Effect of Sintering Additives and Reinforcement on Microhardness Values of Si$_3$N$_4$ Ceramics and Composites

M. F. Wani*, Z. A. Khan **, M. Hadfield **

* Department of Mechanical Engineering, National Institute of Technology Srinagar, Hazratbal Srinagar Kashmir India
telfax: +91 194 2421437
e-mail: mfwani@nitsri.net

** School of Design, Engineering and Computing, Bournemouth University, Ferndown, Talbot Campus, Poole, Dorset, BH12 5BB, United Kingdom
telfax: +44 1202 961645/+44 1202 965314
e-mail: zkhan@bournemouth.ac.uk

Submitted: 11/01/2010
Accepted: 14/02/2010
Appeared: 16/02/2010

© HyperSciences.Publisher

Abstract—In this research study, microhardness values of silicon nitride ceramics and its composites have been obtained by using Vickers and Knoop indenters. Samples of six silicon nitride ceramics were used for this study. These are Si$_3$N$_4$ + Y$_2$O$_3$, Si$_3$N$_4$ + MgO, Si$_3$N$_4$ + TiC, Si$_3$N$_4$ + TiN, Si$_3$N$_4$ + BN and Nano-Si$_3$N$_4$ + Nano-BN. Samples of silicon nitride ceramics (Y$_2$O$_3$ and MgO) and its composites of TiC, TiN and BN were prepared by hot pressing. Nano-Si$_3$N$_4$ + Nano-BN ceramic composite was developed by Spark Plasma Sintering. Vickers and Knoop hardness values were obtained under high load of 0.05 Kg to 2.0 Kg. Fracture toughness of Si$_3$N$_4$ ceramics and its composites was also obtained by Vickers micro-indentation method. Higher hardness and higher fracture toughness was observed in nano-Si$_3$N$_4$ + Nano-BN, as compared to other Si$_3$N$_4$ ceramics and its composites.

Keywords: Vickers hardness, Knoop hardness, Microhardness, Nano-Silicon nitride, Nano-Boron nitride

1. INTRODUCTION

Ceramic/silicon nitride bearing elements are an attractive design solution for high speed turbine, precision machine tools and various automotive applications. High demand of employing these elements in severe conditions of high contact stress, high temperature, high speed and restricted lubrication have put tremendous pressure on design engineers to evaluate the material and advise applicable design strategies, Khan et al. (2005).

Silicon nitride Si$_3$N$_4$ bearing elements have shown practical advantages over traditional steel elements due to their mechanical and physical properties, Hadfield et al. (1993) and Hadfield (1998). Leading technology, demands for high efficiency and importance of sustainable development have caused loading bearing contacts in all kinds of machinery to be subjected to high speeds, high contact stresses and severe conditions of lubrication, Khan et al. (2006).

Engineering ceramics uniquely combine strength, strength retention at high temperature, hardness, dimensional stability, good corrosion resistance, low density, superior thermal shock resistance, high wear resistance, and fracture toughness, Bennewitz (2003). These excellent mechanical and tribological properties make them suitable candidate materials for various applications, ranging from cutting tools to nuclear reactors, Kanimoto et al. (2000) and Kitamura et al. (2006). Typical applications are gas turbine bearings, I. C. Engine components, turbocharger rotors, seals, rocker arms, turbine blades. Compared with other engineering ceramics, silicon nitride has superior mechanical and tribological properties, Hyuga et al. (2005), Nakamura et al. (2001), Xu et al. (2005), Xu et al. (2007). Silicon nitride and its composites have long been used for design and development of hybrid bearings, cutting tools, values, engine parts, turbine blades etc, Andersson et al. (1991). As the use of Si$_3$N$_4$ is increasing at rapid rate, various sintering methods have been used to improve microstructure, mechanical and tribological properties of Si$_3$N$_4$ ceramics Wani et al. (1997). In addition, composites of Si$_3$N$_4$ with BN, TiN and TiC; and also composites of nano-Si$_3$N$_4$ with Nano-BN have been developed to improve microstructure, mechanical and tribological properties of monolithic Si$_3$N$_4$, Xu et al. (2006), Jones et al. (2001), Jones et al. (2001), Hyuga et al. (2003) and Ullner et al. (2001).

