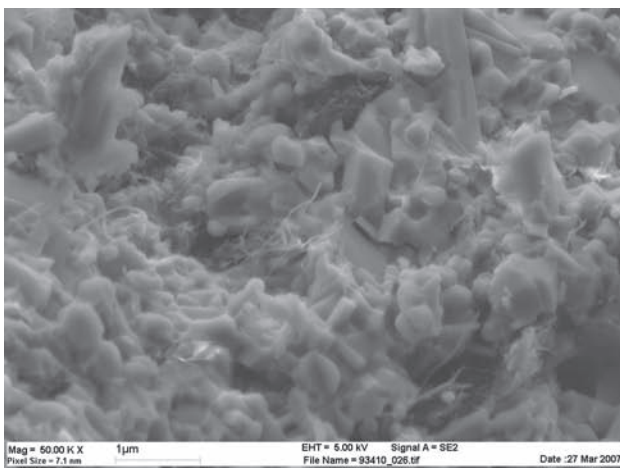
Figure 2. Scanning electron micrographs of MWCNTs (a) and graphene (b)



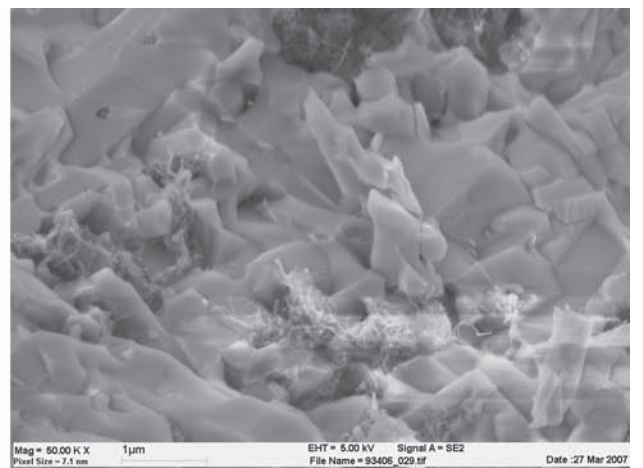
a)



b)

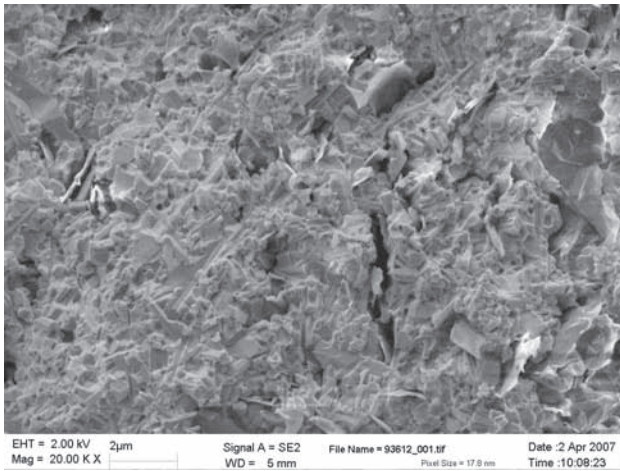


c)

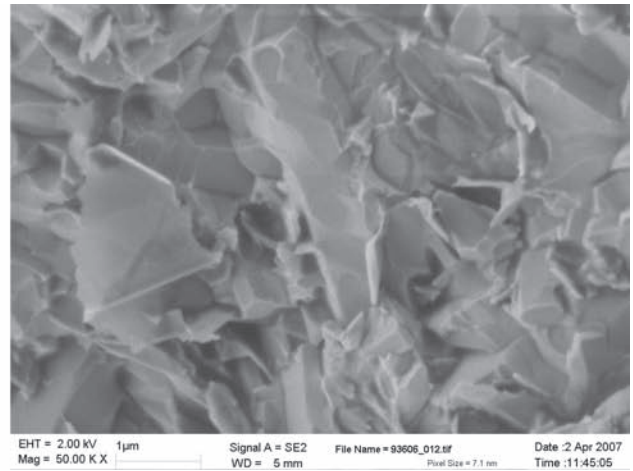


d)

