Engineering Symposium at Bánki
(ESB 2020)
http://bgk.uni-obuda.hu/esb/2020

Tribological behavior of graphene reinforced silicon nitride composites

[1]Awais Qadir, [2]Péter Pinke, [3]Ján Dusza

[1]*Doctoral School of Materials Sciences & Technologies, Óbuda University, Budapest, Hungary, awais.qadir@uni-obuda.hu*
[2]*Institute of Materials & Manufacturing Sciences, Donat Banki Faculty of Mechanical & Safety Engineering, Óbuda University, 1081 Budapest, Hungary; pinke.peter@uni-obuda.hu*
[3]*Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic; duszaj@yahoo.com; jdusza@saske.sk*

Abstract

The tribological properties of silicon nitride + 1 wt. % graphene composites, prepared using gas pressure sintering (GPS) and hot isostatic pressing (HIP) at 1700 °C, were investigated and compared to the wear properties of monolithic Si_3N_4. The tribological measurements were performed using reciprocating ball-on-plate technique under dry conditions in the air with Si_3N_4 ball as a tribological partner at an applied load of 5 N and 13.5 N and sliding speed of 10 cm/s. Scanning electron microscopy (SEM) was used for the characterization of wear mechanisms. The friction coefficient of the systems changed from 0.40 to 0.47 and 0.55 to 0.69 at applied loads of 5 N and 13.5 N, respectively, with the lowest values for monolithic Si_3N_4 in both cases. The wear rates of investigated systems are in the range of $10^{-6} \sim 10^{-7}$ $mm^3/N.m$ with the lowest wear rate for the monolithic silicon nitride prepared by GPS.

Keywords: Si_3N_4, graphene, hot isostatic pressing, tribology, wear

1 Introduction

Silicon nitride (Si_3N_4) based ceramics, because of their excellent properties as hardness, flexural strength, oxidation resistance, tribological and thermal properties, etc., are widely used in different engineering applications as cutting tools, bearings, parts of gas turbines, engines, etc., [1]. However, silicon nitrides also exhibit some negative properties, such as low fracture toughness, low reliability, limited functional properties as electrical conductivity, etc. [2]. Recent advances in carbon-based nanomaterials opened up new opportunities to tailor the microstructures of ceramic materials as Si_3N_4 at a micro/nanometric scale and to develop new classes of silicon nitride-based ceramics with improved mechanical, tribological and functional characteristics [3][4][5].
At the beginning, carbon nanotubes (CNTs) based Si_3N_4 have been developed, and the exceptional mechanical, electrical, thermal, and multifunctional properties of CNTs resulted in the significantly improved properties of the composites [6][7].

Recently graphene nanoplatelets (GPLs) have emerged as a particularly promising nanoscale filler phase for Si_3N_4 ceramics due to their exceptional mechanical and physical properties [8]. GPLs also hold the potential for improving the composites' tribological properties as graphite is known to be an excellent solid lubricant.
The tribological properties of Si_3N_4 + graphene composites were investigated intensively during the last decade, [9][10]. Hvizdos et al. [9] studied the mechanical and tribological properties of nanocomposites with silicon nitride matrix with the addition of 1 and 3 wt. % of various types of

graphene platelets. They observed that such amounts of graphene phases do not decrease the coefficient of friction at dry conditions but 3 wt. % of larger sized graphene addition results in higher wear resistance. Belmonte et al. [10] investigated the tribological properties of graphene nanoplatelets (GNPs)/Si_3N_4 composites using a reciprocating ball-on-plate configuration under isooctane lubrication. They observed that the exfoliated graphene nanoplatelets formed a protective tribofilm, which acted as lubrication and enhanced the wear resistance up to 56%.

The aim of the present work is to study the tribological properties of Si_3N_4 ceramics with 1 wt.% graphene additives, processed with GPS and HIP processing routes.

