

# HIGH TEMPERATURE TRIBOLOGICAL CHARACTERIZATION OF NANO-SIZED SILICON NITRIDE + 5% BORON NITRIDE CERAMIC COMPOSITE

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## ABSTRACT

*Tribological studies on nano-sized  $\beta$ -silicon nitride+5% BN were carried out in dry air at high temperatures to clarify the lack of consensus in the bibliographic data concerning the Tribological behavior of Si<sub>3</sub>N<sub>4</sub> ceramics and effect of doped hexagonal boron nitride on coefficient of friction and wear coefficient at different loads and elevated temperatures. The composites were prepared via high energy mechanical milling and subsequent spark plasma sintering using Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> as sintering additives. After sintering, the average crystalline size of Si<sub>3</sub>N<sub>4</sub> was observed to be 50 nm. Tribological tests were performed with temperature and Friction coefficients 0.16 to 1.183 and 0.54 to 0.71 were observed for Nano-sized  $\beta$ -silicon nitride+5% BN composite under normal load of 10N-70 N and over high temperature range of 350 °C - 550 °C respectively. Specific wear coefficients from  $1.33 \times 10^{-4}$  mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup> to  $4.42 \times 10^{-4}$  mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup> were observed for Nano-sized Si<sub>3</sub>N<sub>4</sub> + 5% BN composite against Si<sub>3</sub>N<sub>4</sub> ball as tribo-pair counterpart over high temperature range of 350 °C - 550 °C while as under normal load of 10N to 70N Specific wear coefficients of  $6.91 \times 10^{-4}$  mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup> to  $1.70 \times 10^{-4}$  were observed. The addition of BN to the Si<sub>3</sub>N<sub>4</sub> composite resulted in a slight reduction of the friction coefficient and lower values of wear coefficient.*

**KEYWORDS:** Ceramics, Tribology, Friction and Wear, Solid Lubrication

## I. INTRODUCTION

Materials serving today's design engineer contain far more than the plain materials and plastics that represent traditional constructional materials. Past few decades have witnessed remarkable developments in structural materials technologies [1]. A reliable engineering design along with appropriate materials selection and the use of an appropriate coating or lubrication system may be sufficient to minimize wear of interacting surfaces or components to an acceptable level. Technological advancements have resulted in products from combination of materials – laminates, composite, fibre-reinforced metals and polymer matrices of various types to provide strength, corrosion resistance, dimensional stability, heat resistance and other properties unavailable from conventional materials. Ceramics are widely used in various engineering and other applications due to their better mechanical and tribological characteristics [2]. Non-oxide ceramics silicon carbide, silicon nitride, partially stabilized zirconia of aluminium oxide, titanium nitride, titanium carbide find their applications in gas turbine bearings, I. C. Engine components, turbocharger rotors, seals, rocker arms, turbine blades. Among all non-oxide ceramics, silicon nitride possesses better tribological properties and is considered one of the most appropriate materials to be used for design and fabrication of machine elements for high temperature applications such as hybrid bearings, I.C engine valves etc. in these applications silicon nitride ceramic is supposed to retain better friction, wear, mechanical properties at elevated temperature which paves a way to study friction and wear properties of silicon nitride at high temperature.