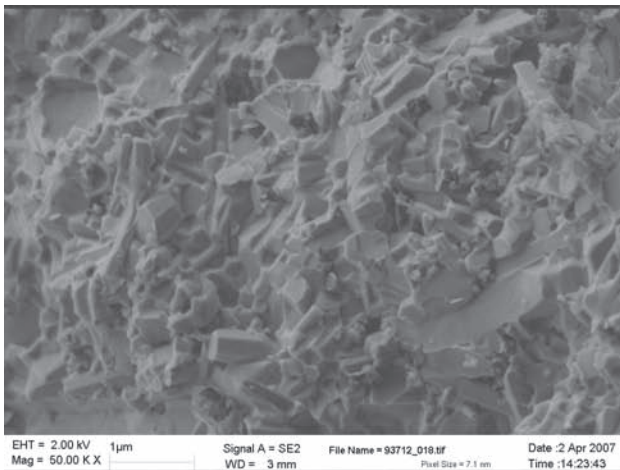
Figure 3. Scanning electron micrographs of fracture surfaces of sintered composites consisting of 3wt% SWCNT (a,b) and 3wt% MWCNT (c,d) prepared at 2 MPa (a,c) and at 20 MPa (b,d).



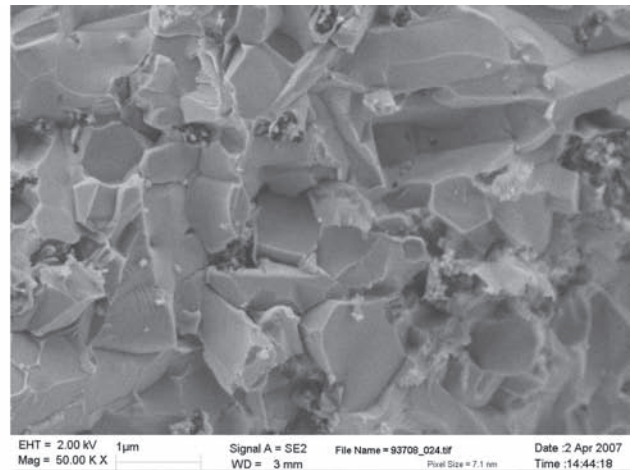
a)



b)

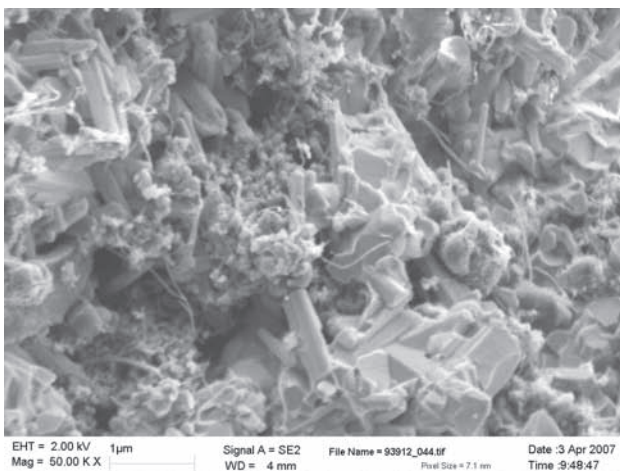


c)

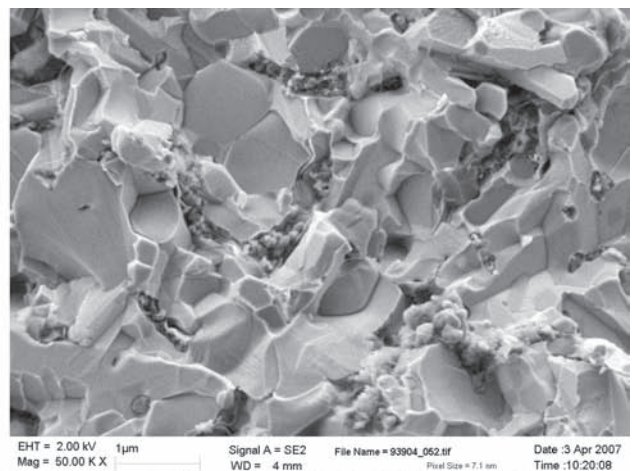


d)

Figure 4. Scanning electron micrographs of fracture surfaces of composite consisting of 3 wt% graphene (a,b) and 3 wt% carbon black (c,d). The samples have been prepared at 2 MPa (a,c) and at 20 MPa (b,d)



a)



b)

