

ÓBUDA UNIVERSITY

Doctoral (Ph.D.) Thesis Booklet



STUDY OF CARBON NANOFILLERS REINFORCED  
SILICON NITRIDE COMPOSITES

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## **Jury for Public Defense**

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## 1. Introduction and objectives of the work

In 1859, Sainte-Claire Deville and F. Wohler reported the synthesis of  $\text{Si}_3\text{N}_4$  for the first time by [1]. In 1955, J. F. Collins and R. W. Gerby found that silicon nitride-based ceramics have potential thermal and mechanical properties at high temperatures [2]. Simultaneously, the silicon nitride was not developed fully dense until then, and it was fabricated by a reaction bonding method only. In the 1960s, Deeley et al. [3] developed, for the first time, highly dense silicon nitride materials with sintering additives by hot pressing (HP). In the early 1970s, researchers focused on silicon nitride-based ceramics for gas turbine application [4]. Later on, different sintering techniques were developed, such as pressureless sintering [5] and gas pressure sintering (GPS) [6] which made it possible to produce complex-shaped components with high density. Silicon nitride is considered a structural ceramic material with several excellent properties such as excellent flexural strength, fracture resistance, high hardness, oxidation resistance, thermal properties at the room, and elevated temperatures. Despite having unique properties, silicon nitride also exhibits some negative properties, such as brittleness, low flaw tolerance, limited-slip systems, and low reliability, limiting its broader applications. To overcome such flaws, the addition of reinforcement in the silicon nitride matrix was proposed.

Another problem is the formation of amorphous glassy phases at grain boundaries of sintered silicon nitride. Due to covalent bonds and low solid-state diffusion in  $\text{Si}_3\text{N}_4$ , sintering is very difficult. Oxide additives such as  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , etc., are used to provide conditions for liquid phase sintering of this ceramic material. These additives create liquid phases that enhance silicon nitride's densification and its transformation from the  $\alpha\text{-Si}_3\text{N}_4$  to the  $\beta\text{-Si}_3\text{N}_4$  (Jack, 1976). Upon cooling, these liquid phases appear in the grain boundaries or at triple points of silicon nitride as amorphous oxide glasses. These glassy phases are detrimental to the mechanical properties of sintered silicon nitride at high temperatures. The glassy phases become soften at grain boundaries at a temperature above 1000 °C and affect the mechanical properties. These glassy phases are needed to eliminate or convert from amorphous to a crystalline phase which could play a role in improving properties at high temperature.

Many researchers developed silicon nitride with different reinforcements and achieved success to some extent. With the discovery of carbon nanotubes (CNTs) in 1991 and graphene in 2004, a new research horizon arose in the materials science field. Since their discoveries, carbon nanofillers are being exploited to improve the mechanical, tribological, and electrical properties

of advanced ceramics, including silicon nitride. The carbon nanofillers are promising candidates as reinforcements in the silicon nitride matrix to improve the composite properties. Therefore, researchers utilize different carbon nanofillers with varying concentrations, adopting various milling methods and parameters and applying different sintering techniques with varying parameters to explore the mechanical, tribological, thermal, and functional properties of silicon nitride composites. The carbon nanofillers are not exploited well yet; there is still a need for much more focused research to exploit the nanofillers as reinforcement to improve silicon nitride's several properties.

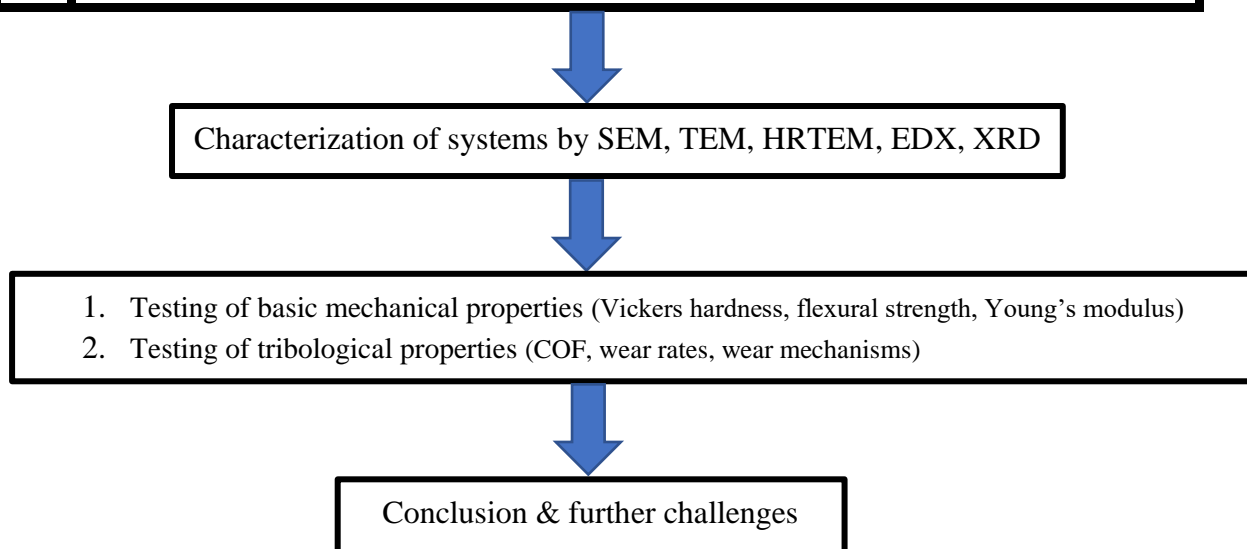
The current work proposed that glassy phases might be eliminated or converted from amorphous to glassy phases by surface oxidation of silicon nitride's starting powders at high temperatures. The current work is also a contribution towards the exploration of silicon nitride's mechanical and tribological properties with the addition of carbon nanofillers. In this work, different techniques and parameters were adopted to optimize and obtain better results. The objectives of the current work are:

- To develop silicon nitride materials without glassy phases at the grain boundaries
- To study the effect of oxidation of starting powders on structural, mechanical, and tribological properties of sintered silicon nitride.
- To develop MWCNTs reinforced silicon nitride composites processed from oxidized  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powders and to study their mechanical and tribological properties.
- To investigate the microstructure of starting powders by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM), and phases analysis by X-ray diffraction (XRD) technique.

## 2. Materials & methods

This thesis focus on the study of brittle ceramic composite materials with various content of different carbon nanofillers in silicon nitride-based matrix and prepared by hot isostatic pressing (HIP) and gas pressure sintering (GPS) techniques. The experimental scheme is given in the diagram (Figure 1). According to the diagram, three different silicon nitride systems were prepared by hot isostatic pressing (HIP) or gas pressure sintering (GPS), these sintered systems were characterized by different techniques (SEM, TEM, HRTEM, EDX, and XRD) and followed by testing of their mechanical and tribological properties. Each system will be discussed in the following chapters separately and followed by a conclusion with future work.