Metal composite self-lubricating composites are among the materials that are currently of great scientific interest. They are being developed to improve friction and wear properties for specific applications in which conventional lubrication does not work: for example, in a vacuum, at extremely high and low temperatures, and for electrical and thermal conductivity of sliding contacts [2]. Self-lubricating composites have also been developed for engineering applications, including gears, bearings, bushings and cams. However, numerous alloys have been replaced by sintered ceramic composites, especially 316L stainless steel due to its superior mechanical properties and high temperature resistance. These solid lubricating materials hexagonal boron nitride (h-BN) possess lamellar structures which in turn are composed of fine, alternating layers of different materials in the form of lamellae. Lamella is a term for a plate like structure appearing in multiples that occur in various situations, such as biology or material sciences, it implies a thin layer (or layers) [3][4]. The ability of a solid to function as a lubricant is determined by the degree of the attraction of its molecules to each other and the sliding surfaces. As a rule, solid lubricant films are more superior to liquid film and provide better surface coverage [5]. These superior lubricating properties of Hexagonal boron nitride (hBN) make it a best available modern day in-situ solid lubricant and can be applied by direct means of impregnating in the metal or ceramic composite subjected to high temperature and wear applications [6][7]. Thus bringing a need for the development of a high temperature sustaining non-oxide ceramic composite combining superior mechanical and tribological properties of Nano-sized silicon nitride and in-situ lubricating effects of hexagonal boron nitride [8]. In this research study, tribological studies were carried out using Reciprocating sliding friction and wear high temperature tribometer (Magnum made). A ceramic ball on ceramic disc configuration was adopted with ceramic ball of Silicon nitride as upper tribo-element in all experimental tests whereas disc of Nano-sized silicon nitride+5% BN was used as counterpart. Experiments were performed with elevated temperature and load as variables. Experimental procedures, results and discussions and future scope are further elaborated in the paper

## II. EXPERIMENTAL PROCEDURE

### 1. Materials

For the experimental characterization following samples are used:

- (i) Nano-sized  $\beta$ - $\text{Si}_3\text{N}_4$  + 5% BN (Disc)
- (ii) Silicon nitride (Ball)

Starting powders were 90.73 wt % sub-nanometer  $\beta$ -silicon nitride powder (NP500 Grade Denki Kagaku Kogyo Co., Tokyo Japan) with an average particle size of 0.5  $\mu\text{m}$ , 7.85 wt %  $\text{Y}_2\text{O}_3$  (99.9 % pure, Shin-estu Chemicals Co., Tokyo Japan) and 1.42 wt %  $\text{Al}_2\text{O}_3$  (99.9 pure, Sumitomo Chemicals Co., Tokyo, Japan). The amount of BN (Woke Pure Chemicals Indus, Japan) was 5 wt % based on the weight of other starting powders. Starting powders were mixed in ethanol using silicon nitride balls for 4 hrs. After drying, the as-received powder mixture was high energy ball milled using  $\text{Si}_3\text{N}_4$  balls of 5 mm diameter and  $\text{Si}_3\text{N}_4$  pots of 359 ml volume. The ball-to-powder weight ratio was 20:1, milling speed 475 rpm, and milling time 6h. Powder mixture was compacted in carbon die (15 mm in inner diameter and 30 mm in outer diameter) and sintered using Spark plasma sintering (Sumitomo Coal Mining Co., Ltd., Tokyo Japan) under a compressive stress of 30 MPa. The temperature was measured using optical pyrometer through a 5.5 mm-depth hole in the outer surface of the graphite die. Heating and cooling were carried out at 300°C/min and 600°C/min, respectively. The linear shrinkage of the specimen was obtained directly by measuring the movement of the crosshead. All processing steps were conducted in a  $\text{N}_2$  atmosphere to avoid oxidation. The composition of  $\text{Si}_3\text{N}_4$  ceramic and their source are shown in Table 1.

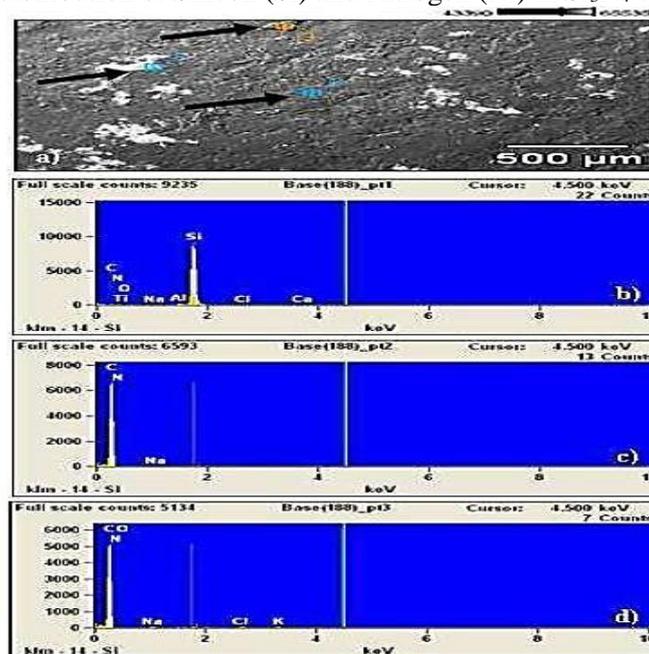
**Table 1:** Composition of nano-sized  $\text{Si}_3\text{N}_4$  +5%BN ceramic

