Key Engineering Materials Vol. 290 (2005) pp. 238-241
online at http://www.scientific.net

Size Effects in Micro- and Nanocarbon added C/Si_3N_4 Composite Prepared by Hot Pressing

Cs. Balázsi[1], F.S. Cinar[2], O. Addemir[2], Zs. Kasztovszky[3], Zs. Kövér[1], F. Wéber[1]

[1]Ceramics and Composites Laboratory, Research Institute for Technical Physics and Materials Science, Hungarian Academy of Sciences, 1121 Konkoly-Thege út 29-33, Budapest, Hungary
[2] Prof. Adnan Tekin High Technological Ceramics and Composites Research Center, 80626 Maslak, Istanbul, Turkey
[3] Department of Nuclear Research, Institute of Isotope and Surface Chemistry, Chemical Research Center, 1121 Konkoly-Thege út 29-33, Budapest, Hungary

Keywords: silicon nitride, carbon black, graphite, mechanical properties

Abstract. Silicon nitride based composites have been fabricated by carbon addition. Carbon black nanograins and graphite micrograins were used as second phase additions. Alumina and yttria were used as sintering aids. Mixing of powders was performed in a ball mill and for comparison in a high efficient attritor mill. For sintering the hot pressing technique has been applied. Experiments at 2 MPa uniaxial pressure have been performed. The Si/N mass fraction after sintering were determined by prompt gamma activation analysis (PGAA). The amount of carbon black and graphite introduced in the silicon nitride matrix increased the porosity and decreased the hardness and bending strength of composites. Lower modulus, and lower strength was obtained for composites with carbon black addition in comparison to graphite added samples. The microstructure of composites consisted mainly of alpha and beta silicon nitride. The formation of silicon carbide was observed only at 10 wt% carbon black addition.

Introduction

Silicon nitride based ceramics have been applied to several structural applications. However, at higher temperatures degradation of grain boundary phases occurs. In general, there are two possibilities to improve the mechanical and physical properties of ceramics: tailoring the microstructure and preparation of composites. Recently, new observations have been performed on structural and morphological development on silicon nitride ceramics in order to understand the governing principles of sintering processes [1]. As resulted, through formation of tough interlocking microstructure mechanical properties may be improved. As an alternate way nanocomposite processing have been performed to develop the physical and mechanical properties of silicon nitride ceramics [2]. Several research groups reported a new type of SiC/Si_3N_4 nanocomposite with improved high temperature strength and fracture toughness [3,4].

In this work silicon nitride based composites have been prepared by carbon black and graphite addition. For a thorough mixing ball milling and for comparison a high efficient attritor mill was employed. The effect of carbon nano- and micro-grains on the microstructure, elastic modulus, bending strength and hardness have been investigated.

Experimental procedure

The compositions of the starting powder mixtures of each of six materials were the same: Si_3N_4 (Ube, SN-ESP), Al_2O_3 (Alcoa, A16) and Y_2O_3 (H. C. Starck, grade C). For composite processing in addition to batches, carbon black (Taurus Carbon black, N330, average particle size between ~50-100 nm) and graphite (Aldrich, synthetic, average particle size 1-2 μm), were added (Table 1).

Table 1. The preparation conditions and composition of starting powder mixtures

Batch	Composition, wt%			Added carbon black/graphite	Ball Milling (ethanol 360rpm	Attritor milling (ethanol) 600rpm	Hot pressing 1800°C, 2h nitrogen atm.
	Si_3N_4	Al_2O_3	Y_2O_3	wt% to batch			MPa
CB0%	90	4	6	-	3h		2
CB1%	90	4	6	1	3h		2
CB10%	90	4	6	10	3h		2
G0%	90	4	6	-		3h	2
G1%	90	4	6	1		3h	2
G10%	90	4	6	10		3h	2

Milling procedure

The powder mixtures with carbon black additions were milled in ethanol in a planetary type alumina ball mill (Fritsch GMBH). As resulted from weight measurements each batch contained approximately 1 wt% alumina as contamination from balls and jars. For graphite added mixtures a high efficient Szegvari attritor mill (Union Process, type 01-HD/HDDM) was employed. This apparatus allowed a higher rotation speed and a contamination free mixing process, because of silicon nitride parts (tank, arm, balls). The mixtures were sieved with 150 μm mesh.