Figure 5. Scanning electron micrographs of fracture surfaces of composites consisting of 1 wt% carbon black and 2 wt% MWCNT, prepared at a) 2 MPa, and b) 20 MPa

IV. Results and Discussion

Results about the morphology of powder mixture and SWCNT samples processed with attritor milling are presented in Fig. 1. As it is shown in Fig. 1a and Fig. 1b (at higher magnification) single wall carbon nanotubes are efficiently dispersed in the mixture of α - Si_3N_4 , and sintering additives Al_2O_3 and Y_2O_3 . In Fig. 2 the scanning electron micrographs of MWCNTs and graphene samples are shown.

In Fig. 3 the scanning electron micrographs of fracture surfaces of sintered samples with 3 wt% SWCNT (a,b) and 3 wt% MWCNT (c,d) prepared at 2 MPa (a,c) and at 20 MPa (b,d) can be seen. After the sintering the CNTs are preserved in the structure. Some degradation of nanotubes may occur during sintering [7,14], but it was not observed in this case. The CNTs are located mainly in the inter-granular places and they are well attached to the silicon nitride grains. In the same time adhered carbon nanotubes to each other can be observed (Fig. 3).

The proper separation and dispersion of carbon nanotubes proved to be a difficult task of the composite preparation. For a better homogeneity, the high efficient attritor milling at high rotation speed (4000 rpm) have been applied. As can be observed, the CNTs in most of the cases are in groups, they can be found as nano- or micrometer sized islands in the matrix after sintering (Figs. 3, 4 and 5). In Fig. 4 the scanning electron micrographs of fracture surfaces of composite consisting of 3 wt% graphene (a,b) and 3 wt% carbon black (c,d) may be observed. In Fig. 5 the scanning electron micrographs of fracture surfaces of composites consisting of 1 wt% carbon black and 2 wt% MWCNT, prepared at a) 2 MPa, and b) 20 MPa are shown.

X-ray diffractograms of sintered samples are presented in Figs. 6 and 7. The main lines of α - Si_3N_4 (JCP-

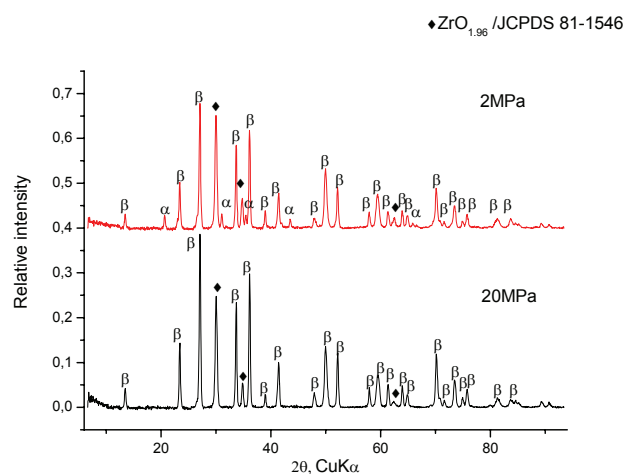


Figure 6. X-ray diffractograms of sintered D samples (with 3 wt% graphene, prepared at 1700°C, 2 and 20 MPa). The main lines of α - Si_3N_4 , β - Si_3N_4 and $\text{ZrO}_{1.96}$ (\blacklozenge / JCPDS 81–1546) can be recognized in all samples

DS-PDF 41–360), β - Si_3N_4 (JCPDS-PDF 33–160) and $\text{ZrO}_{1.96}$ (JCPDS-PDF 81–1546) can be recognized in the case of samples sintered at 2 MPa. The α - Si_3N_4 to β - Si_3N_4 phase transformation was completed in the sample prepared at 20 MPa (Fig. 6). The X-ray diffractions of sintered samples are showing the main lines of β - Si_3N_4 and two zirconia phases (Fig. 7).