No.	Systems	Starting powders	Oxidation time (h)	Sintering method	Sintering Temperature	Detailed Study in
1	Monolithic Si <sub>3</sub> N <sub>4</sub> systems	$\alpha$ - Si <sub>3</sub> N <sub>4</sub>	0	HIP	1500 & 1700 °C	Chapter 4
			10			
			20			
2	Si <sub>3</sub> N <sub>4</sub> + 3 wt% MWCNTs	$\alpha$ - Si <sub>3</sub> N <sub>4</sub>	0	HIP	1700 °C	Chapter 5
			10			
			20			
3	Si <sub>3</sub> N <sub>4</sub> + 1 wt% graphene	$\alpha$ - Si <sub>3</sub> N <sub>4</sub>	0	HIP	1700 °C	Chapter 6
				GPS		



*Figure 1 – experimental program*

## 2.1. Preparation of monolithic Si<sub>3</sub>N<sub>4</sub> composites

Two powdered  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> samples were oxidized at 1000 °C for 10 hours and 20 hours in ambient air, respectively. The starting powders used in experiments were as follows: 90 wt. %  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powders (Unoxidized and 10 & 20 hrs oxidized  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powders) (Ube, SN-ESP), as well 4 wt. % Al<sub>2</sub>O<sub>3</sub> (Alcoa, A16) and 6 wt. % Y<sub>2</sub>O<sub>3</sub> (H.C. Starck, grade C) sintering additives. Polyethylene glycol (PEG) surfactants and ethanol were added to the powder mixture. These mixtures were milled in high-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 cm<sup>3</sup> zirconia tank. Each batch contains zirconia as contamination which originated from media and discs. This milling process has been performed with high rotation speed 4000 rpm for 4 hours.

The powders were dried and sieved through 150  $\mu$ m mesh number. Green samples were produced by dry pressing under 200 MPa pressure. These samples were subjected to the oxidation at 400 °C for the elimination of polyethyleneglycol (PEG) prior to the sintering process.

For analysis of the effect of sintering temperature on the structural and mechanical properties of composites, two hot isostatic pressing sintering temperatures were carefully chosen. The strategies are given below:

- a) First batch of samples was densified at 1700 °C,
- b) And other batch of samples was densified at 1500 °C,

Under 20 MPa in nitrogen (N<sub>2</sub>) gas environment for 3 hours as a holding time.

The heating rate did not exceed 25 °C/ min. The dimensions of the as-sintered specimens were 3.5 mm x 5 mm x 50 mm.

## 2.2. Preparation of Si<sub>3</sub>N<sub>4</sub> + MWCNTs composites

The starting powder,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> (Ube, SN-ESP), used in this investigation was in three forms:

- a) As received  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder (un-oxidized) used as a reference (SN-CNT/0).
- b) 10 h oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder at 1000 °C in ambient air environment (SN-CNT/10).
- c) 20 h oxidation of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder at 1000 °C in ambient air environment (SN-CNT/20).

Each batch with 90 wt. %  $\alpha$ - $\text{Si}_3\text{N}_4$  powders (un-oxidized and 10 & 20 hours oxidized  $\alpha$ - $\text{Si}_3\text{N}_4$  powders) were milled separately with 4 wt. %  $\text{Al}_2\text{O}_3$  (Alcoa, A16), 6 wt. %  $\text{Y}_2\text{O}_3$  (H.C. Starck, grade C) as sintering additives and polyethylene glycol (PEG) surfactants and ethanol in high-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 cm<sup>3</sup> zirconia tank. This milling process was performed with high rotation speed 4000 rpm for 4 hours. The 3 wt. % MWCNTs were added in the mixture and mixed them for 30 minutes on the 600 rpm in attritor mill. The MWCNTs were produced by CCVD method [7]. The low rpm was used to avoid the damaging of MWCNTs in the powder. A similar powder preparation process was used in previous works [8]. The drying and sieving process with 150  $\mu\text{m}$  mesh number were done after the milling process. Each batch of powders were subjected to the dry pressing consolidation process under 200 MPa pressure to produce green samples with the dimensions of 3.5 mm x 5 mm x 50 mm. The heat treatment of green samples was done at 400 °C in the muffle furnace to eliminate the PEG prior to the sintering process. After the heat treatment of green samples, the samples were sintered at 1700 °C, 20 MPa in nitrogen ( $\text{N}_2$ ) gas environment for 3 hours as a holding time with the heating rate of 25 °C/ min similar as in our previous work [8].

### 2.3. Preparation of $\text{Si}_3\text{N}_4$ + Graphene composites

The starting powder 90 wt. %  $\alpha$  -  $\text{Si}_3\text{N}_4$  (Ube, SN-ESP), and sintering aids 4 wt. %  $\text{Al}_2\text{O}_3$  (Alcoa, A16) and 6 wt. %  $\text{Y}_2\text{O}_3$  (H.C. Starck, grade C), polyethyleneglycol (PEG) surfactants, and deionized water were added to the powder mixture. These mixtures were milled in a highly efficient attritor mill (Union Process, type 01-HD/HDDM) equipped with zirconia agitator delta discs (volume of 1400 cm<sup>3</sup>) and zirconia grinding media (diameter of 1 mm) in a 750 ml tank. Each batch contained  $\text{ZrO}_2$  as contamination, which originated from the grinding media. The milling process was performed with a high rotation speed of 3000 rpm until 4.5 h.

Three types of graphene-based materials from commercial companies were added as reinforcements.

1. exfoliated graphene nanoplatelets (xGnP-M-5) [9]
2. exfoliated graphene nanoplatelets (xGnP-M-25) [9]
3. nano graphene platelets (Angstrom N006-010-P) [10]

1 wt. % of each type graphene was added to  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> 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.

The substance was dried and sieved with a filter with a mesh size of 150  $\mu$ m. 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. The sintering processes are given below:

1. Hot isostatic pressing (HIP): 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.
2. Gas pressure sintering (GPS): 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  $\times$  5 mm  $\times$  50 mm.



## 4. Main findings

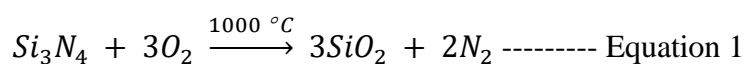
After preparation of composites, following characterization techniques were used: Archimedes method for measuring the density, scanning electron microscopy (SEM) for examining the microstructure, X-ray diffraction (XRD) for phase analysis, transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) for crystallographic structure analysis and confocal microscopy for calculating the material loss due to wearing after tribological tests. The fundamental mechanical properties and tribological properties of the composites were determined. A fractographic analysis was carried out to determine the nature of the fracture. Wear tracks were examined by scanning electron microscope (SEM) to identify the wear mechanisms. Based on the results analysis, following major findings have been published in peer-reviewed journals and documented below:

- 1. I demonstrated that in-situ Si<sub>2</sub>N<sub>2</sub>O could be produced in the Si<sub>3</sub>N<sub>4</sub> matrix by oxidizing the starting powders at 1000 °C, adding oxides (4 wt % Al<sub>2</sub>O<sub>3</sub>, 6 wt% Y<sub>2</sub>O<sub>3</sub>) as sintering aids, and densifying the powders compacts by hot isostatic pressing (HIP) at 1500 or 1700 °C in an N<sub>2</sub> gas environment under 20 MPa pressure for 3 hours.**

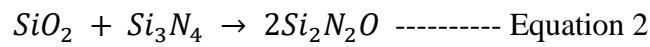
Based on XRD results, Si<sub>2</sub>N<sub>2</sub>O phase was found in sintered composites. It was demonstrated successfully that the production of in-situ Si<sub>2</sub>N<sub>2</sub>O is feasible by oxidizing the starting powders. For the first time, the in-situ Si<sub>2</sub>N<sub>2</sub>O was produced by adopting the described techniques in Chapter 4 of the thesis.