2 Experimental materials and methods

The starting powder 90 wt. % α - Si_3N_4 (Ube, SN-ESP), and sintering aids 4 wt. % Al_2O_3 (Alcoa, A16) and 6 wt. % Y_2O_3 (H.C. Starck, grade C), polyethyleneglycol (PEG) surfactants, and deionized water were added to the powder mixture, and milled in a highly efficient attritor mill (Union Process, type 01-HD/HDDM) equipped with zirconia agitator delta discs and zirconia grinding media (diameter of 1 mm) in a 750 ml tank. The milling process was performed with a high rotation speed of 3000 rpm for 4.5 h. Three commercial graphenes were used: two grades of exfoliated graphene nanoplatelets (xGnP-M-5 – particle size 5 μm, and xGnP-M-25 – particle size 25 μm)[11] by XG Sciences and nanographene platelets (Angstron N006-010-P) by Angstron Materials [12]. 1 wt. % of each type graphene was added to α-Si_3N_4 powders for a separate batch and milled with low rotational speed, 600 rpm until 30 min. The milling with low rotation speed and shorter time was performed to avoid damaging the graphene reinforcements particles. Starting compositions of sintered samples are given in Table 1. The substance was dried and sieved with a filter with a mesh size of 150 mm. Green samples (green bodies) were obtained by dry pressing at 220 MPa. Before sintering processing, the green bodies were fired at 400 °C to eliminate PEG.

Two different sintering processes were performed to densify the powder compacts to observe the effect of the sintering process on the prepared composites' mechanical and tribological properties. Hot isostatic pressing (HIP) was performed at 1700 °C in high purity nitrogen by a two-step sinter-HIP method using BN embedding powder at 20 MPa, with 3 h holding time. The heating rate did not exceed 25 °C/ min. The dimensions of the as-sintered specimens were 3.5mm x 5mm x 50mm. Gas pressure sintering (GPS) was performed at 1700 °C in high purity nitrogen using BN embedding powder at 2 MPa, with no holding time. The heating rate did not exceed 25 °C/min. The dimensions of the as-sintered specimens were 3.5 mm × 5 mm × 50 mm.

The sintered samples' apparent density was measured by a standard Archimedes method using distilled water as an immersion medium at room temperature. For graphene reinforced Si_3N_4, the tribology measurements were carried out on equipment UMT 3 (Bruker) using the reciprocating ball-on-plate technique. The wear behavior of the experimental materials was studied in dry sliding in the air. The tribological partner was a highly polished (roughness Ra < 0.10 μm according to ISO 3290) Si_3N_4 ball with a 6.35 mm diameter. The applied load was 13.5 N, the sliding speed 10 cm/s, and the sliding distance was 720 m. The experiments were realized at room temperature at the relative humidity of 40 ± 5%.

Table 1 - Details of materials and parameters of processing

No.	Starting Powders (wt. %)			Graphene (wt. %)	Type of additives	Sintering Conditions			Sintering Technique	App. density (g/cm^3)
	Si_3N_4	Al_2O_3	Y_2O_3			T (°C)	Holding time	Pressure (MPa)		
SN-1	90	4	6	0	-	1700	-	2	GPS	3.329
SN-2	90	4	6	1	xGnP-M-25	1700	-	2	GPS	3.301
SN-3	90	4	6	1	Angstron N006-010-P	1700	-	2	GPS	3.297
SN-4	90	4	6	1	xGnP-M-25	1700	3 h	20	HIP	3.375
SN-5	90	4	6	1	xGnP-M-5	1700	3 h	20	HIP	3.379

3 Results and Discussion

The density values of the sintered samples are illustrated in Table 1. As it is visible the samples prepared by HIP method show higher density in comparison to the samples processed by GPS and the different GPLs addition results in similar density values.

Coefficient of friction (COF): Figure 1 shows the friction coefficient under 5 N and 13.5 N loads in the *run-in* stage (0 – 40 m) and *steady-state stage* (40 – 720 m) for the investigated systems. After the run-in stage the coefficient of friction under the testing conditions was stable for all investigated systems. The friction coefficient was between 0.40 to 0.47 under 5 N load and between 0.55 to 0.69 under the load of 13.5 N. The lowest coefficient of friction under both loads 5 N and 13.5 N was recorded for monolithic Si_3N_4 material (SN-1) prepared by gas pressure sintering. From composites at 5 N load similar COF value as for monolithic material was measured for Si_3N_4 + 1% xGnP-M-25 prepared by HIP and at 13.5 N load for Si_3N_4 + 1% Angstron N006-010-P, prepared by GPS.