	$\text{Si}_3\text{N}_4$	$\text{Y}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	BN
Material composition (wt.%)	NP 500 grade, 9.73wt %, $\beta$ - $\text{Si}_3\text{N}_4$ , average particle size 0.5 $\mu\text{m}$	7.85 wt %, (99.9 % pure)	1.42 wt %, (99.9 % pure)	5 wt % of other powders (99.0 % pure)

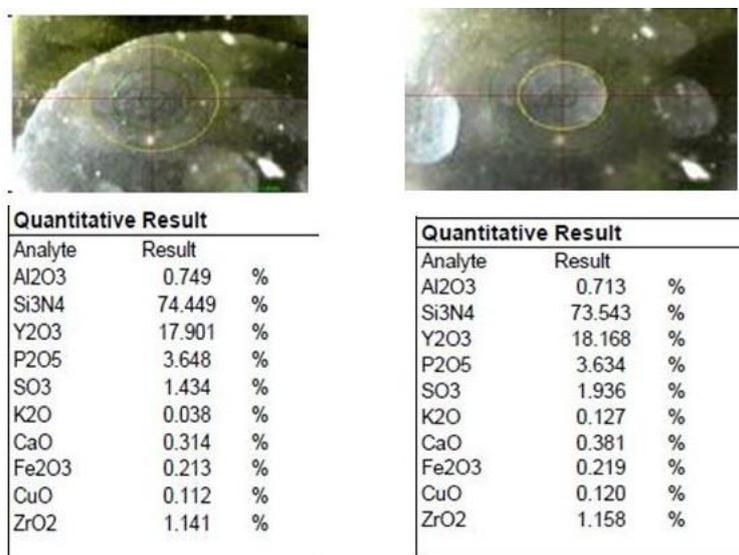
Source	Denki Kagaku, Kogoyo CO., Tokyo Japan	Shin-estu Chemicals CO., Tokyo Japan)	Sumitomo chemicals co., Tokyo , Japan).	Woke pure chemical Indus, Japan
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**2. Characterization**

Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) studies were carried out to study Nanostructure of ceramic surfaces and also to carry out elemental analysis of Si<sub>3</sub>N<sub>4</sub> ceramic samples. SEM studies were carried out on Hitachi SEM S -3600, equipped with EDS. Energy Dispersive X-ray Spectroscopy (EDX) studies were carried out on Shimadzu Energy Dispersive X-ray Fluorescence Spectrometer (EDX-7000). Typical results of SEM with EDX and XRD are shown in Figure 1.1 and Figure 1.2 respectively. EDX results of worn and unworn Silicon nitride+5% BN surfaces evidence that there is no compositional change at high temperatures. SEM results reveal uniform distribution of Silicon (Si) and Nitrogen (Ni) in Si<sub>3</sub>N<sub>4</sub> composite.



**Figure 1.1.**Scanning electron Nanograph (SEM) and Energy Dispersive Spectroscopy (EDS) of Nano-sized Si<sub>3</sub>N<sub>4</sub> +5%BN Ceramic



**Figure 1.2** EDX results of unworn and worn Silicon nitride+5% BN surfaces

X-ray diffraction (XRD) studies were carried on M/s Philips, The Netherlands Compact X-ray Diffraction System. XRD patterns and analysis of Nano  $\text{Si}_3\text{N}_4$ + 5wt % BN are shown in Figure 1.3 and Figure 1.4. Average grain size of  $\text{Si}_3\text{N}_4$  in Nano  $\text{Si}_3\text{N}_4$ + 5wt % Nano BN disc sample is 56.5 nm. X-ray diffraction pattern (Figure 2) indicates that major phase present in the Nano composite is  $\beta$ -silicon nitride.