Figure 2 illustrates the mechanism of the *in-situ* growth of Si<sub>2</sub>N<sub>2</sub>O in the silicon nitride matrix. Si<sub>2</sub>N<sub>2</sub>O was formed from the reaction of SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> in the presence of the liquid phase. The oxidized powders contained oxygen, which caused the formation of Si<sub>2</sub>N<sub>2</sub>O in the presence of the liquid phase. The starting powders α - Si<sub>3</sub>N<sub>4</sub> were oxidized at 1000 °C in an ambient environment for 10 and 20 hours. As a result of oxidation, a nanolayer of amorphous SiO<sub>2</sub> was formed on α - Si<sub>3</sub>N<sub>4</sub> particles, according to this reaction (Equation 1).

In the first stage, the SiO<sub>2</sub> was formed on the Si<sub>3</sub>N<sub>4</sub> powder particles' surface (Equation 1).



In the second stage, Si<sub>2</sub>N<sub>2</sub>O was formed as a result of a reaction between SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> in the presence of an N<sub>2</sub> gas environment during the sintering process (Equation 2)[11][12][13].



During the sintering process, an Al-Y-O-N based supersaturated liquid was formed, and the reaction between SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> occurred (Equation 2). In the first step, Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> were dissolved into the liquid phase as Si, N, and O. Then in the second step, these (Si, N, O) diffused through the liquid phase towards the growth of Si<sub>2</sub>N<sub>2</sub>O and finally attached to the growing Si<sub>2</sub>N<sub>2</sub>O crystals. Tsai and Raj [11] proposed a model for the Si<sub>2</sub>N<sub>2</sub>O growth through the dissolution of Si<sub>3</sub>N<sub>4</sub> in a glassy phase based on Mg-Si-O-N. The proposed model by Tsai and Raj, with a slight modification, validates the growth mechanism of Si<sub>2</sub>N<sub>2</sub>O in the present study. Moreover, α- to β- Si<sub>3</sub>N<sub>4</sub> transformation also happened simultaneously with the formation of Si<sub>2</sub>N<sub>2</sub>O. During the sintering, a supersaturated liquid phase based on Si-Al-Y-O formed, and α-Si<sub>3</sub>N<sub>4</sub> was dissolved in this liquid and re-precipitated as a β phase. This hypothesis supports Hampshire and Jack's work [14].

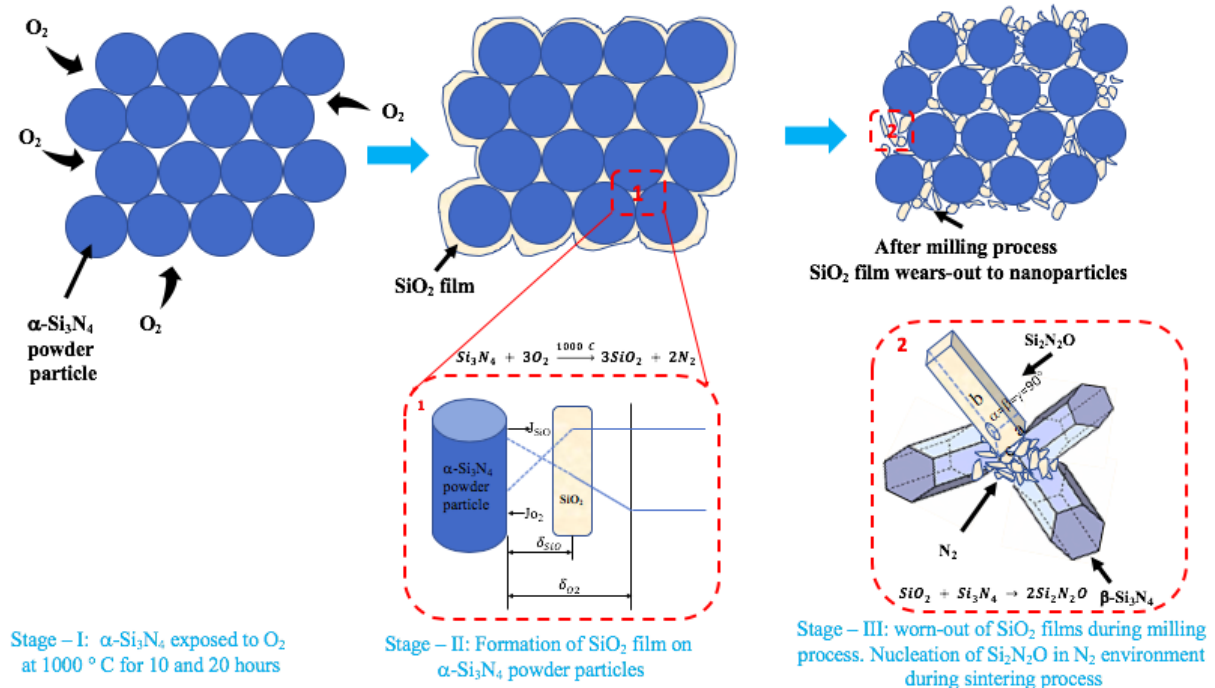
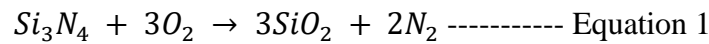
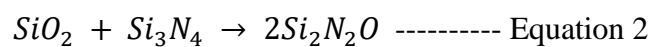


Figure 2 - Illustration of mechanism of in-situ growth of Si<sub>2</sub>N<sub>2</sub>O in Si<sub>3</sub>N<sub>4</sub> matrix (Author's work).

The starting powders  $\alpha$  -  $\text{Si}_3\text{N}_4$  were oxidized at 1000 °C in an ambient environment for 10 and 20 hours. As a result of oxidation, a nanolayer of amorphous  $\text{SiO}_2$  was formed on  $\alpha$  -  $\text{Si}_3\text{N}_4$  particles, according to this reaction (Equation 1):



The formation of the  $\text{SiO}_2$  layer was confirmed by HRTEM results and EDX analysis. During the sintering process, the  $\text{Si}_2\text{N}_2\text{O}$  was nucleated due to a reaction between  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  (Equation 2).



The presence of the  $\text{Si}_2\text{N}_2\text{O}$  phase was confirmed by XRD analysis (**Figure 5**). The mechanism of the in-situ growth of  $\text{Si}_2\text{N}_2\text{O}$  has been described in **Figure 2**. The amount of  $\text{Si}_2\text{N}_2\text{O}$  increased with an increasing amount of oxygen content in starting powders, which is a function of oxidation time (**Figure 3**).

