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Spark plasma sintering of Si_3N_4 /multilayer graphene composites

Abstract: Multilayer graphene reinforced silicon nitride composites were prepared by spark plasma sintering to investigate the effect of the graphene addition on mechanical properties. The composites contained multilayer graphene (MLG) in various (0, 1, 3 and 5 wt%) content. Significantly higher fracture toughness of $8.0 \text{ MPa m}^{1/2}$ was obtained at 1% MLG content, however, on further increasing the graphene content the toughness did not increase, but dropped to the value of the monolithic silicon nitride. The maximum hardness of 18.8 MPa was also obtained at 1% MLG, while at higher MLG contents it gradually decreased.

Keywords: spark plasma sintering, silicon nitride, multilayer graphene

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1 Introduction

Silicon nitride is one of the most well-known advanced structural ceramics, due to its unique combination of properties including the low density, high strength even

at elevated temperatures, good resistance to corrosive environments, excellent wear resistance, etc. The ceramics are used in several high tech applications and are expected to be suitable substitutes for high-temperature metal alloys in a range of gas turbine engines [1]. The greatest barrier for their more widespread application is their liability to sudden fracture. Over the previous decades lots of research has been conducted to overcome this problem. Most approaches tried to create a microstructure with reinforcing phases evenly dispersed in the matrix. The reinforcing phases included rod-like $\beta\text{-Si}_3\text{N}_4$ [2-3], various particles or carbon structures such as carbon fibers, nanotubes [4-5] or most recently graphenes [6] or more precisely graphene nanoplatelets (GNP). By the virtue of its outstanding mechanical properties including high tensile strength and Young modulus graphene shows great promise as a nanofiller in composite materials [7]. In addition, they possess excellent electric, thermal and optical properties, too. In the last decade a number of studies with polymer [8], metal and ceramic-based matrices [9-10] have been demonstrated that graphene can significantly improve the charge transport, thermal, and mechanical properties of the composites, even at relatively low nanofiller loadings [11-12].

Recently a few papers have also been published on graphene nanoplatelets reinforced silicon nitride ceramics. Ramirez et al. [13] studied the electrical conductivity, which could be improved with a maximum of 40 S cm^{-1} by 25 vol.% multilayer graphene (MLG) addition. Dusza [14] and Kvetková et al. [15] studied the various types MLG added in 1 wt% to the Si_3N_4 composite. They both reported considerable improvement on the mechanical properties regardless of the type of the used MLG. Tapasztó et al. [16] compared the performance of the various carbon nanostructures in Si_3N_4 matrix using 3 wt% additives, however, they did not find any improvement for the graphene incorporated silicon nitride composites. Ramirez et al. [17] also studied the fracture toughness for Si_3N_4 composites containing commercial graphene, and they reported a 40% improvement in the fracture

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toughness at 4.3 vol.% GNP addition. These unambiguous findings call for more investigation on the effect of the graphene content on the mechanical properties. Such a comprehensive study has not been published up to now.

In this work, silicon nitride-based nanocomposites incorporated with multilayer graphene (MLG) in various amounts (1, 3 and 5 wt%) have been fabricated by spark plasma sintering. The aim of the work was to study the effect of graphene incorporation on the toughening of Si_3N_4 and determine the optimal content. The mechanical properties can also be influenced by the applied sintering method. Spark plasma sintering has become an increasingly widespread method only over the last decade. On heating the samples innumerable microdischarges are generated among the particles to be consolidated on the effect of the time varying electric pulses. Compared to other sintering methods, SPS allows much faster heating rates and shorter sintering times, accompanied with commonly lower sintering temperatures [18]. Although, there is still a harsh dispute over the exact mechanism of the discharge generation, the benefit of this method on the microstructure of the sintered pieces and on the shortness of the process is indisputable. It is also considered that grain growth will be eliminated because of lower temperature and shorter holding time thus nanostructured ceramics could be produced [19].

2 Experimental Procedure

90 wt% Si_3N_4 (Ube, SN-ESP) has been used as starting powder, whereas for sintering aids we used the following powers: 6 wt% Y_2O_3 (H.C. Starck, grade C) and 4 wt% Al_2O_3 (Alcoa, A16). The powder mixtures were milled in ethanol in a high efficiency attritor mill (Union Process, type 01-HD/HDDM) with high rotation speed, 4000 rpm for 5 h. After milling multilayer graphene was added to the silicon nitride-based powder mixtures in 1, 3 and 5 wt%, respectively. As reference graphene free silicon nitride was also sintered. The MLG additions were prepared by the mechanical milling method [20], similar to the method used by Knieke et al. [21]. These mixtures were milled in an attritor mill equipped with Si_3N_4 grinding media (diameter of 20 mm) in a 750 ml silicon nitride tank. The milling process has been performed with high rotation speed, 4000 rpm for 5 h.

