FRACTURE MECHANISM IN Si_3N_4 – GRAPHENE PLATELETS COMPOSITES

Lenka Kvetková[1)], Annamaria Duszová[1)], Monika Kašiarová[1)], Františka Dorčáková[1)], Ján Dusza[1,2)], Csaba Balázsi[3)]*
[1)] *Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04353 Košice, Slovakia*
[2)] Óbuda University, Donát Bánki Faculty of Mechanical and Safety Engineering, *Népszínház street 8, 1428 Budapest, Hungary*
[3)] *Institute for Technical Physics and Materials Science, Hungarian Academy of Sciences, Budapest, 49, H-1525, Hungary*

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[*]*Corresponding author: e-mail: kvetkova@mail.telekom.sk, Tel.:+421 55 792 2457, Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04353 Košice, Slovak*ia

Abstract
Silicon nitride + 1 wt% graphene platelet composites were prepared using various graphene platelets (GPLs) as a filler. Two different sintering routes were applied which resulted in different microstructure: hot isostatic pressing (1700°C/3h/20 MPa) and gas pressure sintering (1700°C/0h/2 MPa). The influence of the GPLs addition and of processing routes on the fracture toughness and fracture mechanism of Si_3N_4+GPLs was investigated. The main toughening mechanisms, which originated from the presence of the graphene platelets are crack deflection, crack branching and crack bridging**.** These mechanisms are responsible for the increase of fracture toughness which is higher than that of monolithic Si_3N_4. The highest value of fracture toughness was obtained in the case of the composite processed by hot isostatic pressing using the GPLs with lowest dimension.

Keywords: ceramic matrix composites, toughness, fracture

1 Introduction

During the last few years new cost effective, high quality carbon based filamentous was developed in the form of graphene platelets (GPLs), also called graphene nanoplatelets (GNP), multilayer graphene nanosheets (MGN) or graphene nanosheets (GNS). These platelets demonstrate exceptional high thermal and electrical conductivity and an exceptional combination of mechanical properties [1, 2]. Number of authors have reported improved mechanical and functional properties in the case of these composites compared to the monolithic ceramics [3-5]. Graphene, as a monolayer of sp2-hybridized carbon atom arranged in a two-dimensional lattice, has attracted tremendous attention in recent years owing to its exceptional mechanical, thermal and electrical properties [6].
Graphene has been produced by several routes [7], including growth by chemical vapor deposition, micro-mechanical exfoliation of graphite, and growth on crystalline silicon carbide. While these approaches can yield a defect-free material with exceptional properties, until recently techniques of making powdered samples of graphene have not yielded large enough quantities for use as filler for different materials [8].

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These platelets usually contain several graphene layers in contrast to the mono-layered graphene. Nano-scaled graphene plates of several desired size ranges (e.g., length and width of approximately 0.05 to 10 microns and thickness of approximately 1 to 10 nm) demonstrates exceptional high thermal and electrical conductivity and exceptional combination of mechanical properties [9].

There are up to now only a few reports used of graphene platelet additives to improve the mechanical properties of bulk silicon nitride ceramics. Walker et al [10] used spark plasma sintering for preparation of Si_3N_4 + GPLs composites with fracture toughness of 6.6 MPa.m$^{0.5}$ for the systems with 1.5 vol% of GPLs. This value is significantly higher than the value measured for the monolithic silicon nitride with globular grains of alfa phase due to the toughening mechanisms in the form of graphene necking and crack bridging, crack deflection and graphene sheet pull-out.

Kun et al [11] prepared and characterized silicon nitride based nanocomposites with different amount of carbon reinforcement in the form of graphene fillers. According to their results both the bending strength and elastic modulus decreased by addition of carbon based fillers.

Kvetkova et al [12] and Dusza et al [13] reported significantly improved fracture toughness of hot isostatic pressed silicon nitride ceramics reinforced with various graphene platelets. The indentified toughening were crack deflection, crack branching, crack bridging and graphene sheet pull-out..

This work deals with fracture mechanism in Si_3N_4 with different types of graphene platelets and their fracture toughening.