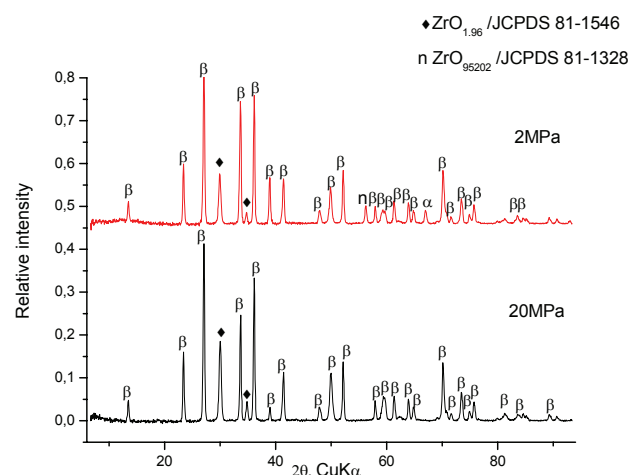


Figure 7. X-ray diffractograms of sintered E samples (with 3 wt% carbon black, prepared at 1700°C, 2 and 20 MPa). The main lines of β - Si_3N_4 and two zirconia phases (\blacklozenge / JCPDS 81–1546; n / JCPDS 81–1328) can be recognized in all samples

The mechanical observations are presented in Figs. 8 and 9. By increasing the gas pressure to 20 MPa the similar level of densification and higher strength values can be achieved for composites with MWCNT, graphene and carbon black additions then in the case of lower (2 MPa) gas pressure.

Fig. 10 depict the thermophysical properties of composite sample with CNT (sample H in Table 1, with 3.222 g/cm³ density, 233 GPa modulus of elasticity and 678 MPa four point bending strength). The specific heat increased with temperature as expected from the Debye theory. The thermal diffusivity decreased over the entire temperature range. Typical for phonon conductors is a maximum value in the thermal conductivity nearly at room temperature. This trend can clearly be seen at both of samples. The thermal conductivity values in the case of the sample H (with 3% MWCNT) are slightly higher than the values of the reference sample. The standard deviation of 5 shots at each temperature is less than 1%.

V. Conclusions

Optimisation of the manufacturing processes has been performed in order to thoroughly disperse the carbon nanotube in matrix, to assure a good nanotube-silicon nitride contact and to keep intact the nanotubes during high temperature processing.

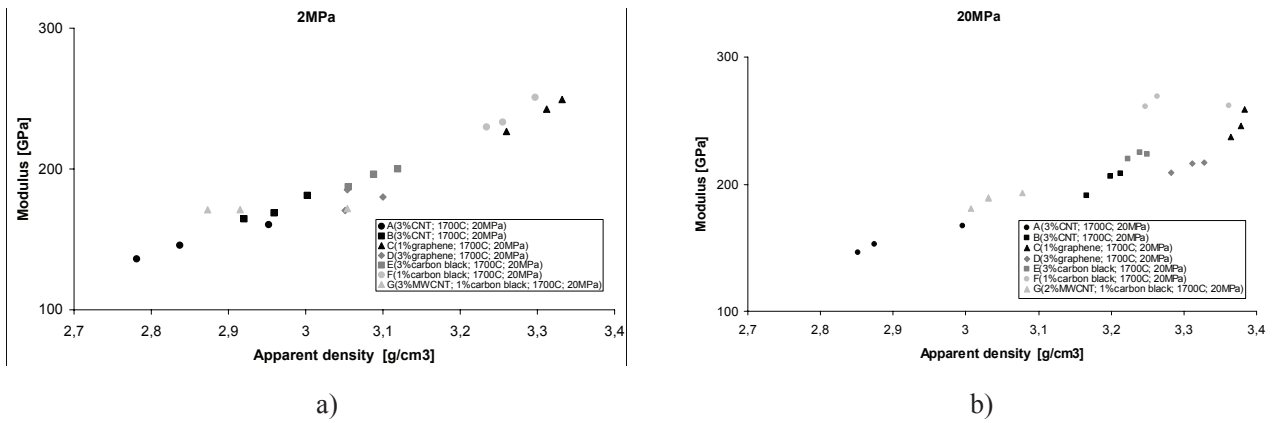


Figure 8. Modulus of elasticity in function of apparent density, in case of (a) 2 MPa (b) 20 MPa sintering pressure