The as-obtained mixtures were then sintered to discs of 2 cm in diameter and 5 mm in thickness by spark plasma sintering apparatus (HD P5, FCT GmbH). Composites with different sintering temperatures (1500°C and 1600°C) and holding times (3 and 10 minutes) were prepared. The

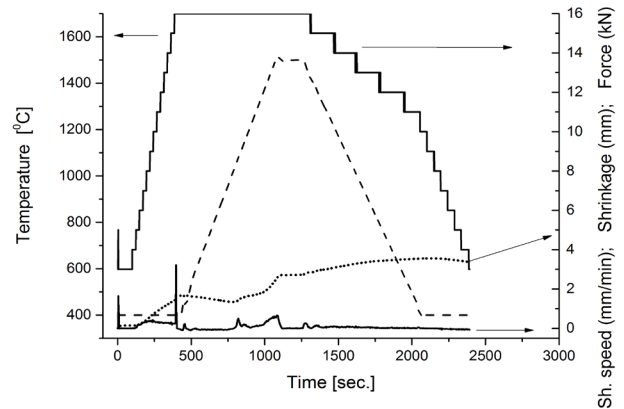


Figure 1: The applied temperature and load profile on the sintering

powders were heated with $100^\circ\text{C min}^{-1}$ heating rate for all the experiments using on/off current pulses of 12/2, 3500 A and 5 V. An applied uniaxial compression of 50 MPa and a chamber pressure of 1 mbar were maintained during sintering. Shrinkage, displacement, heating current and voltage were monitored and recorded during sintering. Fig. 1 shows the shrinkage displacement curve and the heating profile curve measured during the process.

The density of the sintered materials was measured by Archimedes method. Morphology and microstructure of the sintered samples were characterized by scanning electron microscopy (SEM, LEO 1540 XB with a heated field emission tungsten cathode) and by X-ray diffraction (XRD) performed on a Bruker AXD 8D using $\text{CuK}\alpha 1$ radiation. The hardness was measured using Vickers indentation method [HV0.2 (19,61 N; 10 sec.)]. The small specimen size did not allow the use of a standard fracture toughness test, therefore fracture toughness was calculated according to the Shetty formula [22]:

$$K_{\text{Icnd}} = 0.0899(H \cdot P/4l)^{1/2}$$

where H is the hardness, P is the indentation load and l is the length of the indentation crack.

However, this calculated fracture toughness does not determine absolute values for fracture toughness but it can be used for simply comparing the fracture toughness and behaviour of different materials [23].

3 Results and Discussion

The microstructure of the composites (Fig. 2a) consists of a fine grained Si_3N_4 matrix, in which multilayer graphene are evenly distributed in all investigated