Sintering method

Samples for hot pressing (HP, CENTORR Vacuum Industries) were prepared as follows. After 10^{-4} Torr vacuum, at 20°C, nitrogen gas were introduced at 1 atm. Heating rate was 20°C/min till 1800°C. At 1000°C a uniaxial pressure of 2 MPa was applied and kept the same until 1800°C. At 1800°C, the pressure was applied for 2h. The samples were cooled down together with the furnace.

Microstructural observations

All surfaces of the test bars were finely ground on a diamond wheel, and the edges were bevelled. The direction of both the diamond grinding and of the bevelling was parallel with the bar lengths. The density of the as-sintered materials was measured by the Archimedes method. To identify the crystalline phases X-ray diffraction (CuKα radiation) was applied. Morphology of the solid products was studied by scanning electron microscopy, with a JEOL-25 microscope. Hardness measurements were performed on micro Vickers Model LL, Tukor Tester, by applying 1kg load. Compositional analyses were performed by prompt gamma activation analysis (PGAA). Details about this nuclear method were presented in an earlier study [5].

Results and Discussions

In Fig. 1a and Fig. 1c the fine microstructures of hot pressed reference samples as resulted from ball and attritor milling and sintering are shown. Both structures are consisting of submicron grains, however in the case of refernce sample CB0% small hexagonal shaped β-Si_3N_4 grains have appeared. Indeed, as presented in Fig. 2, in the structure of sample CB0% a considerable amount of β-Si_3N_4 lines appeared. A porous structure and an enhanced grain (β-Si_3N_4) growing process can be observed in the CB10% scnning micrograph (Fig. 2b). Graphite platelets are included in the structure even after sintering as it is shown in Fig. 2d, sample G10%. By adding 1wt% carbon black the structure remains the same as for reference sample, α-Si_3N_4 (PDF-JCPDS 41-0360) and β-Si_3N_4 (PDF-JCPDS 33-1160) are the main phases (Fig 2. sample CB1%). But, with carbon black increase (CB10%) SiC lines have appeared ((PDF-JCPDS 31-1231). This observation was confirmed by PGAA analysis as well. We found a nitrogen exhaust from CB10% structure according to following reaction taking place around 1435ºC: $3C(s) + Si_3N_4(s) \rightarrow 3SiC(s) + 2N_2(g)$ [6].