* This work was supported by Government of India Department of Science & Technology, under SERC financial assistance NO.SR/S3/MERC/24/2007.
Mechanical and tribological properties, such as, hardness, strength and wear resistance of Si$_3$N$_4$ ceramics depend upon (a) sintering additives (b) type of reinforcement and (c) sintering conditions (i.e. temperature, pressure etc.) used for fabrication of Si$_3$N$_4$ ceramics and its composites, Xu et al. (2006), Jones et al. (2001), Jones et al. (2001), Hyuga et al. (2003) and Ullner et al. (2001). Hardness plays a significant role, in increasing the wear resistance of Si$_3$N$_4$ ceramic, Rendtel et al. (2005) Higher hardness means higher wear resistance and vice-versa. Hardness is crucial for cutting tools, wear and abrasion-resistant parts, prosthetic hip-joint balls and sockets, optical lens glasses, ballistic armor, molds and dies, valves, and seals, Quinn (2006) and Swab (2004). Different techniques for measuring hardness of ceramics have been used, Sun et al. (2007). However, microhardness technique for measuring the hardness of ceramics have been used, Sun et al. (2007), Hyuga et al (2003) and Ullner et al. (2001). Hardness plays a significant role, in increasing the wear resistance of Si$_3$N$_4$ ceramic, Rendtel et al. (2005) Higher hardness means higher wear resistance and vice-versa. Hardness is crucial for cutting tools, wear and abrasion-resistant parts, prosthetic hip-joint balls and sockets, optical lens glasses, ballistic armor, molds and dies, valves, and seals, Quinn (2006) and Swab (2004). Different techniques for measuring hardness of ceramics have been used, Sun et al. (2007). However, microhardness technique for measuring the hardness of ceramics has shown promising results Rendtel et al. (2005), Quinn (2006), Swab (2004) and Sun et al. (2007). In order to understand the influence of sintering additives and the composites on hardness values and wear resistance, it is essential to measure hardness of Si$_3$N$_4$ ceramics and its composites.

Microhardness research studies on three advanced ceramic materials Si$_3$N$_4$, SiC Al$_2$O$_3$ have been carried out, Ullner et al. (2001). In this research study, three different indentation techniques Vickers, Knoop and Rockwell have been used, to evaluate the hardness of these three ceramics. It was observed that there is no significant difference between the abilities of these hardness techniques. Influence of BN particulate on microstructure and mechanical properties of Si$_3$N$_4$ has been studied, Kasiarova et al. (2006). In this research study, it was observed that the particulate of BN reinforced into the Si$_3$N$_4$ improves tribological properties of Si$_3$N$_4$. Silicon nitride composite of SiC has been developed to study the influence of reinforcement on the properties of monolithic Si$_3$N$_4$, Blugan et al. (2005). Researchers observed that intergranular SiC Nano-particles hinder the Si$_3$N$_4$ grain growth and thus change the chemical composition of grain boundary phase. Mechanical properties of Si$_3$N$_4$/C fibre composite have been carried to study the influence of C reinforcement on the properties of monolithic Si$_3$N$_4$, Blugan et al. (2005) Hadad et al. (2006). In this research study, it has been observed that the strength and toughness of the composite is higher comparing to monolithic Si$_3$N$_4$. Multilayered laminates of Si$_3$N$_4$ –TiN have been used to develop the Si$_3$N$_4$ / TiN composite Bai et al. (2008). Friction and wear study results have shown that wear resistance of laminates remain unchanged, however, fracture toughness of laminates is higher than that of Si$_3$N$_4$ composite. Recently, Nano-silicon nitride composites of BN have been developed for self lubrication of Si$_3$N$_4$ / Si$_3$N$_4$ tribopair, Xu et al. (2005) and Wani (2009).