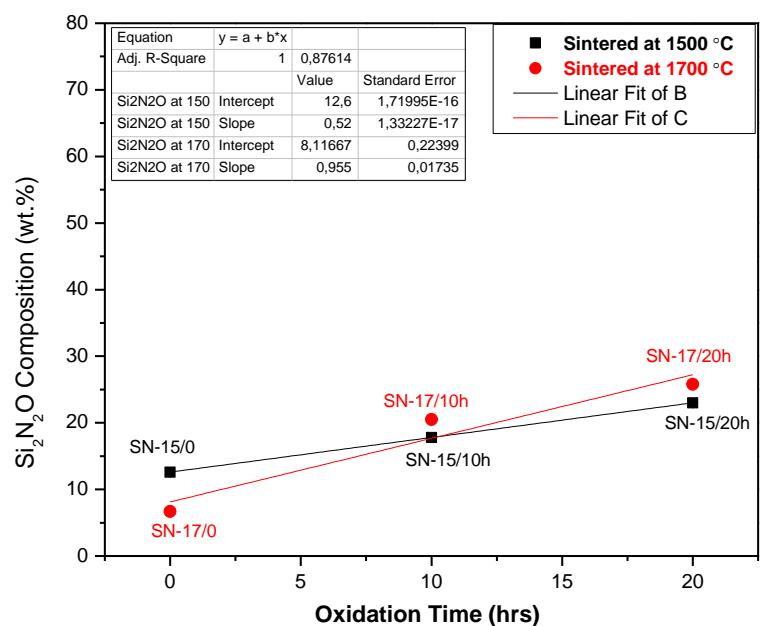
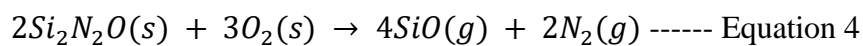
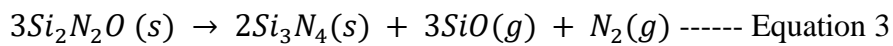


Figure 3 -  $\text{Si}_2\text{N}_2\text{O}$  phase is increasing with the oxidation time.

- I demonstrated that the  $\text{Si}_2\text{N}_2\text{O}$  phase could be preserved above 1500 °C by applying a high pressure of  $\text{N}_2$  (20 MPa) gas during sintering and a suitable selection of sintering aids ( $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ ).

It is proven that the formation of  $\text{Si}_2\text{N}_2\text{O}$  started at a lower temperature than the  $\alpha$  to  $\beta$ -transformation temperature, and the higher concentration of oxygen in starting powders favored the formation of  $\text{Si}_2\text{N}_2\text{O}$  and hindered the crystallite growth of  $\beta$ -  $\text{Si}_3\text{N}_4$  (**Figure 4**). Contrary to other researchers' findings,  $\text{Si}_2\text{N}_2\text{O}$  was found stable above 1500 °C in the current work. A few researchers reported the decomposition of  $\text{Si}_2\text{N}_2\text{O}$  phase above 1500 °C (according to Equations 3 and 4) due to the addition of sintering aids of  $\text{Li}_2\text{O}$  above their threshold amount [15][16].



The  $\text{Si}_2\text{N}_2\text{O}$  phase above 1500 °C can be preserved by adopting a high pressure of  $\text{N}_2$  (20 MPa) gas during sintering and a suitable selection of sintering aids ( $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ ).

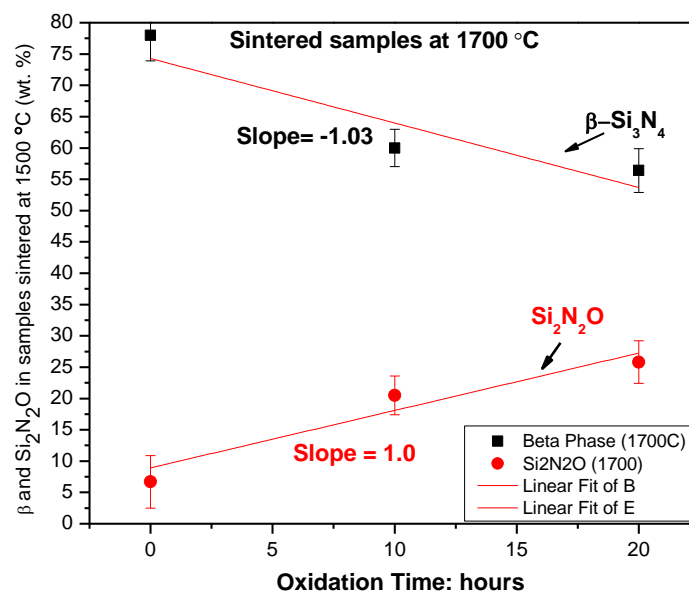


Figure 4 -  $\text{Si}_2\text{N}_2\text{O}$  is increasing and  $\beta$ - $\text{Si}_3\text{N}_4$  phase is decreasing simultaneously at same rate with the oxidation time.

**3. I demonstrated that  $\alpha$  -  $\text{Si}_3\text{N}_4$  can be fully transformed to  $\beta$  -  $\text{Si}_3\text{N}_4$  phase during hot isostatic pressing at 1700 °C under a pressure of 20 MPa of  $\text{N}_2$  gas.**

The complete transformation of  $\alpha$ - $\text{Si}_3\text{N}_4$  to  $\beta$ - $\text{Si}_3\text{N}_4$  phase is possible by optimum conditions hot isostatic pressing (HIP) at 1700 °C for 3 hours holding time under the pressure of 20 MPa of  $\text{N}_2$  gas (**Figure 5**).  $\beta$ - $\text{Si}_3\text{N}_4$  is tougher than that of  $\alpha$ - $\text{Si}_3\text{N}_4$  because of its elongated

hexagonal structure and  $\beta$  phase acts a self-reinforcing agent in the matrix and its presence induced the toughening effect and enhanced the fracture toughness. The amount of  $\beta$  phase is crucial to improve the fracture toughness. The  $\beta$  phase was decreased, and the indentation fracture resistance was also decreased in the samples produced by HIP at 1700 °C. The highest fracture resistance values were achieved in the sample, which contained the highest amount of  $\beta$  phase. Here, it was proven that sintering temperature 1500 °C is lower for the complete phase transformation and mixed  $\alpha$  and  $\beta$  phases were achieved. By optimizing the sintering temperature, the mixed phases  $\alpha$  and  $\beta$  can be achieved in the composite, and the desired ration of  $\alpha/\beta$  can be achieved by optimizing the sintering temperature, holding time, and gas pressure.