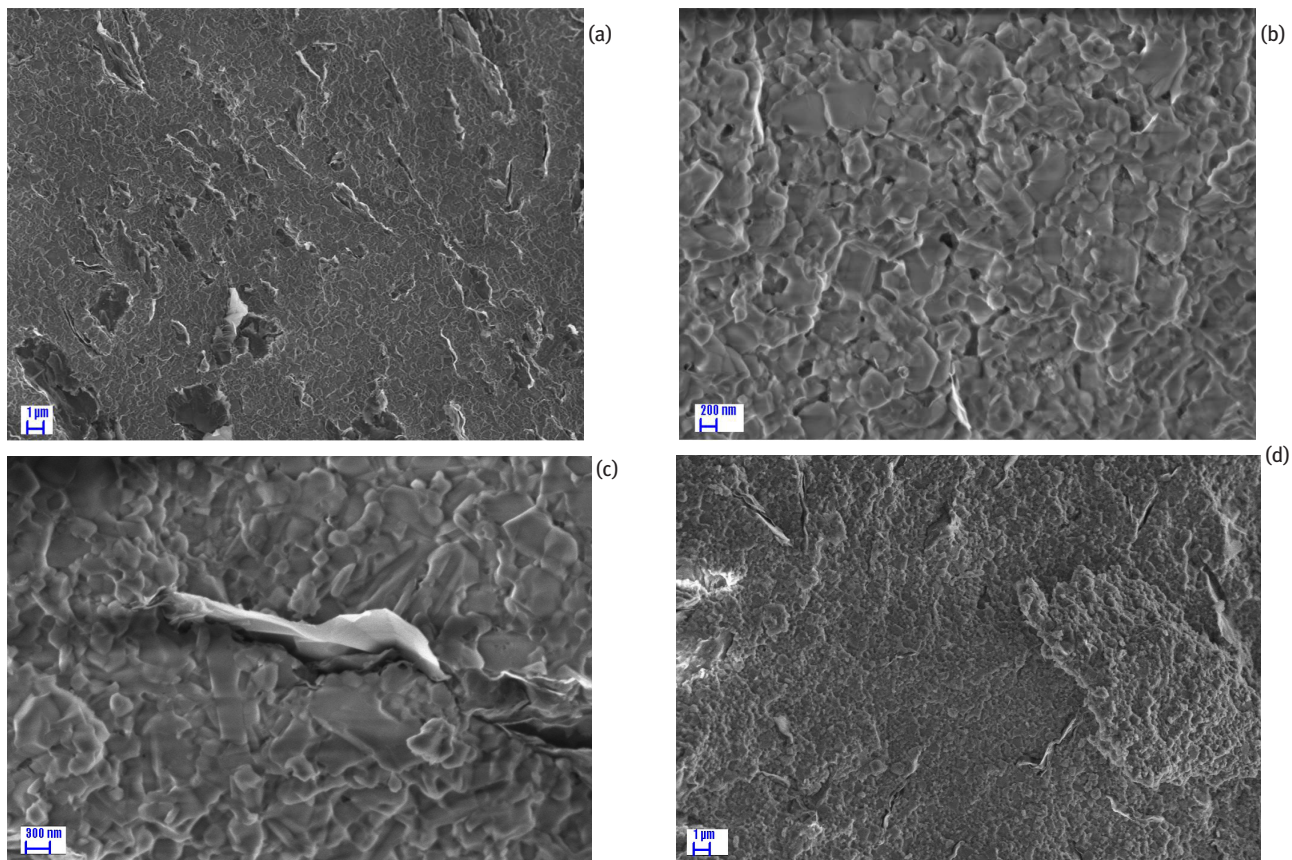


Figure 2: SEM micrographs of fracture surfaces of $\text{Si}_3\text{N}_4/\text{MLG}$ composites (a) Fracture surfaces of the sample with 5 wt% MLG sintered at $1600^\circ\text{C}/3$ min. (b) Sample with 1 wt% MLG content, sintered at $1500^\circ\text{C}/10$ min showing pores. (c) Sample with 3 wt% MLG, sintered at $1600^\circ\text{C}/10$ min revealing β grains between α -phase. (d) Samples with 3 wt% MLG, sintered at $1500^\circ\text{C}/3$ min showing the pores along the graphene-matrix interface.

composites without creating large agglomerates and are located at an intergranular position. It is apparent that the nanosheets are more or less oriented and they situated parallel to each other and perpendicularly to the direction of the compacting pressure. This orientation of one or two dimensional reinforcing phases is not unusual when before or during sintering uniaxial compression is applied. This may lead to anisotropic mechanical properties. In higher magnification (Fig. 2b) several pores are perceptible on the fractured surface. It cannot be unambiguously decided whether these pores are the result of the uncompleted consolidation or they formed during fracture when the rod-like hexagonal β crystals were pulled out. In Fig. 2c it is apparent that the matrix structure is composed of two types of crystalline phases with globular and columnar shaped grains, respectively. At this magnification (Figs. 2c and 2d) no pores could be detected in the matrix just along the graphene-matrix interface implying that porosity is associated only to the graphene addition. Kvetková

et al. [15] also found that clustered graphene sheets accumulate pores and in this way they are the main source of the porosity.

XRD analysis (Fig. 3) revealed that the matrix is composed of both α and β crystalline Si_3N_4 phases. The β -phase ratio was varied between 8-15 vol.%, so the α to β phase transformation occurred only in minor extent with increasing temperature and time. Accordingly, samples sintered at 1600°C for 10 min contained the most β -phase (16 vol.%), while the main component remained the α - Si_3N_4 . ZrO_2 could also be detected in the sample, though in very small amounts. It comes from the grinding process as contamination.