In this research study, microhardness tests on Si$_3$N$_4$ ceramics and its composites have been carried out, to study influence of sintering additives and reinforcement on Vickers and Knoop hardness values of silicon nitride ceramics. In addition, fracture toughness of these ceramic materials has also been evaluated, based on Vickers indentation method.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and manufacturing process

The following powders were used as raw materials for the fabrication of Si$_3$N$_4$: Si$_3$N$_4$, 86% α-phase, with specific area of 8.78 m$^2$/g, containing 0.538 % calcium, 0.01 % magnesium, 0.084% sodium, 0.13 % iron, 38.6% nitrogen and 2.2% oxygen ( H. C. Starck, Goslar, Germany); CeO$_2$ and Y$_2$O$_3$, both 99.9% ( Indian Rare-Earths Ltd., Udyogmandal, India); MgO > 97% ( E. Merck, Darmstadt, Germany); AlN, 65.5% aluminium and 32.4% nitrogen ( H. C. Starck); and SiO$_2$ 99.8%, Hasla Minerals, Ranchi, India). Batches of Si$_3$N$_4$ powder (100g), mixed with the requisite amounts of additives, and were attrition-milled with aluminium balls in normal hexane. The uniform powder mixture, after final sieving to remove the aluminium balls and grit, were hot pressed ( GCA Vacuum industries Inc., Somerville, U.S.) as 25 mm diameter x 8 mm thick disks in a BN-Coated graphite die at 1650°C-1700°C under pressure of 25 MPa until shrinkage ceased. The composite of Si$_3$N$_4$ and TiC was made from nitrogen–rich, liquid- phase pressure sintered Si$_3$N$_4$ and Y$_2$O$_3$. The surfaces of samples were polished and finished with 4 µm and 2 µm diamond grit in an automatic polisher (Pedemax, Struers, and Copenhagen Denmark). The typical surface had an average surface roughness of 0.6 µm. Similarly, the composition of powders and preparation of Si$_3$N$_4$ + 30 wt % TiN composite is provided in Blugan et al. (2005) Hadad et al. (2006).

The composition of powders and preparation of Nano- Si$_3$N$_4$ +5 wt % Nano- BN and micro Si$_3$N$_4$ + 5 wt % BN ceramics samples is given elsewhere, Xu et al. (2007) and Wani (2009).

2.2. Characterization

Scanning Electron microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) studies were carried out to study microstructure of ceramic surfaces and also to carry out elemental analysis of Si$_3$N$_4$ ceramic samples. SEM and EDS studies were carried out on Hitachi SEM S -3600, equipped with EDS. X-ray diffraction (XRD) studies were carried out on M/S Philips, The Netherlands Compact X-ray Diffraction System. Typical results of SEM with EDS and XRD are shown in Figures 1-3. Figure 1 (a - d) shows SEM and EDS of Si$_3$N$_4$. It is obvious from Fig. 1 (a) that the surface of Si$_3$N$_4$ sample contains uniform grain structure of the ceramic material. EDS analysis of the Si$_3$N$_4$ surface was carried out at three different spots (marked as 1, 2 and 3) and is shown in Figure 1 (b, c and d). Figure 1 (b) shows EDS of spot 1. Similarly, Figure 1(c and d) shows EDS of spot 2 and 3. It is evident from EDS analysis of these three spots that Si$_3$N$_4$ is evenly distributed over the surface of the Si$_3$N$_4$ ceramic.

XRD patterns and analysis of nano-Si$_3$N$_4$+ 5wt % nano- BN are shown in Figures 2 and 3 respectively. It is obvious from Figure 2 that average grain size of Si$_3$N$_4$ in nano- Si$_3$N$_4$+ 5wt % Nano-BN disc sample is 56.5 nm. X-ray diffraction
pattern shown in Figure 3 indicates that major phase present in the Nano-composite is $\beta$-silicon nitride.