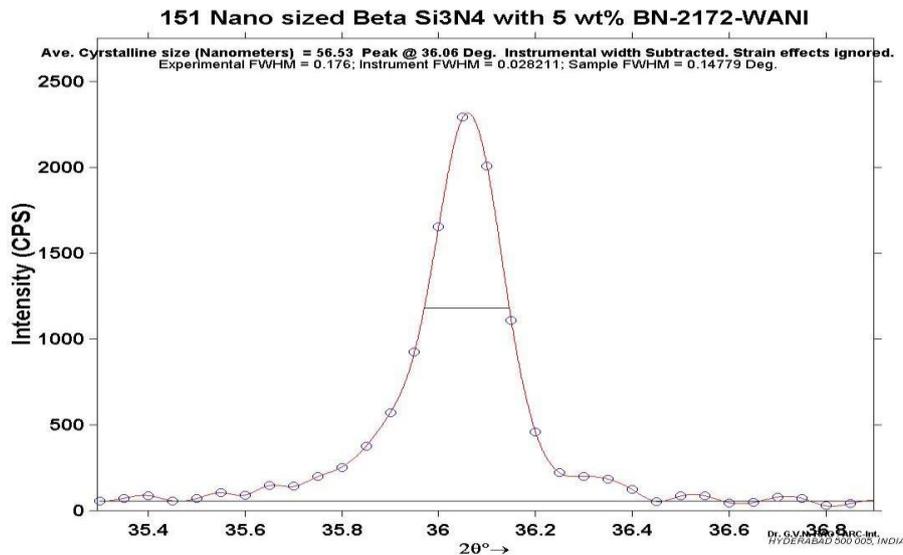


Figure 1.3 XRD image of unworn nano-sized Silicon nitride+5% BN showing average crystalline size to be 56.53 nm

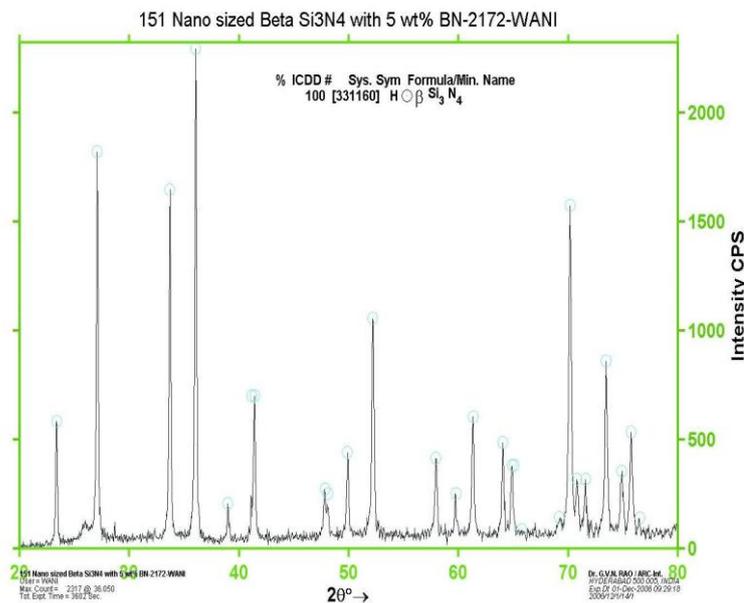


Figure 1.4 XRD image of unworn nano-sized Silicon nitride+5% BN showing  $\text{Si}_3\text{N}_4$  as major phase present in the composite

