

**Silicon nitride nanocomposites with carbon
nanostructure additions**

PhD thesis booklet

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Budapest

2012

Introduction

Technical ceramics possess exceptional physical properties and can provide a viable alternative for metals in several applications. For specific applications ceramic materials provide a substantial improvement in functionality and efficiency that compensates their relatively higher fabrication costs.

Nevertheless, technical ceramics have their own drawbacks, mainly originating from their mechanical rigidity. Nowadays, a promising method that could offer a solution for the above mentioned problem, as well as tailor the mechanical, electrical and thermal properties of the ceramics for different applications is adding carbon nanostructures to the ceramic matrix. However, there are several technical challenges one has to face upon preparing carbon nanostructures reinforced ceramic composites. First, one has to assure an efficient mechanical load (and electrical charge) transfer at the interface between the nanostructures and the ceramic matrix. On the other hand a homogenous dispersion of the nanoscale filler material has to be achieved. Due to their high specific surface, nanostructures show a strong tendency towards aggregation. These aggregates ranging in size from a few tens of nanometers to microns substantially degrade the resulting mechanical properties of the nanocomposites. In contrast to polymer based composites where the dispersion of the nanostructures can be realized in the liquid phase of the matrix, in ceramic composites the uniform dispersion of the nanoscale filler phase is still a highly challenging task. This is the main reason that ceramic composites were not able to fully exploit the potential offered by carbon nanostructures for mechanical reinforcement. Overcoming this issue is particularly challenging as there are no reliable experimental methods available, to quantitatively characterize the dispersion degree of the nanoscale filler phase within the matrix material.

Aims

The subject of my PhD work is the synthesis and characterization of silicon nitride based ceramic composites reinforced with different carbon nanostructures (single- and multi-walled carbon nanotubes, few layer graphene and carbon black). The aim is to establish the essential relationships between the synthesis parameters, microstructure and mechanical properties of the resulting nanocomposites. To achieve this we have investigated both the effect of the ceramic matrix microstructure and the dispersion patterns of different carbon nanostructures on various mechanical parameters of the composites (strength, toughness, hardness).

We have studied the role of the ceramic powder grain size after milling on the microstructure and phase composition of the sintered ceramic matrix; as well as compared two different sintering methods (hot isostatic pressing, and spark plasma sintering) from the point of view of the resulting microstructure and mechanical properties.

On the characterization side, we have applied for the first time the small angle neutron scattering technique to characterize the dispersion of carbon nanostructures within ceramic matrix composites. This method allowed us to acquire data representative for the whole sample volume, in contrast to the previously used electron microscopy methods providing only local information. In all cases my main goal was to explore relationships between the microstructure of the matrix, dispersion patterns of the nanoscale filler and the mechanical properties of the resulting nanocomposites.

Novel scientific results

The new scientific results are summarized in the following thesis points:

1. **We have investigated the effect of milling time of the ceramic powder with the phase composition and mechanical properties of the resulting silicon nitride nanocomposites reinforced with multi-walled carbon nanotubes. [T1]**
 - a. We have shown that depending on the sintering conditions the milling time can have a substantial influence on the final phase composition and mechanical properties of the sintered Si_3N_4 nanocomposites.
 - b. We found that it is possible to improve the mechanical properties of the silicon nitride nanocomposites by optimizing the milling time of the starting powder. However, to control the properties of the nanocomposites one has to consider that the phase composition after sintering is a function of both the milling time and sintering pressure.

2. **We have compared silicon nitride based composites with various carbon nanostructure additions (single- and multi-walled carbon nanotubes, few layer graphene, carbon black) prepared by two different sintering methods (hot isostatic pressing and spark plasma sintering). We have shown that by choosing the suitable sintering method different mechanical properties of the nanocomposites can be improved. [T2]**
 - a. We have shown that the samples prepared by spark plasma sintering mainly consist of alpha silicon nitride grains and independent of the type of the carbon nanostructure filler, provide harder and stiffer nanocomposites.
 - b. We have found that the samples prepared by hot isostatic pressing mainly consist of beta silicon nitride grains and independent of the type of the carbon filler, provide tougher nanocomposites.

3. We applied for the first time small angle neutron scattering measurements to investigate the dispersion patterns of carbon nanostructures in ceramic matrix composites. We have shown that neutron scattering experiments are able to provide information about the dispersion of the nanostructures representative for the whole volume of the sample, in contrast to the electron microscopy methods applied so far. [T3,T4]

- a. We have demonstrated that single-walled carbon nanotubes display a surface fractal behavior in the ceramic matrix, which can be attributed to the disordered 2D nanotube networks wrapping the Si_3N_4 crystallites at the grain boundaries.
- b. We have shown that in contrast to single-walled nanotubes, multi-walled nanotubes display a mass fractal behavior in neutron scattering experiments, indicative of 3D disordered nanotube aggregates within the ceramic matrix.
- c. We have demonstrated that under similar preparation conditions few layer graphene flakes can be much more homogeneously dispersed within the ceramic matrix than multi-walled carbon nanotubes. Even individual dispersion could be achieved with few layer graphene, while carbon nanotubes were always found in the form of disordered aggregates.
- d. By comparing few layer graphene and multi-walled carbon nanotube composites, we have shown that a direct correlation can be established between the dispersion patterns of the nanostructures and the resulting mechanical properties of the nanocomposites. The more homogeneously dispersed graphene samples displayed a 10 to 50 % improvement in the mechanical properties as compared to their carbon nanotubes reinforced counterparts.

Publications used in the thesis points

T1. O. Tapasztó , Cs. Balázs, The effect of milling time on the sintering kinetics of Si₃N₄ based nanocomposites. *Ceram. Internat.* **36**, 2247-2251. (2010)

T2. O. Tapasztó, P. Kun, F. Wéber, G. Gergely, K. Balázs, J. Pfeifer, P. Arató, A. Kidari, S. Hampshire, Cs. Balázs. Silicon nitride based nanocomposites produced by two different sintering methods. *Ceram. Internat.* **37**, 3457-3461. (2011)

T3. O. Koszor, L. Tapasztó, M. Markó, Cs. Balázs. Characterizing the global dispersion of carbon nanotubes in ceramic matrix nanocomposites. *Appl. Phys. Lett.* **93**, 201910. (2008)

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Other related publications

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6. A Kovalčíková, Cs Balázs, J Dusza , **O Tapasztó**. Mechanical properties and electrical conductivity in a carbon nanotube reinforced silicon nitride composite. *Ceram. Internat.* **38**, 527-533. (2012)

7. A Kovalčíková, O Tapasztó, Cs Balázs, J Dusza. Indentation thermal shock resistance of Si₃N₄/CNT composites. *Chemické Listy* **105**, s824-s825. (2011)

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11. **O Koszor**, A Lindemann, F Davin, C Balázsi. Observation of thermophysical and tribological properties of CNT reinforced Si₃N₄. *Key Engineer. Mater.* **409**, 354-357. (2009)

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New York: Nova Science Publishers Inc., 2008. pp. 200-224.