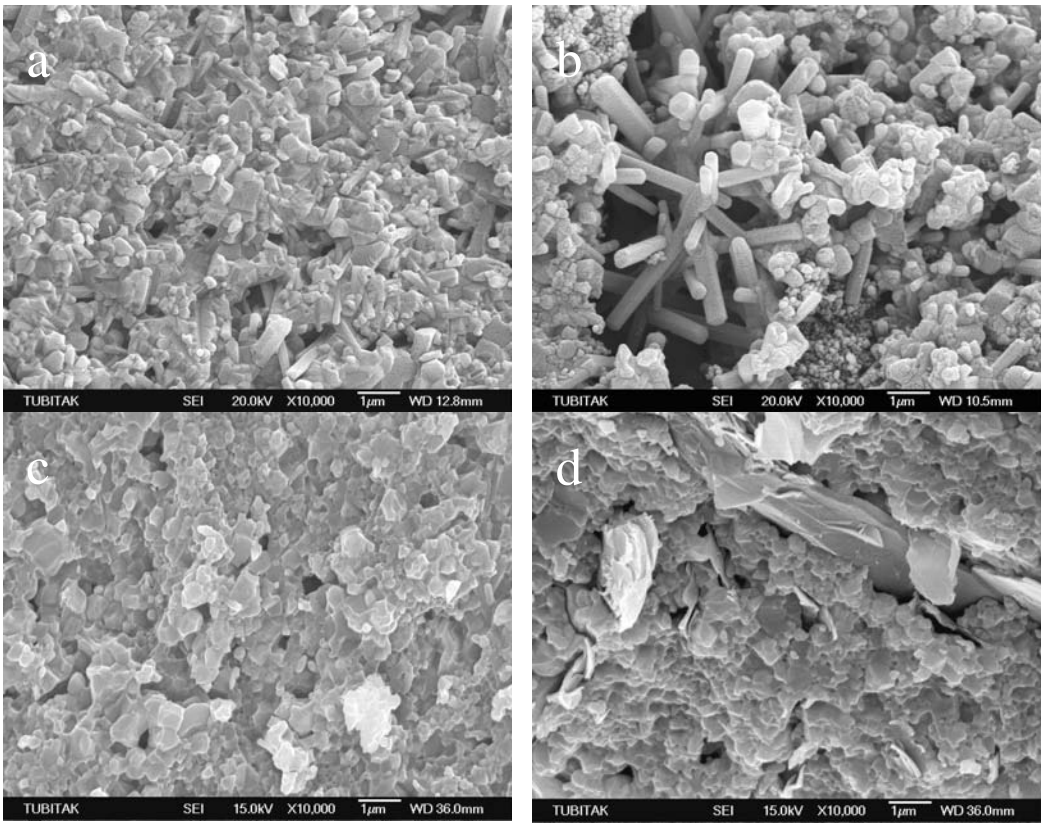

Figure 1. Micrographs of fracture surfaces. a – reference sample CB0%. b – sample CB10%. c – reference sample G0%. d – sample G10%. Bar: 1 μm for all of the micrographs.

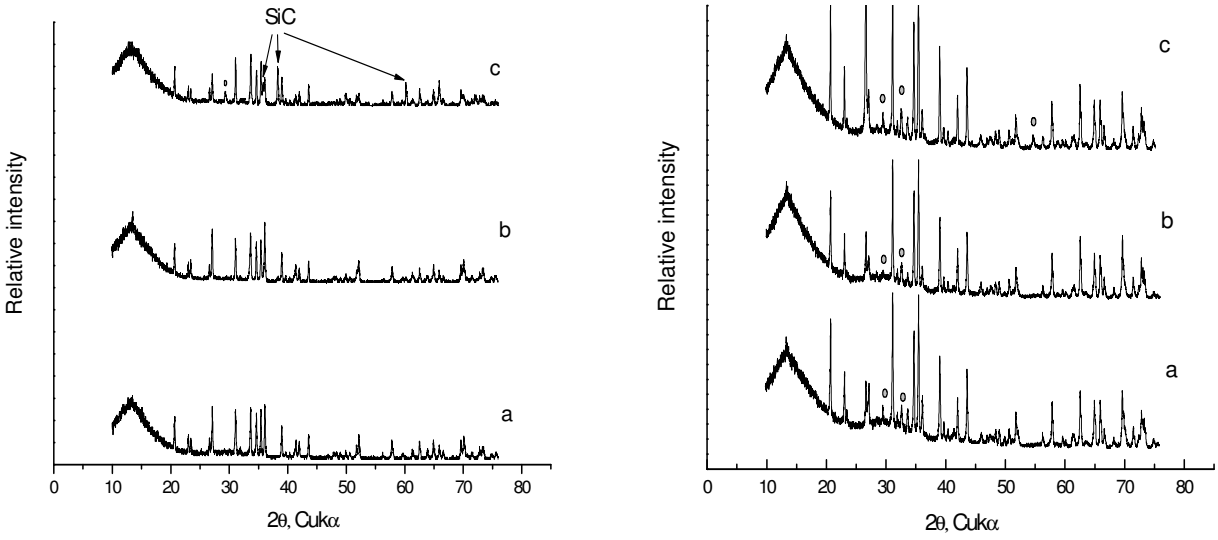

Figure 2. X-ray diffractograms of sintered samples. (left) a – reference sample CB0%. b - sample CB1%. c – sample CB10%. (right) a – reference sample G0%. b - sample G1%. c – sample G10%.