### 3. Friction and wear tests

A reciprocating sliding ball-on-disk Tribometer (Magnum Engineers made) as shown in Figure 2.1 was used for carrying out the Tribological tests on polished surfaces with average surface roughness of 0.25  $\mu\text{m}$ . Since our main concern was to study the friction and wear of the Nano-sized  $\text{Si}_3\text{N}_4$ / $\text{Si}_3\text{N}_4$ tribopair at elevated temperatures, such a test rig was sufficient to serve the purpose. The holder holds the disk which could be of varying size and shape. The ball has a stable contact point

with the disk. As shown in the figure, a pin/ball is moved over the sample by means of a stage which could either be rotating or reciprocating but rotating in this case. . Load and Temperature variations were made in order ascertain the effects of temperature and load on coefficient of friction and wear coefficient. Wear was measured by the weight loss method. Before mounting the tribo-elements (counter parts) to the clamping on tribometer, the samples were washed and degreased in acetone (being volatile and non reactive to the samples) followed by ultrasonic cleaning in an ultrasonic bath for about 10 minutes. Further the samples were preheated in a furnace at 50 °C for evaporation and elimination of acetone or impurities if any. Samples were repeatedly weighed on an electronic weighing balance with a 0.1 mg resolution before and after the every test prior to mounting on the test machine. A constant plot of friction coefficient was taken throughout the experiments.

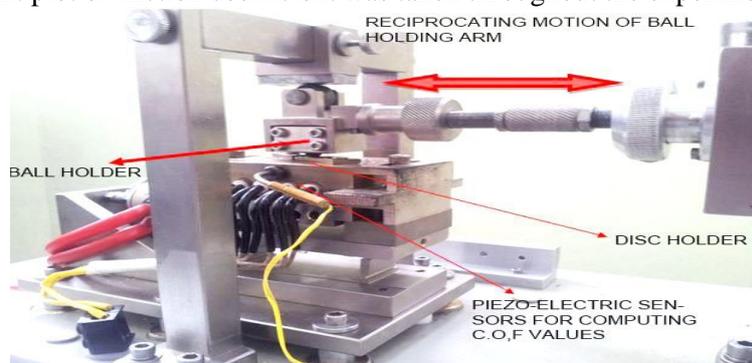


Figure 2.1 Schematic of Pin on Disc tribometer setup

### III. RESULTS AND DISCUSSIONS

Wear volume of ceramic disc was calculated from cumulative weight loss and density. The wear volume of ceramic Si<sub>3</sub>N<sub>4</sub> ball of diameter 8 mm was calculated from wear scar diameter using the following equations:

$$\text{Wear Volume} = \pi h^2 (r - h/3) \dots \dots \dots (1)$$

$$\text{Scar depth} = \frac{(d/2)^2}{r + \sqrt{r^2 - (d/2)^2}} \dots \dots \dots (2)$$

$$K_w = V_w / D_s \times P \text{ (mm}^3 \text{ N}^{-1} \text{ m}^{-1}) \dots \dots \dots (3)$$

Where;

$K_w$  = Specific Wear Coefficient (mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>),  $V_w$  = Wear Volume (mm<sup>3</sup>),  $D_s$  = Sliding Distance (m),  $P$  = Normal load (N),  $r$  is radius of the ball;  $d$  is diameter of wear scar. The coefficient of wear specific wear commonly used for comparison was calculated by the following Archard’s wear equation (3). Following results obtained are shown in Table 2 and Table 3.

**Table 2:** Coefficient of Friction and wear coefficient obtained during Temperature Tests for nano-sized silicon nitride+5% BN discs

Sample	Temperature °C	Coefficient of friction $\mu$	Wear Coefficient $K_w$
Nanosized $\beta$ -Si <sub>3</sub> N <sub>4</sub> +5% wt BN	350.7197	0.5444	0.000133
	400.6414	0.6793	0.000301
	447.1277	0.6851	0.000401
	496.6733	0.7101	0.000442