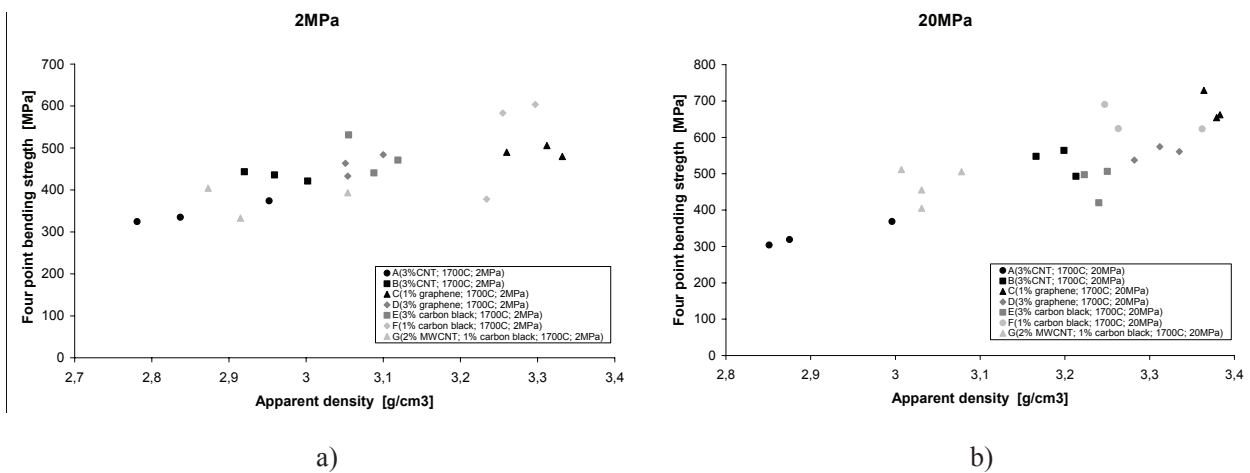


Figure 9. Four point bending strength of composites in function of apparent density, in case of (a) 2 MPa (b) 20 MPa sintering pressure