Wear rate: Figure 2 shows the wear rates under loads of 5 N and 13.5 N for the investigated systems. The investigated systems' wear rates are in the range of $10^{-6} \sim 10^{-7}$ mm^3/N.m. Overall the wear rates of systems under 5N loads are lower than that of systems under 13.5 N. The lowest wear rate was observed for the monolithic silicon nitride prepared by GPS. From composites similar wear rates as for the monolithic Si_3N_4 was measured at 5 N load for the composites Si_3N_4 + 1% Angstron N006-010-P, prepared by GPS and Si_3N_4 + 1 wt. % xGnP-M-25, prepared by HIP and at 13.5 N load for the composite Si_3N_4 + 1 wt. %xGnP-M-25, prepared by GPS. The wear resistance of these composites is higher than the reported values by several researchers [13], [14].

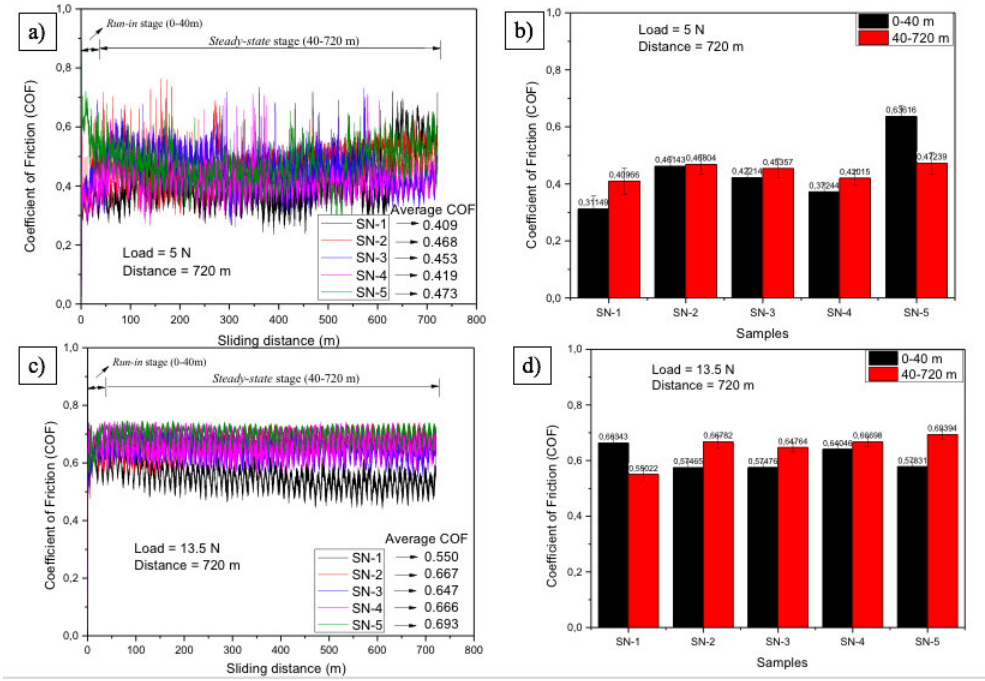

Figure 1 – Coefficient of friction of investigated composites: a) COF under 5 N loads; b) COF of composites during (0-40 m) and 40-720 m) under 5 N load; c) COF under 13.5 N loads; d) COF of composites during (0-40 m) and 40-720 m) under 13.5 N load.

Wear Mechanism: SEM observation of the wear track of investigated systems was used to identify the wear mechanisms. Similar wear mechanism was identified in all investigated systems. The worn surface of the monolithic Si_3N_4 was relatively smooth with only a small amount of abrasion groves and adhered debris can be identified. Under higher load of 13.5N, micro-crack formation and spalling layers were also observed. In wear track of composites only a very limited formation of tribolayer, thanks to the present graphene phase is visible.