Normal Load=40 N, Test duration=15 mins, Stroke=2mm

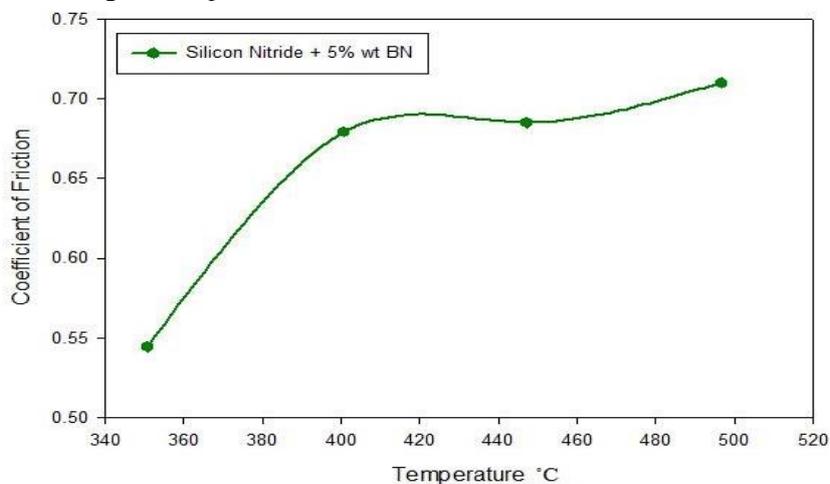
**Table3 :** Coefficient of Friction and wear coefficient obtained during load Tests for nano-sized silicon nitride+5% BN discs

Sample	Load (N)	Coefficient of friction $\mu$	Wear Coefficient $K_w$
Nanosized $\beta$ -Si <sub>3</sub> N <sub>4</sub> +5% wt BN	10	0.167	0.000902
	30	0.46	0.000700
	50	0.789	0.000452
	70	1.183	0.000257

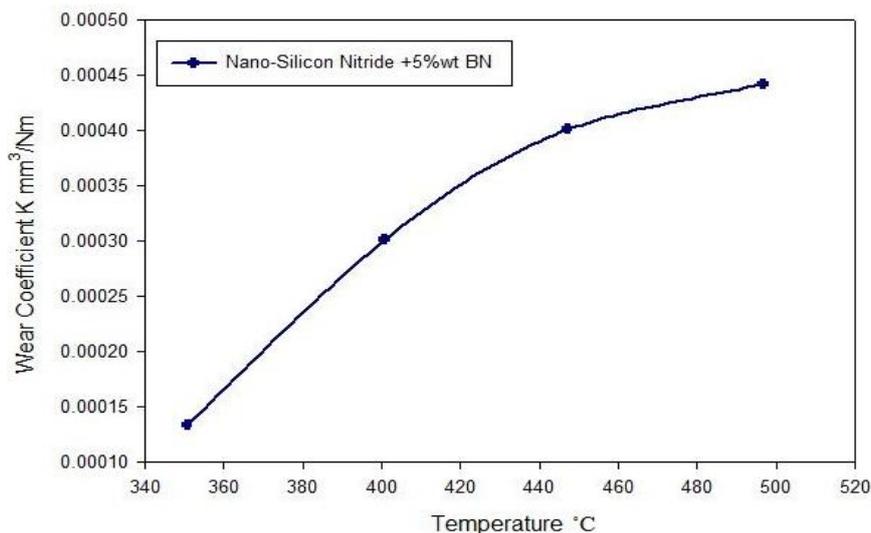
Temperature:500°C Test duration=15 mins, Stroke=2mm

### Variation of Frictional Coefficient and Wear Coefficient with elevation in Temperature:

Figures 3.1 and 3.2 presents the tribological study of nano-sized silicon nitride+5% BN composite which indicate the linear increment of frictional coefficient and wear coefficient with elevation in temperature. The friction coefficient varies from  $0.54 < \mu < 0.71$  for the composite with elevation in temperature. Meanwhile the wear coefficients even vary linearly with increment in temperature indicating the value being  $> K \approx 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ . Obtained Specific wear coefficients of  $1.33 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  to  $4.42 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  were observed for Nano-sized  $\text{Si}_3\text{N}_4$  against  $\text{Si}_3\text{N}_4$  ball as tribo-pair counterpart over high temperature range of  $350^\circ\text{C} - 550^\circ\text{C}$ . It indicates loss of wear resistance of Nano-sized  $\text{Si}_3\text{N}_4$  at higher temperatures.