The relative density values are illustrated in Fig. 4. In an increasing order of the graphene content. Relative densities ranged from 88% to 98%, the highest value of which was obtained for monolithic Si_3N_4 sintered at 1600°C , 10 min holding time. The most striking tendency apparent from this figure is that the higher proportion of graphene additives resulted in lower relative density values.

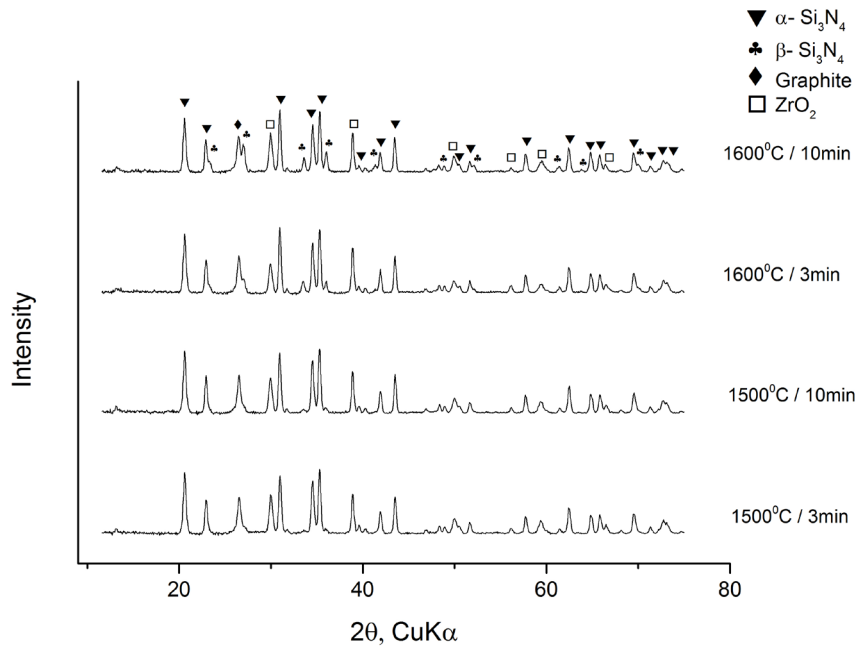


Figure 3: XRD diffractograms of 3 wt% MLG/Si₃N₄ composites are presented.

It confirms former findings that graphene makes it difficult to remove pores from the composite and is the main cause of the porosity. The density also changes in the function of sintering temperature, i.e. increasing temperature resulted in higher densities, although the variation is smaller. Holding times apparently had no influence on the density.

Most relevant mechanical properties including hardness (HV) and fracture toughness (K_{IC}) are illustrated in Figs. 5a and 5b in the function of the incorporated graphene content. The hardness values varied between 14 and 19 GPa. Up to 1% graphene addition the hardness was constant or perhaps a little bit higher but on full scale the graphene made the hardness poorer even smaller than monolithic Si₃N₄. Considering the main properties of graphene not much of improvement in the hardness was expected, but this declining trend was not foreseen either, even though similar decline of hardness was reported in (Fig. 5a) on graphene addition. This effect can be attributed to the increased remaining porosity in the structure with the higher graphene content. Among samples sintered at the same temperature the lowest hardness was exhibited by the one made at 1600°C for 10 minutes. This probably can be attributed to the fact that the $\alpha \rightarrow \beta$ phase transformation took place in the biggest proportion for this sample, and the β phase possesses lower hardness.

The primary aim of graphene reinforcement was the assessed improved resistance to fracture. In Fig. 5b the correlation of fracture toughness with respect to the graphene content is not so obvious. It is quite apparent that 1% of graphene increased the toughness even up to 8.0 MPa m^{1/2} in two experiments, which is a 60% increase as compared to pure Si₃N₄. This is in very good agreement with Kvetková's finding who measured fracture a toughness of 8.9 MPa m^{1/2} [15] for the composite with 1 wt% of MLG. However, the increasing trend did not continue and the fracture toughness did not correlate linearly with graphene content, but seems to have a maximum at 1%. Further increasing the graphene content did not cause significant change in the fracture toughness, which stayed around 5 MPa m^{1/2}. It is in line with findings of Walker et al. [24], who fabricated composite with 1.5 wt% of GPL and the achieved fracture toughness was of 6.6 MPa m^{1/2} which is little higher than that of monolithic composite was not spectacular. Tapasztó et al. [25] fabricated Si₃N₄ with 3 wt% graphene and obtained a paltry 3.2 MPa m^{1/2} value for the toughness.