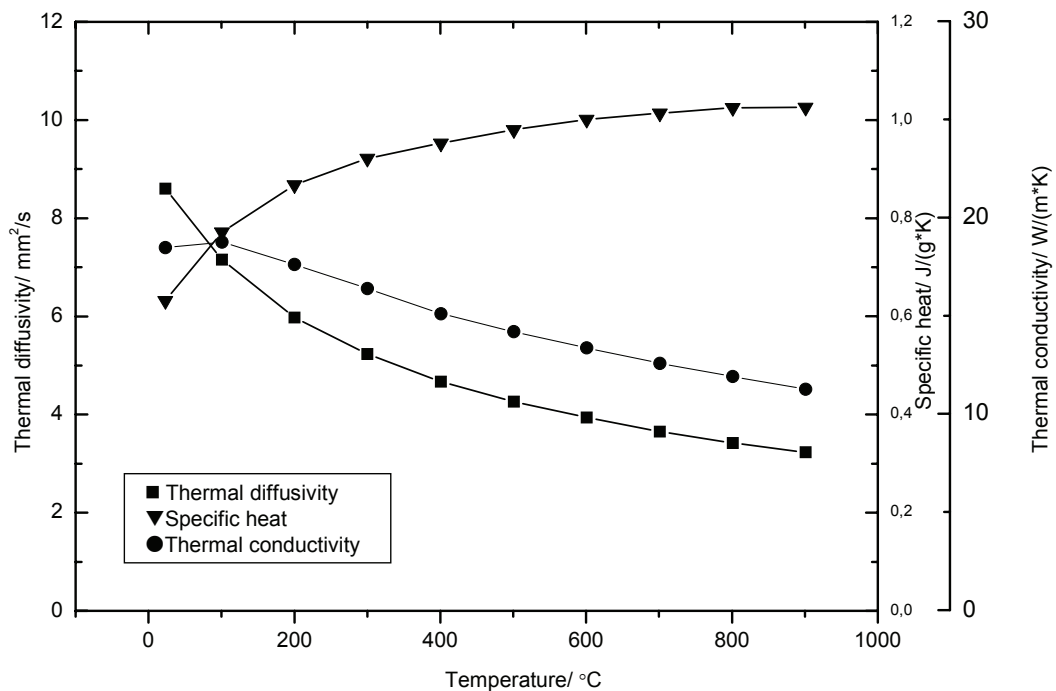


Figure 10. Thermophysical properties of sample H with MWCNT

The mechanical properties of composites with different amount of CNT, carbon black and graphene have been investigated. The grouping of the strength and modulus values as a function of apparent density was observed in the case of samples, sintered at higher pressure, as compared to the lower pressure sintered samples. At 20 MPa, the highest densification grade, modulus and strength values were found for the case of the sample with 1 wt% graphene, 3 wt% graphene and 1 wt% carbon black, at 2 MPa for the case of the sample with 1 wt% carbon black and 1 wt% graphene.

Acknowledgements: Dr. Csaba Balázs and Dr. Zoltán Kónya acknowledges the support of the Bolyai Janos Research Grant.

References

1. S. Rochie, “Carbon nanotubes: exceptional mechanical and electrical properties”, *Ann. Chim. Sci. Mater.*, **25** (2000) 529–532.
2. E.T. Thostenson, Z. Ren, T.W. Chou, “Advances in the science and technology of carbon nanotubes and their composites: a review”, *Comp. Sci. and Techn.* **61** (2001) 1899–1912.
3. K.T. Lau, D. Hui, “The revolutionary creation of new advanced materials-carbon nanotube composites”, *Composites: Part B*, **33** (2002) 263–277.
4. K.T. Lau, D. Hui, “Effectiveness of using carbon nanotubes as nano-reinforcements for advanced composite structures”, *Carbon*, **40** (2002) 1597–1617.
5. S.R. Dong, J.P. Tu, X.B. Zhang, “An investigation of the sliding wear behavior of Cu-matrix composite reinforced by carbon nanotubes”, *Mater. Sci. Eng.* **A 313** (2001) 83.
6. R.Z. Ma, J. Wu, B.Q. Wei, J. Liang, D.H. Wu, “Processing and properties of carbon nanotubes–nano-SiC ceramic”, *J. Mater. Sci.*, **33** (1998) 5243–5263.
7. Cs. Balázs, Z. Kónya, F. Wéber, L.P. Biró, P. Arató, “Preparation and characterization of carbon nanotube reinforced silicon nitride composites”, *Mater. Sci. Eng. C 23* [6–8] (2003) 1133–1137.
8. G.-D. Zhan, J.D. Kuntz, J. Wan, A.K. Mukherjee, “Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites”, *Nature Mater.*, **2** (2003) 38–42.
9. G.-D. Zhan, J.D. Kuntz, J.E. Garay, A.K. Mukherjee, “Electrical properties of nanoceramics reinforced with ropes of single-walled carbon nanotubes”, *Appl. Phys. Lett.*, **83** [6] (2003) 11.
10. W.A. Curtin, B.W. Sheldon, “CNT-reinforced ceramics and metals”, *Mater. Today*, **7** [11] (2004) 44–49.
11. X. Wang, N.P. Padture, H. Tanaka, “Contact-damage-resistant ceramic/single-wall carbon nanotubes and ceramic/graphite composites”, *Nature Mater.*, **3** (2004) 539–544.
12. J.D. Kuntz, G.-D. Zhan, A.K. Mukherjee, “Nanocrystalline-matrix ceramic composites for improved fracture toughness”, *Mater. Res. Soc. Bull.*, **29** [1] (2004) 22–27.
13. Z. Kónya, I. Vesselényi, K. Niesz, A. Kukovecz, A. Demortier, A. Fonseca, J. Delhalle, Z. Mekhalif, J. B. Nagy, A.A. Koós, Z. Osváth, A. Kocsonya, L.P. Biró, I. Kiricsi, “Large scale production of short functionalized carbon nanotubes”, *Chem. Phys. Lett.*, **360** (2002) 429–435.
14. Cs. Balázs, Z. Kónya, Zs. Kasztovszky, F. Wéber, Z. Vértesy, L.P. Biró, I. Kiricsi, P. Arató, “Examination of carbon nanotube reinforced silicon nitride composites”, *Proceedings of Fifth International Conference on High Temperature Ceramic Matrix Composites (HTC-MC-5) New Frontiers and Horizons*, Seattle, Washington, USA (published by The American Ceramic Society), (2004) 107–112.