**Figure 3.1:** Variation Of Frictional coefficient with Temperature for Nano-sized Silicon nitride+5% BN disc

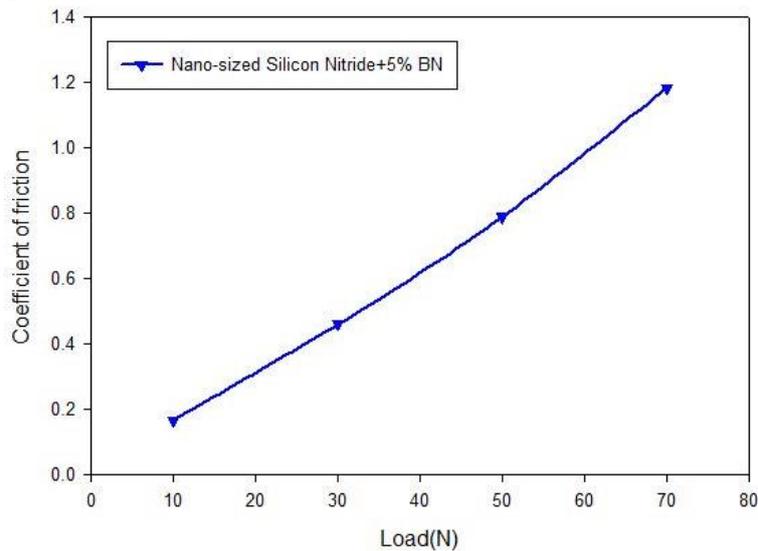


**Figure 3.2:** Variation Of Wear coefficient with Temperature for Nano-sized Silicon nitride+5% BN disc

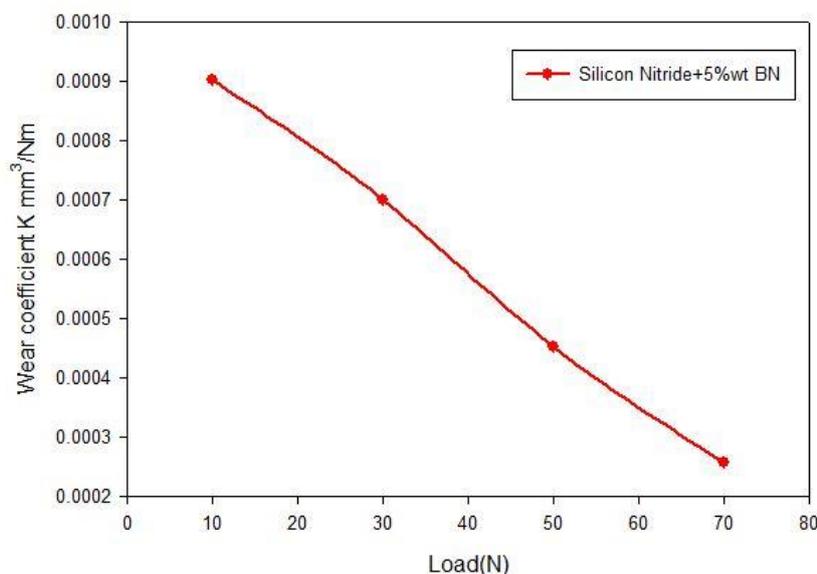
### Variation of Frictional coefficient and Wear Coefficient with variation in Load:

Figures 3.3 and 3.4 present the tribological study of nano-sized silicon nitride+5% BN composite samples which indicate the linear increment of frictional coefficient and logarithmic decrement of wear coefficient with increase in load as such the friction coefficient varies from  $0.16 < \mu < 1.183$  for the composite, with increase in load. Meanwhile the wear coefficients show logarithmic decrement with increment in load. Obtained wear coefficients vary in a range of  $6.91 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  to  $1.70 \times 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  being  $> K \approx 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  over a load range of  $10-70 \text{ N}$ . The reason for logarithmic decrement being that the wear coefficient varies inversely with load as suggested by

Archard's Wear Model. It can now be concluded that Nano-sized  $\text{Si}_3\text{N}_4$  presents higher wear resistance at higher loads.