Although the GLPs was found to participate in several toughening mechanisms including crack branching, crack deflection and crack bridging, their more frequent occurrence seemingly does not provide additional advantage. This behavior may probably be also related to the higher porosity but needs more research.

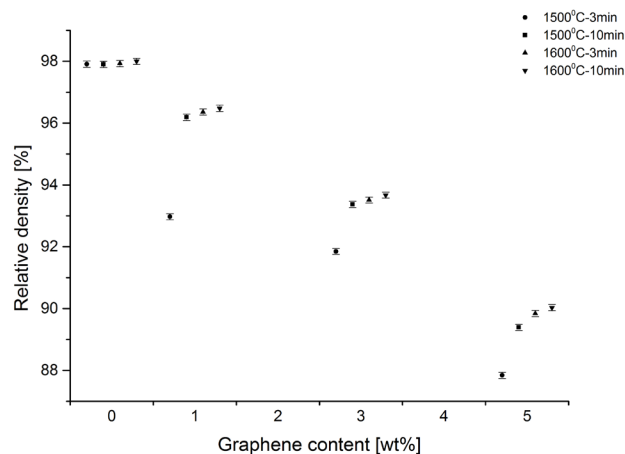


Figure 4: Relative density as a function of graphene content.

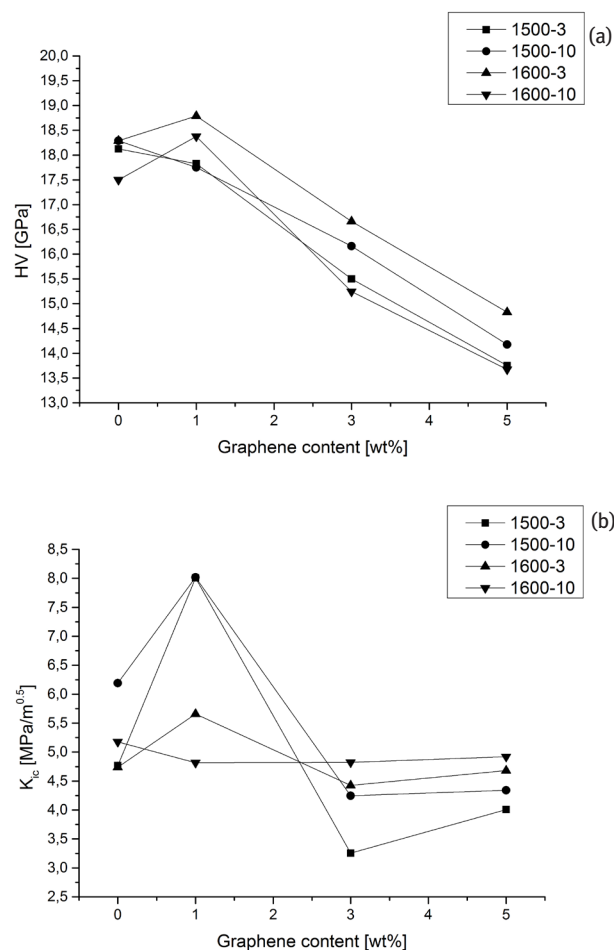


Figure 5: Results of the mechanical analysis hardness (a), and fracture toughness (b) on the different graphene concentration and sintering temperatures.

4 Conclusions

In this work we studied the effect of the multilayer graphene platelets content on the mechanical properties in silicon nitride matrix. The nanocomposites with varying graphene content (1, 3 and 5 wt%) have been fabricated by spark plasma sintering at different temperatures (1500°C and 1600°C) and holding times (3 min and 10 min). A very evident trend could be observed between the graphene content and the obtained density. The increasing graphene gave rise to lower density values. The hardness followed a similar trend to density. Although, it achieved a maximum value of 18,8 GPa at 1 wt% graphene content, but the increasing porosity of the composite eventually resulted in lower hardness values above 1 wt% of MLG. A minor $\alpha \rightarrow \beta$ phase transformation took place in all MLG/Si₃N₄ samples, while the prevailing phase remained the α -one. Fracture toughness greatly improved for all samples at 1 wt% multilayer graphene content having an average of 8.0 MPa m^{1/2}. This value is more than 60% improvement as compared to the monolithic Si₃N₄ composite. The fracture toughness, however, exhibited a maximum relation as it was decreased to the value of the monolithic silicon nitride. The exact reason of it could not be revealed but probably is also related to the higher porosity of the composite.

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