2 Experimental material(s) and methods

The starting powders used in this experiments were: 90 wt% Si_3N_4 (Ube, SN-ESP), 4 wt% Al_2O_3 (Alcoa, A16) and 6 wt% Y_2O_3 (H.C. Starck, grade C). The powder mix and green samples have been prepared in the same way as it is described in [13]. Four different carbon based fillers were used; GPL-1 (multilayer graphene nanosheets), prepared by mechanical milling method, GPL-2 (exfoliated graphene nanoplatelets, xGnP-M-5), GPL-3 (exfoliated graphene nanoplatelets, xGnP-M-25 and GPL-4 (nano graphene platelets Angstron N006-010-P), [12], **Fig 1**.

Two different processing route have been applied for the densification. Hot isostatic pressing (HIP) was performed at 1700°C in high purity nitrogen using BN embedding powder at 20 MPa, with a 3 h holding time. The heating rate did not exceed 25°C/min. Gas pressure sintering (GPS) was employed at 1700°C in high purity nitrogen using BN embedding powder at 2 MPa, without holding time.

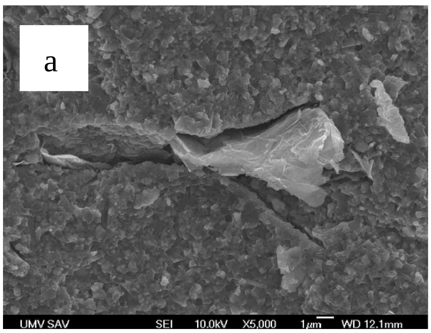

Fig.1 a Type of used GPLs: GPL-1: Multilayer graphene nanosheets

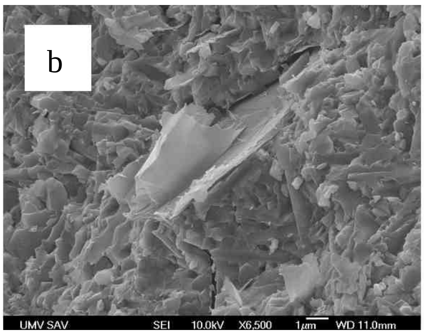

Fig.1 b Type of used GPLs: GPL-2: Exfol. graphene nanoplatelets xGnP-M-5

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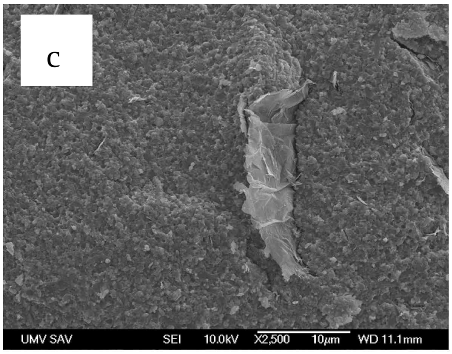

Fig.1 c Type of used GPLs: GPL-3: Exfol. graphene nanoplatelets xGnP-M-25

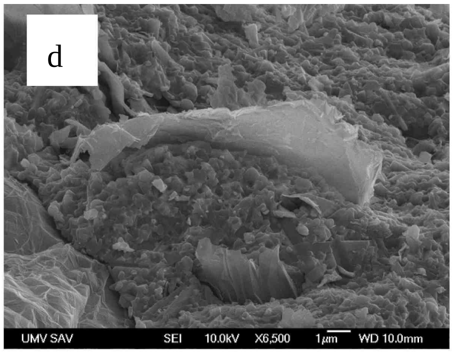

Fig.1 d Type of used GPLs: GPL-4: Nano graphene platelet Angstron N006-010-P

The experimental materials were characterized by X-ray, SEM, TEM and HREM. Specimens for microstructure examination were prepared by diamond cutting, grinding and polishing. The distribution of GPLs in the Si_3N_4 matrix was investigated using a carefully polished un-etched ceramographic section at magnifications from 500X to 2000X. Microstructure analysis has been made on chemical etched polished surface using SEM, JSM – JEOL 7000F. Images at magnification of 20 000x were used for estimation the mean diameter and aspect ratio of the Si_3N_4 grains and the volume fraction of ZrO_2 as well.
The microhardness (Leco Instruments) and hardness were measured using the Vickers indentation method at loads from 9.81 N to 150 N. The small specimen size did not allowed to use standard fracture toughness test, therefore indentation fracture toughness testing was performed at loads of 147 N using a Vickers indenter, and the K_{IC} was calculation was calculated using the Shetty equation,[14].

$$K_{ICInd} = 0.0899(H.P/4l)^{0.5} \qquad (1.)$$

where: H - Vicker hardness
P - indentation load and
l - length of the indentation crack.
Microfractography was used to study the fracture lines and surfaces of the specimens and to identify the toughening micromechanisms in the monolithic materials and in the composites.