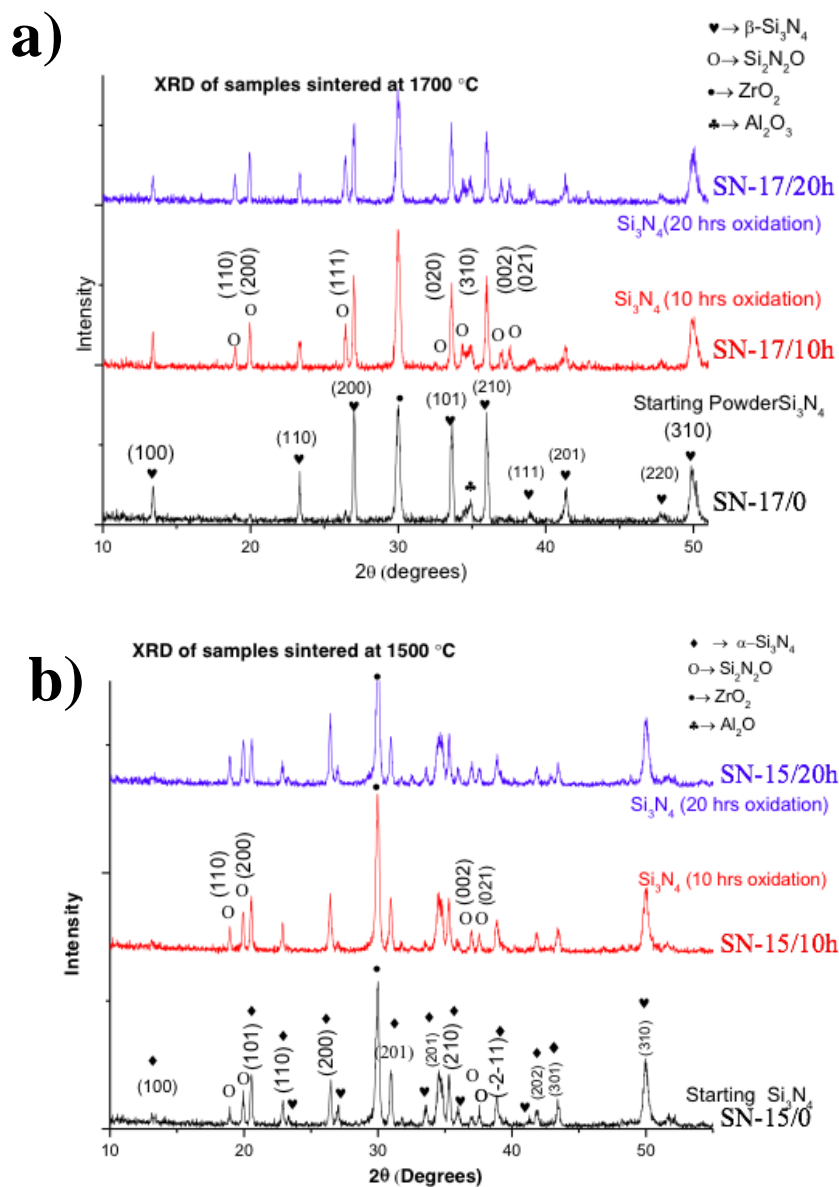


Figure 5 - XRD spectra of sintered samples: a) samples sintered at 1700 °C and b) samples sintered at 1500 °C.

4. Monolithic  $\text{Si}_3\text{N}_4$  – processed from oxidized and un-oxidized  $\alpha\text{-Si}_3\text{N}_4$  powders sintered at 1500 °C and 1700 °C by HIP under a pressure of 20 MPa of  $\text{N}_2$  gas – exhibited higher values of Vickers hardness, flexural strength and Young’s modulus as compared to MWCNTs reinforced silicon nitride composites processed from oxidized and un-oxidized  $\alpha\text{-Si}_3\text{N}_4$  powders sintered at 1700 °C by HIP under a pressure of 20 MPa of  $\text{N}_2$  gas. The addition of carbon nanotubes was detrimental to the mechanical properties of silicon nitride.

Comparatively, higher mechanical properties (Vickers hardness, flexural strength, Young’s modulus) were achieved in the case of monolithic silicon nitride systems, and the mechanical properties were decreased with the addition of 3 wt% multi-walled carbon nanotubes (MWCNTs).

Figure 6 shows that all monolithic silicon nitride systems densified by HIP either at 1500 or 1700 °C exhibited higher Vickers hardness under 10 N applied load than the silicon nitride with 3 wt% MWCNTs prepared by HIP at 1700 °C.

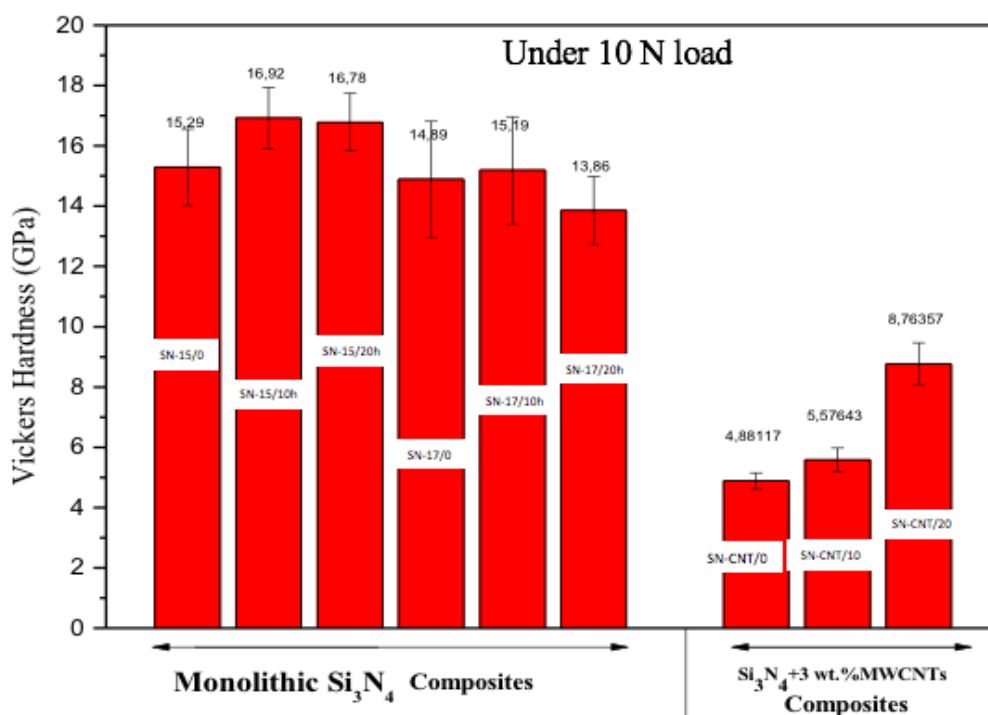


Figure 6 – Vickers hardness of monolithic and MWCNTs reinforced silicon nitride composites.

Monolithic  $\text{Si}_3\text{N}_4$  systems showed higher Flexural strength (based on 4 – point bending strength) than that of 3 wt% MWCNTs reinforced silicon nitride composites (**Figure 7**).

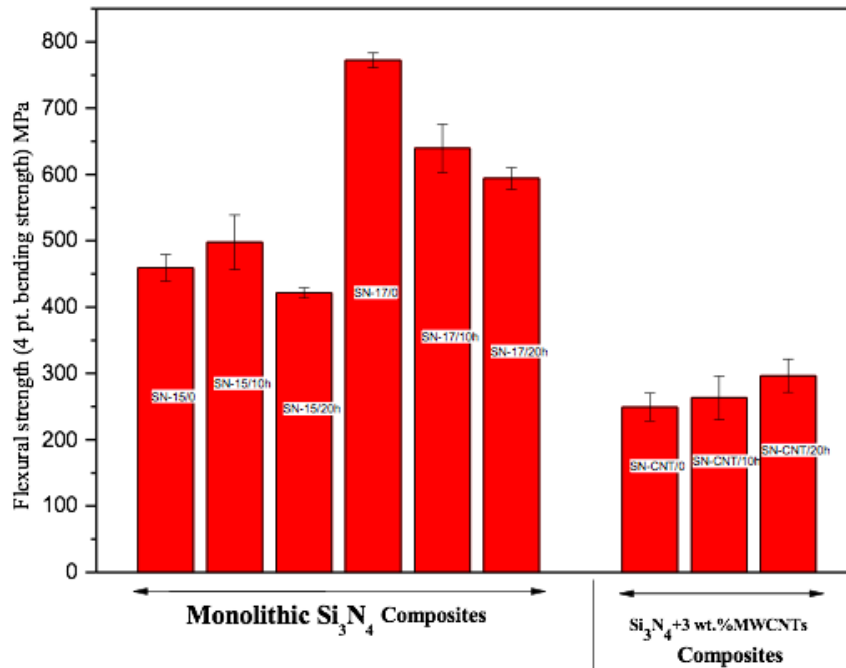


Figure 7 – Flexural strength of monolithic systems and 3 wt % MWCNTs added silicon nitride systems.

Monolithic silicon nitride systems exhibited the higher Young's modulus than that of 3 wt% MWCNTs reinforced silicon nitride composites, respectively (**Figure 8**).