**Figure 3.3:** Variation Of Frictional coefficient with Load for Nano-sized Silicon nitride+5% BN



**Figure 3.4:** Variation Of Wear coefficient with Load for Nano-sized Silicon nitride+5% BN

The tribological characteristics of monolithic  $\text{Si}_3\text{N}_4$  or  $\text{Si}_3\text{N}_4$  composite ceramics sliding against themselves is a well-known matter. In the present test conditions, the ceramic wear resistance is low, with friction and wear coefficients unacceptable for practical applications, i.e., higher than 0.5 and  $10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ , respectively. The dominant wear mechanism may be the mechanical failure of the material. Compared to the balls, the  $\text{Si}_3\text{N}_4$  composite discs show a higher wear loss and surface damage due to intermittent loading.

#### IV. CONCLUSIONS

Nano-sized  $\text{Si}_3\text{N}_4$  ceramics were developed using high energy mechanical milling followed by subsequent spark plasma sintering. Tribological tests on nano-sized  $\text{Si}_3\text{N}_4$  +5% BN composites against monolithic  $\text{Si}_3\text{N}_4$  were conducted to assess tribological properties of these ceramics. The following conclusions were derived

1. Increase in Coefficient Of friction Values and wear coefficient values with subsequent increase in temperature for Nano-sized  $\text{Si}_3\text{N}_4$  +5% BN while as increase in coefficient of friction and logarithmic decrement with increase in load.
2. Wear resistance drops with increase in temperature while as it increases with increase in load.
3. The friction coefficient varies from  $0.54 < \mu < 0.71$  for the Nano-sized  $\text{Si}_3\text{N}_4$  composite+ 5% BN, with elevation in temperature.
4. The friction coefficient varies from  $0.23 < \mu < 1.31$  for the composite with increase in load.
5. Wear coefficients being  $> K \approx 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ .
6. In the present test conditions, the wear resistance of nano-sized  $\text{Si}_3\text{N}_4$  is low, with friction and wear coefficients unacceptable for practical applications, i.e., higher than 0.5 and  $10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ , respectively
7. The addition of BN to the  $\text{Si}_3\text{N}_4$  matrix resulted in a slight reduction of the frictional and wear coefficient.

## V. FUTURE SCOPE

Silicon nitride ceramic materials exhibit a high potential for structural applications at room and elevated temperatures. This is due to their excellent mechanical properties in combination with good corrosion and thermal shock resistance. The development of the silicon nitride materials in the future will be divided in two main directions; the increased penetration in the market of the state of the art silicon nitride materials by improving the technology and reliability and decreasing the production costs and the development of new materials with improved wear, corrosion, high temperature properties. In the last decade a continuously increase in the number of application fields was observed. The technical feasibility and the reliability of the materials and components were shown in many applications, such as valves and other parts for the automotive industry, bearings and household applications. For the wider penetration into the market there is a engineering work necessary to optimize the production, stabilize the reliability and reduce the production cost.

An intensive development of high fracture toughness  $\alpha$ -SiAlON-materials can be expected. The better understanding of the microstructure formation of these materials and a further improvement of strength and toughness by a reduced grain size are main topics of the investigations.

Frequently, there is a need to make a compromise between the different properties due to the opposite dependencies on the microstructure. How such compromise looks like depends on the technological possibilities and on the powder properties, which developments offer new possibilities. An improvement of the materials behavior can be expected by the development of homogeneous composite materials based on silicon nitride, as it was shown for  $\text{Si}_3\text{N}_4/\text{MoSi}_2$  or  $\text{Si}_3\text{N}_4/\text{SiC}$  composites for the high temperature long term applications. Especially in this area the use of metal organic precursors can lead to an improvement of the materials. The reduction of sintering temperature and in some modifications the shrinkage (concept of active filler) can allow the production of composites of thermodynamic unstable components. The development in this direction is only at the beginning.

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