3 Results and discussion

The hardness and indentation fracture toughness of the investigated materials are illustrated in **Table 1**.

Table 1 The hardness and indentation fracture toughness of the GPS investigated materials

Composition of investigated materials [wt%]				GPLs aditives	Hardness HV1 [GPa]		Fracture Toughness K_{Ic} [$MPa.m^{0.5}$]	
Si_3N_4	Al_2O_3	Y_2O_3	C		GPS	HIP	GPS	HIP
90	4	6	0	-	16.2 ± 0.3	16.4 ± 0.4	6.3± 0.2	6.5 ± 0.2
90	4	6	1	GPL - 2	14.9 ± 0.5	14.6 ± 0.3	6.7 ± 0.4	7.8 ± 0.4
90	4	6	1	GPL - 3	14.7 ± 0.4	15.1 ± 0.3	6.1 ± 0.3	8.6 ± 0.2
90	4	6	1	GPL - 4	15.3 ± 0,2	14.6 ± 0.4	7.6 ± 0.2	8.9 ± 0.4
90	4	6	1	GPL - 1	16.3 ± 0.4	16,4 ± 0,4	8.5 ± 0.4	9,9 ± 0,4

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According to the results beside the system reinforced by multilayer graphene nanosheets all composites exhibit lower hardness in comparison to the hardness of monolith. This is a result of the un-sufficient sintering and the present porosity around the graphene platelets. The GPS monolithic silicon nitride show slightly lower fracture toughness in comparison to the silicon nitride prepared by HIP. This is connected with the different microstructure of these systems and with the observed toughening mechanisms on the fracture line and fracture surface during the crack propagation. In Si_3N_4 prepared by GPS we found only a limited number of toughening mechanisms, why in material prepared by HIP we found toughening mechanisms in the form of crack deflection and mechanical and frictional interlocking. This behavior is connected with the different grain diameter of the materials. Characteristic fracture surface of the two monolithic materials is illustrated in **Fig. 2**. All composites exhibit higher indentation fracture toughness compared to the monolithic ceramics however the composites prepared by GPS exhibits lower fracture toughness in comparison to that prepared by HIP.