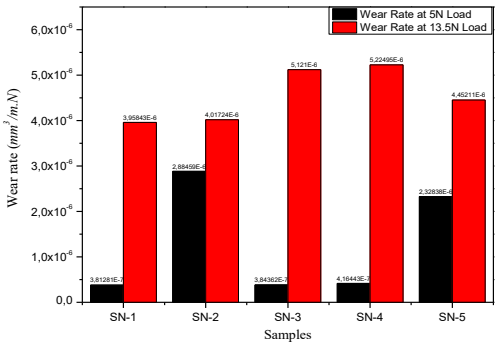

Figure 2 – Wear rates of silicon nitride composites with 1 wt. of different types of graphene under 5 N loads and 13.5 N loads.

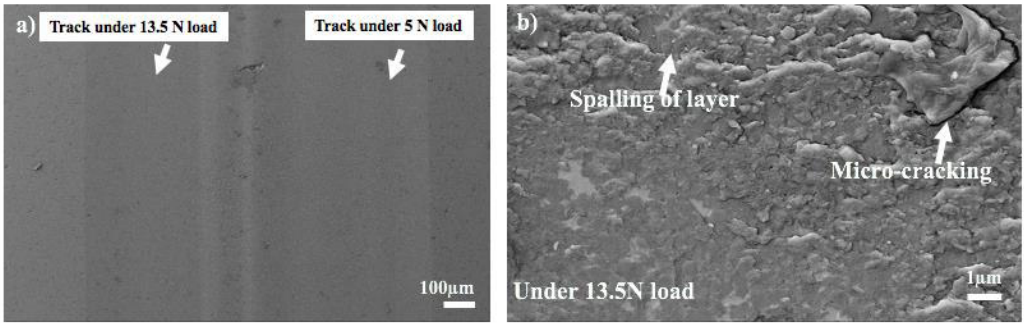

Figure 3 – Wear mechanism of monolithic Si_3N_4 prepared by GPS, studied by SEM: a) wear tracks under 5 and 13.5 N, looks smooth surface; and b) wear track under 13.5 N with higher magnification, microcracking and chipping off material in the wear track are visible.

4 Conclusions

The aim of the present contribution was to investigate the tribological properties of silicon nitride + 1 wt. % graphene composites prepared using gas pressure sintering (GPS) and hot isostatic pressing (HIP) and compare to the wear properties of monolithic Si_3N_4.

1. The friction coefficient of the systems changing from 0.40 to 0.47 and 0.55 to 0.69 at applied loads of 5 N and 13.5 N, respectively, with the lowest values for monolithic Si_3N_4 in both cases.

2. The wear rate of investigated systems at the applied load of 5 N changing from 3.8 x 10^{-7} mm^3/N.m to 2.8 x 10^{-6} mm^3/N.m with the lowest value for monolithic Si_3N_4 and Si_3N_4 + graphene/Angstron composite.

3. The wear rates of investigated systems at the applied load of 13.5 N changing from 3.9 x 10^{-6} mm^3/N.m to 5.2 x 10^{-6} mm^3/N.m with the lowest value for monolithic Si_3N_4 and Si_3N_4 + graphene/xGnP composite.

4. The dominant wear mechanisms were abrasion, microcrack formation, and spalling with minimal tribo-layer formation.

5. The volume fraction of the graphene platelets in the Si_3N_4 matrix is probably not enough to improve the tribological characteristics of the investigated silicon nitride based composites.

Acknowledgement

One of the authors, Awais Qadir, would like to express his thanks to the following project: ÚNKP-20-3 NEW NATIONAL EXCELLENCE PROGRAM of the MINISTRY FOR INNOVATION AND TECHNOLOGY from the source of the NATIONAL RESEARCH, DEVELOPMENT AND INNOVATION FUND, which provided support for the research. Authors thank to Mr. V. Varga, and S. Gurban for sample preparation, Dr. Dávid Medved and Ing. Michal Ivor for performing the tribological testing and SEM of worn surfaces.