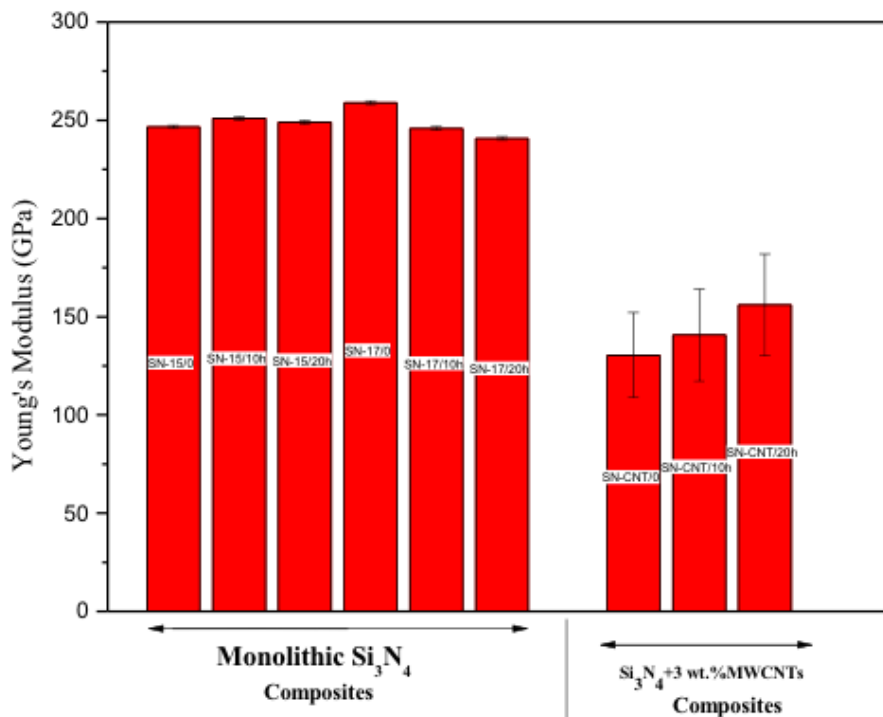


Figure 8 – Young's modulus of composites: monolithic  $\text{Si}_3\text{N}_4$  and  $\text{Si}_3\text{N}_4 + 3 \text{ wt \% MWCNTs}$ .

5. I reported the detailed study of wear characteristics of monolithic  $\text{Si}_3\text{N}_4$  ceramics containing in-situ grown  $\text{Si}_2\text{N}_2\text{O}$  processed from oxidized  $\alpha$  -  $\text{Si}_3\text{N}_4$  powders for the first time. Monolithic  $\text{Si}_3\text{N}_4$  with in-situ grown  $\text{Si}_2\text{N}_2\text{O}$  prepared by HIP at 1500 °C under 20 MPa pressure of  $\text{N}_2$  for 3 hours have lower wear rates in dry conditions that that of monolithic  $\text{Si}_3\text{N}_4$  with in-situ grown  $\text{Si}_2\text{N}_2\text{O}$  prepared by HIP at 1700 °C under 20 MPa pressure of  $\text{N}_2$  for 3 hours.

Best to author's knowledge, the tribological behavior of silicon nitride systems containing in-situ grown  $\text{Si}_2\text{N}_2\text{O}$  is not reported yet in the literature. Following main findings have been reported: i) the wear rates of the systems sintered at 1500 °C were lower in comparison to the wear rates for the systems sintered at 1700 °C, ii) The lowest wear rate,  $1.224 \times 10^{-4} \text{ mm}^3/\text{N}\cdot\text{m}$ , was measured for the system with 10 hours oxidized  $\alpha$  - $\text{Si}_3\text{N}_4$  powder sintered at 1500 °C, iii) the wear rates decreased exponentially after the running-in stage for all investigated systems, iv) the main wear mechanisms were identified in the form of abrasive wear with grain pull-out, micro-cracking, and debris formation together with tribo-film formation (**Figure 9**).

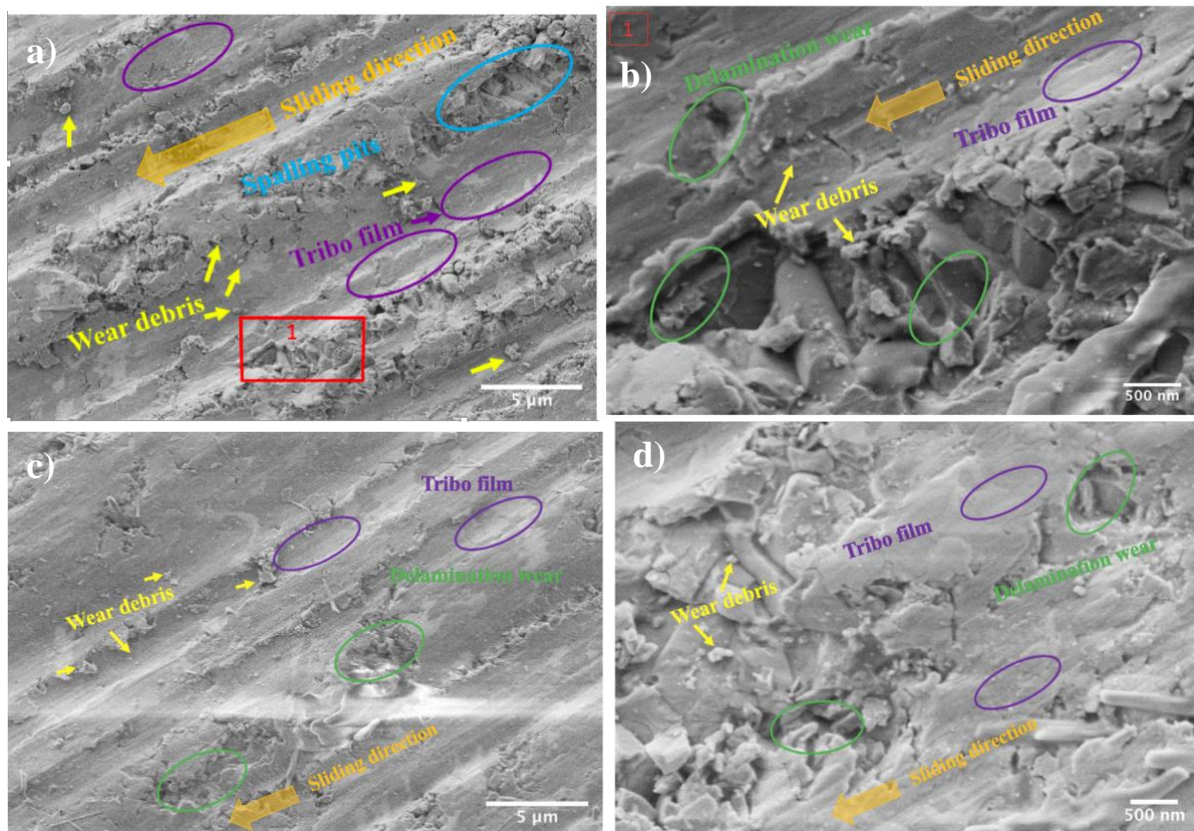


Figure 9 – SEM image of wear track and the worn areas are labeled with arrows and elliptical circles to identify its respective wear mechanisms: a) wear track of SN-17/0 and b) wear track of SN-17/0 at higher magnification; c) wear track of SN-17/20h and d) wear track of SN-17/20h at higher magnification.