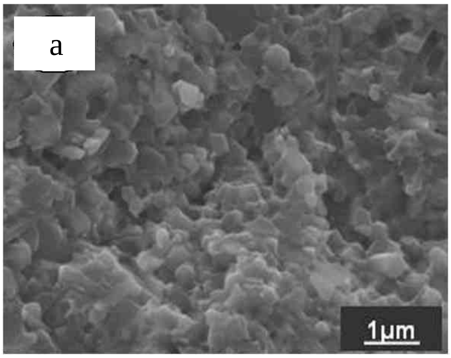

Fig.2 a Fracture surface of Si_3N_4 - processed by GPS

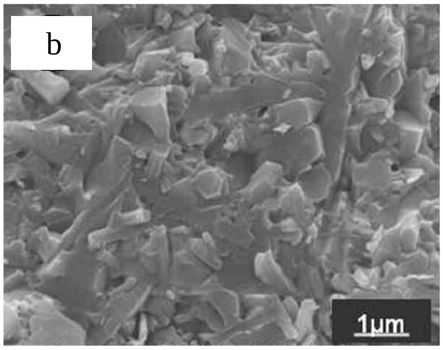

Fig.2 b Fracture surface of Si_3N_4 – processed by HIP

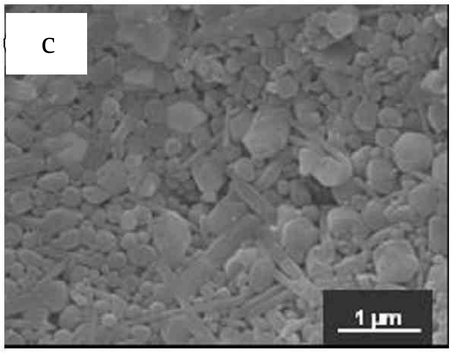

Fig.2 c Microstructure of Si_3N_4 processed by GPS

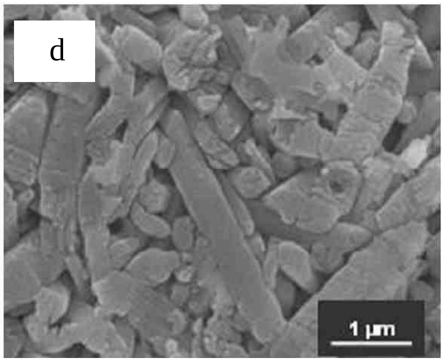

Fig.2 d Microstructure of Si_3N_4 processed by HIP

All composites exhibit higher indentation fracture toughness compared to the monolith, thanks to the more frequently occurred toughening mechanisms during the crack propagation. Fractographic examination of the fracture lines and fracture surfaces revealed different toughening mechanisms due to the present GPLs. These are very similar for all systems

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reinforced by different GPLs, only the frequency of their occurrence during the crack propagation or their effectiveness in toughening process is different. The main toughening mechanisms are; crack deflection (**Fig. 3a**), crack branching (**Fig. 3b**), and crack bridging (**Fig. 3c**).

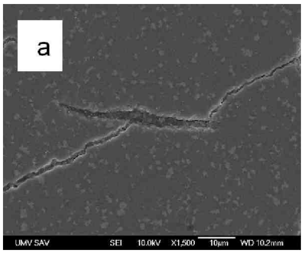

Fig.3 a Crack deflection at platelet with larger dimension and with the plane oriented nearly parallel to the plane of section

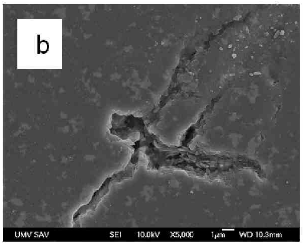

Fig.3 b Crack branching at platelets with larger dimension

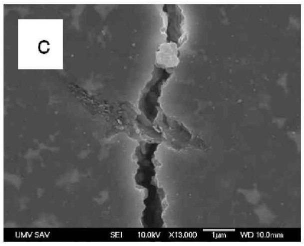

Fig.3 c Crack bridging by platelet with the plane orientated nearly perpendicularly to the plane of the section

Crack deflection and the slow down of the crack propagation were observed at the interaction of the crack with larger GPLs, **Fig. 3a**. At such an interaction the process zone of the crack is rapidly arises and after the increase of the outer applied load crack branching or/and crack twisting occurs in different direction to the main crack. Crack branching is very frequently observed toughening mechanisms in all investigated composites. The origin of this mechanism is the interaction of the propagating crack and GPLs with smaller size. The length of the secondary cracks is several micron and the frequency of occurrence of this mechanism is very high, **Fig. 3b**. Crack bridging was observed after the crack interaction with large GPLs as well as with smaller one. Characteristic crack bridging by larger GPL is visible in **Fig. 3c** on the fracture line with the plane of the graphene sheets nearly parallel to the plane of the polished surface. In spite of the fact that the GPL was destroyed during the grinding/polishing (ceramographic preparation of the sample) the effectiveness of the crack bridging by GPL is clearly visible.

4 Conclusion

Graphene platelets added silicon nitride (GPL/Si_3N_4) composites with various GPLs have been prepared and the influence of the type of GPLs and processing on the fractography, toughening mechanisms and fracture toughness was studed.

- The matrix of the composites prepared by GPS consists of Si_3N_4 grains with smaller diameter and aspect ratio in comparison to the composite prepared by HIP.
- The indentation fracture toughness of the composites was in the range 6.69 – 9.92 $MPam^{0.5}$, which is significantly higher compared to the monolithic silicon nitride 6.9 and 6.8 $MPam^{0.5}$.The highest value of K_{IC} was 9.92 $MPam^{0.5}$ in the case of composite reinforced by smallest multilayer graphene nanosheets, prepared by HIP.The composites prepared by GPS exhibit lower fracture toughness from 6.69 to 8.1 $MPam^{0.5}$.

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- The toughening mechanisms were similar in all composites in the form of crack deflection, crack branching and crack bridging.

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