5 Reference

[1] S. Hampshire, "Silicon Nitride Ceramics," in *Engineered Ceramics: Current Status and Future Prospects*, Jansen M., Heidelberg: Springer, Berlin, Heidelberg, 2016, pp. 77–97.

[2] F. L. Riley, "Silicon Nitride and Related Materials," *J. Am. Ceram. Soc.*, vol. 83, no. 2, pp. 245–265, Dec. 2004, doi: 10.1111/j.1151-2916.2000.tb01182.x.

[3] C. Balazsi, "Silicon Nitride Composites with Different Nanocarbon Additives," *J. Korean Ceram. Soc.*, vol. 49, no. 4, pp. 352–362, Jan. 2012, doi: 10.4191/kcers.2012.49.4.352.

[4] A. Qadir, P. Pinke, and J. Dusza, "Silicon Nitride-Based Composites with the Addition of CNTs—A Review of Recent Progress, Challenges, and Future Prospects," *Mater. 2020, Vol. 13, Page 2799*, vol. 13, no. 12, p. 2799, Jun. 2020, doi: 10.3390/MA13122799.

[5] W. Zhai, N. Srikanth, L. B. Kong, and K. Zhou, "Carbon nanomaterials in tribology," *Carbon*, vol. 119. Elsevier Ltd, pp. 150–171, Aug. 01, 2017, doi: 10.1016/j.carbon.2017.04.027.

[6] M. Matsuoka, S. Yoshio, T. Yamakawa, J. Tatami, T. Wakihara, K. Komeya, and T. Meguro, "Development of CNT-Si3N4 Composites with High Strength and Electrical Conductivity by Adding HfO2," *Trans. Mater. Res. Soc. Japan*, vol. 37, no. 1, pp. 11–14, Mar. 2012, doi: 10.14723/tmrsj.37.11.

[7] E. T. Thostenson, Z. Ren, and T.-W. Chou, "Advances in the science and technology of carbon nanotubes and their composites: a review," *Compos. Sci. Technol.*, vol. 61, no. 13, pp. 1899–1912, Mar. 2001, doi: 10.1016/S0266-3538(01)00094-X.

[8] L. S. Walker, V. R. Marotto, M. A. Rafiee, N. Koratkar, and E. L. Corral, "Toughening in Graphene Ceramic Composites," *ACS Nano*, vol. 5, no. 4, pp. 3182–3190, Apr. 2011, doi: 10.1021/nn200319d.

[9] P. Hvizdoš, J. Dusza, and C. Balázsi, "Tribological properties of Si3N4–graphene nanocomposites," *J. Eur. Ceram. Soc.*, vol. 33, no. 12, pp. 2359–2364, 2013, doi: https://doi.org/10.1016/j.jeurceramsoc.2013.03.035.

[10] M. Belmonte, C. Ramírez, J. González-Julián, J. Schneider, P. Miranzo, and M. I. Osendi, "The beneficial effect of graphene nanofillers on the tribological performance of ceramics," *Carbon N. Y.*, vol. 61, pp. 431–435, 2013, doi: https://doi.org/10.1016/j.carbon.2013.04.102.

[11] "(No Title)." https://xgsciences.com/wp-content/uploads/2018/10/xGnP-M-Grade-XG-Sciences.pdf (accessed Aug. 13, 2020).

[12] "nano graphene platelets, http://angstronmaterials.com." .

[13] J. Gonzalez-Julian, J. Schneider, P. Miranzo, M. I. Osendi, and M. Belmonte, "Enhanced Tribological Performance of Silicon Nitride-Based Materials by Adding Carbon Nanotubes," *J. Am. Ceram. Soc.*, vol. 94, no. 8, pp. 2542–2548, Mar. 2011, doi: 10.1111/j.1551-2916.2011.04391.x.

[14] J. Balko, P. Hvizdoš, and C. Balázsi, "WEAR DAMAGE IN SILICON NITRIDE COMPOSITES WITH GRAPHENE AND CARBON NANOTUBES," *Acta Metall. Slovaca - Conf.*, vol. 3, no. 0, pp. 276–281, May 2013, doi: 10.12776/amsc.v3i0.140.