6. Based on results, 1 wt % graphene nanoplates (GnPs) are more promising candidates than 3 wt% MWCNTs as reinforcements in the silicon nitride matrix for robust tribological properties tested by identical parameters.

Based on available tribological results for MWCNT and graphene reinforced  $\text{Si}_3\text{N}_4$  systems, the 1 wt% graphene reinforced  $\text{Si}_3\text{N}_4$  composites showed lower wear rates under identical testing parameters (**Figure 10**). Tribological properties for both systems were tested under the same parameters as follows:

- Test configuration = Ball-on-Plate.
- Tribometer = UMT 3 (Bruker),
- Counter body =  $\text{Si}_3\text{N}_4$  ball (D=6.35 mm),
- Sliding Conditions = dry,
- Load = 13.5 N & 5 N,
- Sliding speed = 0.1 m/s,
- Total sliding Distance = 720 m,
- Average Hertzian pressure ~ 2 GPa.

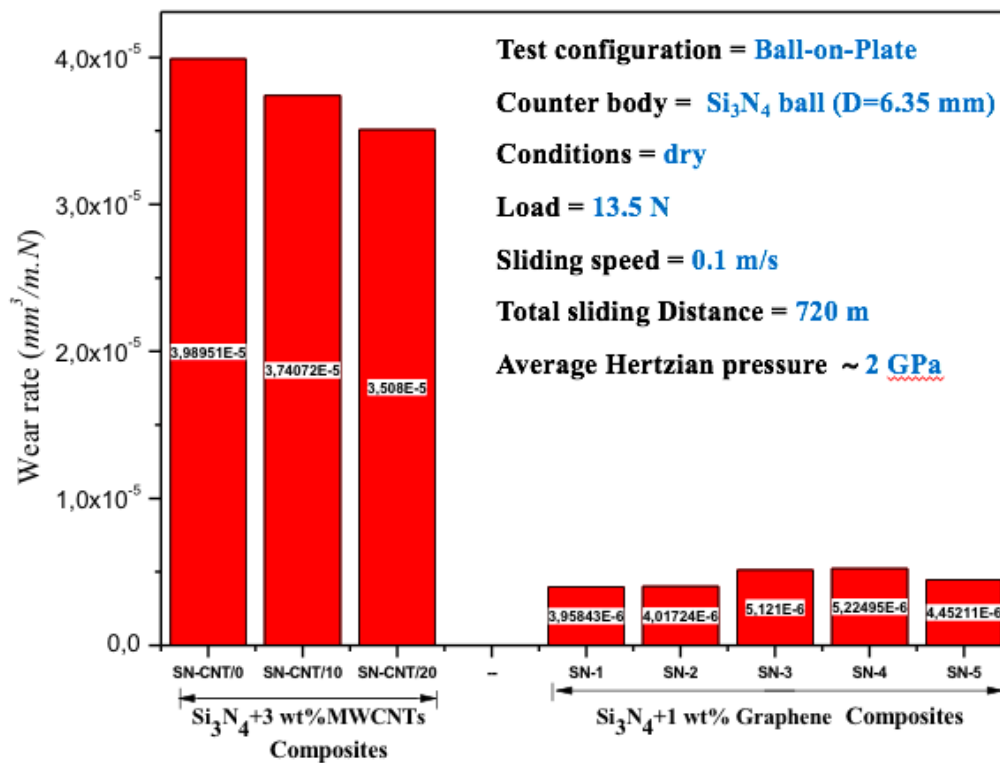


Figure 10 – Wear rates of investigated systems.

#### 4.1. Further challenges

Further progress is expected in the development of monolithic and carbon nanofillers reinforced  $\text{Si}_3\text{N}_4$  composites with the aim:

- Further investigative study is needed for graphene reinforced silicon nitride systems in order to define the wear mechanisms,
- To achieve an optimized amount of in-situ  $\text{Si}_2\text{N}_2\text{O}$  can be possible by optimizing the oxidation of starting powders. The desired amount of  $\text{Si}_2\text{N}_2\text{O}$  can be achieved by optimizing the oxidation of starting powders. In other words, the amount of the desired  $\text{Si}_2\text{N}_2\text{O}$  can be achieved by optimizing the amount of oxide phase ( $\text{SiO}_2$ ) in the starting powders,
- To achieve the desired amount of  $\beta\text{-Si}_3\text{N}_4$  can be possible by optimizing the sintering parameters such as sintering technique, temperature, pressure, and holding time,
- To solve the problem of difficulties relating to dispersing carbon nanofillers mainly with an increasing concentration of nanofillers by the help of advanced processing such as colloidal processing, etc. This will help not only in the elimination/limitation of strength-decreasing defects in the composites, but also in increasing the number of active nanofillers in the toughening process and an increased number of constituents for increasing the tribological and functional properties as well,
- To realize an effective carbon nanofillers reinforcement strategy while optimizing the nanofillers/matrix interface in such a way as to have the adhesion between the nanotube and the matrix be not so strong as to introduce nanotube failure before debonding, but to have the adhesion be not so weak that the frictional resistance to sliding is minimal,
- To make advances in improving the properties of modified carbon nanofillers and in the field of *in-situ* reinforced composites with the aim to offer processing of  $\text{Si}_3\text{N}_4 + \text{CNT/graphene}$  composites with improved functional, tribological and mechanical properties,
- To improve the most promising processing methods such as aqueous colloidal processing, ultrasonication, bead milling, improved SPS, electric field-assisted pressure-less sintering, usually named flash sintering, etc.
- To introduce new characterization and testing methods in the area of Raman spectroscopy, focused ion-beam (FIB) technique, microcantilever technique for fracture toughness testing, etc.

- To design new systems in the form of carbon nanofillers-concentrated, functionally graded and layered carbon–ceramic composites, etc., in combination with other carbon-based fillers as graphene platelets which would surely offer multi-functional properties for challenging functional, bio-medical and structural applications,
- To improve the applications of carbon-ceramic matrix nanocomposites such as: load-bearing structural parts, wear or friction surfaces, medical devices and implants, automotive, aerospace, power generation applications, tool and die materials, and military field applications.

## 5. Publications

### 5.1. Publications related to PhD topic

[S-1] **Awais Qadir**, Zsolt Fogarassy, Zsolt E. Horvath, Katalin Balazsi, Csaba Balazsi, Effect of the oxidization of Si<sub>3</sub>N<sub>4</sub> powder on the microstructural and mechanical properties of hot isostatic pressed silicon nitride, *Ceramics International*, 2018 Aug 15;44(12):14601-9.

**Impact Factor: 3.830 (Q1)**

DOI: <https://doi.org/10.1016/j.ceramint.2018.05.081>

[S-2] **Awais Qadir**, B. H Rachid, P. Pinke, J. Dusza, Tribology of Si<sub>3</sub>N<sub>4</sub> containing in-situ grown Si<sub>2</sub>N<sub>2</sub>O processed from oxidized  $\alpha$  - Si<sub>3</sub>N<sub>4</sub> powders, *Ceramics International*, 2021 47 (12) 17417-17426.

**Impact Factor: 3.830 (Q1)**

DOI: <https://doi.org/10.1016/j.ceramint.2021.03.058>

[S-3] **Awais Qadir**, Pinke Peter, Jan Dusza, Silicon nitride with the addition of carbon nanotubes: A review of progress, challenges and future prospects, *Materials* 2020, 13, 2799.