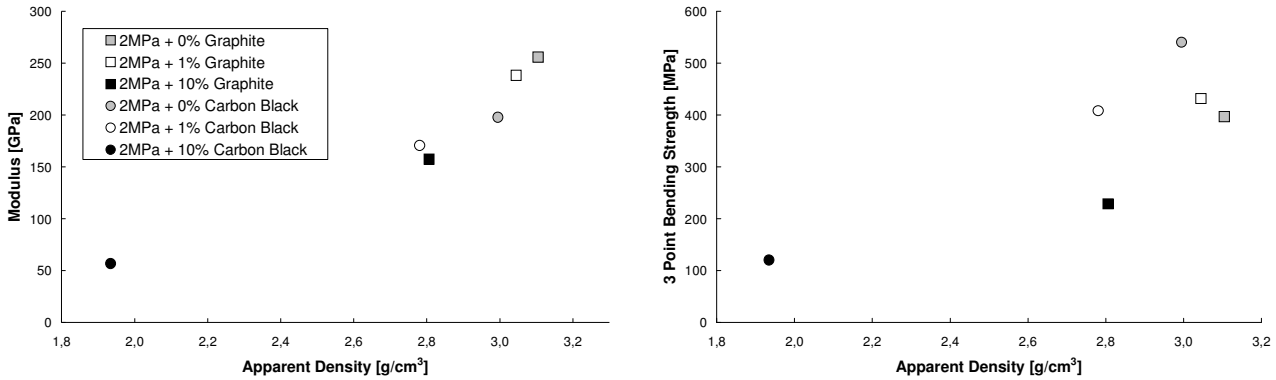

Figure 4. Modulus of elasticity and three point bending strength in function of density.

Table 2. Hardness of composites

Batch	Hardness, HVI, GPa	Batch	Hardness, HVI, GPa
CB0%	13.07±0.6	G0%	16.27±0.6
CB1%	9.22±0.7	G1%	14.72±1.2
CB10%	1.21±0.5	G10%	8.94±2.1

In the case of graphite additions α-Si_3N_4, β-Si_3N_4 and β-$Y_2Si_2O_7$ (PDF 21-1454 JCPDS) lines can be observed (Fig 2. sample G1%, G10%). SiC phase was not formed in graphite composites. Graphite addition assured an increase of hardness in comparison to carbon black added samples (Table 2). Addition of graphite resulted in more densified samples than for carbon black containing samples (Fig. 4). All modulus values have been found to be higher for graphite than for carbon black added composites at the same carbon level. As regards bending strengths although, the reference has higher strength, for graphite added composites a higher strength was obtained than for carbon black added samples (Fig. 4). We found an increase in strength for G1% in comparison to reference G0%. It seems because of the high specific surface area of carbon black nanograins agglomeration occurs that cause a more porous structure after sintering with lower mechanical properties.

Acknowledgements

Dr. Csaba Balázsi thanks for OTKA Postdoctoral Research Grant (D38478), János Bolyai Research Grant and Hungarian State Eötvös Fellowhsip. Support from OTKA T043704 is greatly acknowledged.

References

[1] Z. Shen, Z. Zhao, H. Peng, M. Nygren, Nature, 16 May 2002, Vol. 417, 266-269.
[2] K. Niihara, J. Jpn. Ceram. Soc., 99 (1991) 974-982.
[3] P. Sajgalik, M. Hnatko, F. Lofaj, P. Hvizdos, J. Dusza, P. Warbichler, F. Hofer, R. Riedel, E. Lecomte, M.J. Hoffmann, J. Eur. Ceram. Soc., 20 (2000) 453-462.
[4] M. Hnatko, D. Galusek, P. Sajgalik, J. Eur. Ceram. Soc. in print.
[5] Cs. Balázsi, Z. Kónya, Zs. Kasztovszky, F. Wéber, Z. Vértesy, L. P. Biró, I. Kiricsi, P. Arató, Proceedings of the Fifth International Conference on High Temperature Ceramic Matrix Composites (HTCMC-5) New Frontiers and Horizons, Seattle, Washington, USA, Ceramic Transactions, published by The American Ceramic Society, (2004) 107-112.
[6] Cs. Balázsi *etal,* Silicates Industriels 69/7-8 (2004) 293-298.
[7] Cs. Balázsi, F.S. Cinar, O. Addemir, F. Wéber, P. Arató, J. of Eur. Cer. Soc., 24 (2004) 3287.