**Impact Factor: 3.057 (Q2)**

DOI: <https://doi.org/10.3390/ma13122799>

[S-4] **Awais Qadir**, Katalin Balazsi, Csaba Balazsi, Michal Ivor, Jan Dusza, Properties of MWCNTs added Si<sub>3</sub>N<sub>4</sub> composites processed from oxidized silicon nitride powders. *Processing and Application of Ceramics*. 2020;14(1):25-31.

**Impact Factor: 0.968 (Q3)**

DOI: <https://doi.org/10.2298/PAC2001025Q>

[S-5] **Awais Qadir**, Jan Dusza, Pinke Péter, Tribological Behavior of Silicon Nitride and Carbon Based Filler Composites – a Review, In: Horváth, Richárd; Beke, Éva; Stadler, Róbert Gábor (szerk.) *Mérnöki Szimpózium a Bánkin előadásai: Proceedings of the Engineering Symposium at Bánki (ESB 2019)*, Budapest, Magyarország : Óbudai Egyetem, (2019) pp. 7-16. , 10 p.

[S-6] **Awais Qadir**, Jan Dusza, Pinke Péter, Tribological behavior of graphene reinforced silicon nitride composites, In: Horváth, Richárd; Beke, Éva; Stadler, Róbert Gábor (szerk.) Mérnöki Szimpózium a Bánkin előadásai: Proceedings of the Engineering Symposium at Bánki (ESB 2020), Budapest, Magyarország : Óbudai Egyetem, (2020) pp. 48-53.

[S-7] **Awais Qadir**, Pinke Péter, Jan Dusza, Graphene reinforced silicon nitride composites – A review, 2021 (**In progress**).

## 5.2. Other publications

[S-5] Kumar Sunil, **Qadir Awais**, Maury Francis, Bahlawane Naoufal, “Visible thermochromism in vanadium pentoxide coatings”, ACS Appl. Mater. Interfaces, 2017, 9 (25), pp 21447–21456

**Impact Factor: 7.145 (Q1)**

DOI: <https://pubs.acs.org/doi/abs/10.1021/acsami.7b04484>

[S-6] Pozdniakov, A. V., A. Lotfy, **A. Qadir**, E. Shalaby, M. G. Khomutov, A. Yu Churyumov, and V. S. Zolotarevskiy. "Development of Al-5Cu/B4C Composites with low Coefficient of Thermal Expansion for Automotive Application." Materials Science and Engineering: A (2017).

**Impact Factor: 4.652 (Q1)**

DOI: <https://doi.org/10.1016/j.msea.2017.01.075>

[S-7] Pozdniakov, A. V., A. Lotfy, A. Qadir, and V. S. Zolotarevskiy. "Effect of the B4C content on the structure and thermal expansion coefficient of the Al–5% Cu alloy-based metal-matrix composite material." The Physics of Metals and Metallography 117, no. 8 (2016): 783-788.

**Impact Factor: 1.064 (Q2)**

DOI: <https://link.springer.com/article/10.1134/S0031918X16060107>

## 5.3. PhD work presentation in conferences

[C – 1] **Awais Qadir**, Katalin Balazsi, Csaba Balazsi, Poster Presentation, Development of silicon nitride-based CNT/graphene composite using hot isostatic pressing (HIP) technique

*(Poster Presentation)*, ECerS 2017, 15<sup>th</sup> Conference & Exhibition of the European Ceramic Society, Budapest, Hungary, July 9-13, 2017. page 98.  
<http://static.akcongress.com/downloads/ecers/ecers2017-programme-book.pdf>

[C – 2] **Awais Qadir**, Zsolt Fogarassy, Zsolt E. Horváth, Katalin Balázsi, Csaba Balázsi, Poster: Effect of oxidized Si<sub>3</sub>N<sub>4</sub> powder particles on mechanical properties of sintered Si<sub>3</sub>N<sub>4</sub> material (*Poster Presentation*), International Conference Deformation and Fracture in PM Materials, High Tatras, 2017. Oct. 22-25.  
<http://www.imr.saske.sk/confer/dfpm2017/dfpm2017.html>

[C – 3] **Awais Qadir**, Zsolt Fogarassy, Zsolt E. Horváth, Katalin Balázsi, Csaba Balázsi, Poster: Effect of oxidized Si<sub>3</sub>N<sub>4</sub> powder particles on mechanical properties of sintered Si<sub>3</sub>N<sub>4</sub> material (*Poster Presentation*), Joint ICTP-IAEA Workshop on Fundamentals of Vitrification and Vitreous Materials for Nuclear Waste Immobilization, The Abdus Salam Centre for Theoretical Physics (ICTP), Trieste Italy. Nov. 06 -10, 2017.  
<http://indico.ictp.it/event/8002/session/41/contribution/303>

[C – 4] **Awais Qadir**, Zsolt Fogarassy, Zsolt E. Horvath, Katalin Balazsi , Csaba Balazsi, The effect of oxidized nanosized silicon nitride powder particles on the structural and mechanical properties of Si<sub>3</sub>N<sub>4</sub>/CNTs composite by hot isostatic pressing (*Oral Talk*), FEMS JUNIOR EUROMAT CONFERENCE 2018, Budapest, Hungary, July 8 –12, 2018, page 64.  
[https://static.akcongress.com/downloads/euromat/JuniorEuromat2018\\_Bookofabstracts.pdf](https://static.akcongress.com/downloads/euromat/JuniorEuromat2018_Bookofabstracts.pdf)

[C – 5] **Awais Qadir**, Zsolt Fogarassy, Zsolt E. Horváth, Katalin Balázsi, Csaba Balázsi, Effect of oxidized Si<sub>3</sub>N<sub>4</sub> powder particles on structural and mechanical properties of sintered Si<sub>3</sub>N<sub>4</sub> material (*Oral Talk*), Fine Ceramics Day 2018, Hungarian Academy of Sciences, Budapest, Hungary, April 12, 2018.

[C – 6] **Awais Qadir**, Zsolt Fogarassy, Zsolt E. Horváth, Katalin Balázsi, Csaba Balázsi, Effect of oxidized Si<sub>3</sub>N<sub>4</sub> powder particles on structural and mechanical properties of sintered Si<sub>3</sub>N<sub>4</sub> material (*Oral Talk*), “17th PhD Students Materials Science Day”, University of Pannon, Veszprem, Hungary, Dec. 4. 2017.

[C – 7] **Awais Qadir**, Jan Dusza, Processing and properties of silicon nitride + MWCNTs composites prepared from oxidized  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> starting powder, (*Poster Presentation*) 6th international conference “Fractography of Advanced Ceramics” in the Smolenice Castle Congress Center, Smolenice SAS on September 08 - 11, 2019. <http://www.imr.saske.sk/confer/fac2019/index.htm>

[S – 8] **Awais Qadir**, Jan Dusza, Processing and properties of silicon nitride + MWCNTs composites prepared from oxidized  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> starting powder, 13th Conference for Young Scientists in Ceramics, CYSC-2019, Novi Sad, Serbia, October 16-19, 2019 <http://cysc.mima.solutions/wp-content/uploads/2019/10/Book-of-Abstarcts-CYSC-2019.pdf>

#### 5.4. Scientific Impact of my research

Impact of research has been calculated and presented below.

Total Publications = 9	PhD work-related Publications = 6
Cumulative Impact Factor = 26.159	PhD work Cumulative Impact Factor = 11.685
All Citations = 74	PhD work-related Citations = 10

## 6. Reference

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