2.3 Microhardness tests

Hardness tests were performed on polished surfaces (mirror like finish, 1 µm diamond polish) using Vickers and Knoop diamonds. Vickers hardness (VH) and Knoop hardness (HK) tests were performed on Universal high-load hardness tester (Model UHL VMHT MoT, Walter UHi, Gmbh & Co. KG, Germany). The indentation was observed under 50 to 100 magnification. VH and HK were measured to study the influence of indentation load and time on hardness values. The indentation load was varied from 2.943 N (0.3 Kg) to 19.62 N (2.0 Kg) and indentation time was changed from 6 seconds to 12 seconds. In order to understand the influence of indentation time on hardness values (HVand HK), indentation tests were performed on selected Si$_3$N$_4$ ceramics. Each indentation test was repeated 3 to 5 times for better repeatability.

Fig. 2. XRD of Nano Si$_3$N$_4$+ 5wt % Nano BN.

Fig. 3. XRD of Nano Si$_3$N$_4$+ 5wt % Nano BN

3. RESULTS AND DISCUSSIONS

Hardness values (HVand HK) of Si$_3$N$_4$ ceramics and its composites against indentation load and indentation time are shown in Figures 4-8. The influence of indentation load (0.05 Kg – 2.0 Kg) on HV and HK of Si$_3$N$_4$ ceramic sintered with Y$_2$O$_3$ and MgO is shown in Figure 4. Figure 5 indicates the influence of indentation load (0.05 Kg – 2.0 Kg) on HV and HK of Si$_3$N$_4$ + TiN and Si$_3$N$_4$ + TiC ceramic composite. Whereas, the influence of indentation load (0.05 Kg – 2.0 Kg) on HV and HK of nano-Si$_3$N$_4$ + Nano BN and micro-Si$_3$N$_4$ + BN ceramics is shown in Figure 6. As can be seen in Figures 4-6, the hardness decreases with the increase in load in Si$_3$N$_4$ ceramics of Y$_2$O$_3$ and MgO; and its composites of TiN, TiC and BN. However, higher hardness values were obtained in the case of Nano-Si$_3$N$_4$ + 5 wt% Nano-BN composite, as compared to other Si$_3$N$_4$ ceramics and its composites. It is evident from Figure 4, that Si$_3$N$_4$ ceramic sintered with Y$_2$O$_3$ possesses higher hardness, as compared to Si$_3$N$_4$ sintered with MgO. This is attributed to the formation of liquid phase in presence of sintering additive Y$_2$O$_3$ in the case of Si$_3$N$_4$ +Y$_2$O$_3$. Sintering additive Y$_2$O$_3$
aids in the formation of liquid phase during sintering, which on solidification produces more intergranular refractory phase, as compared to MgO. Xu et al. (2006) and Jone et al. (2001). However, higher sintering temperature is required for $Y_2O_3$, as compared to MgO.

Fig. 4. Vickers hardness (HV) and Knoop hardness (HK) versus Load (\(\DeltaHV \) & *HK of Si$_3$N$_4$ + Y$_2$O$_3$, & HV & HK of Si$_3$N$_4$ + MgO).

Fig. 5. Vickers hardness (HV) and Knoop hardness (HK) versus Load: (HV & HK of Si$_3$N$_4$ + TiN and HV & HK of Si$_3$N$_4$ + TiC).

Fig. 6. Vickers hardness (HV) and Knoop hardness (HK) versus \(\DeltaHV\) & *HK of Si$_3$N$_4$ + Nano-BN & +HV, \(\DeltaHK\) -Si$_3$N$_4$ + BN

In the case of Si$_3$N$_4$ + 30 wt % TiN and Si$_3$N$_4$ + 10 wt % TiC composites, Si$_3$N$_4$ + TiN possesses higher hardness, as compared to Si$_3$N$_4$ + TiC composite, as shown in Figure 5. This is attributed to the fact that cracks deflection, micro crack deflection and crack impedance exists in the case of Si$_3$N$_4$ + TiC. The increase in micro cracks easily leads to excessive connection of micro cracks, which reduces hardness and strength of the ceramic composite, Quinn et al. (2006). As can be seen in Figure 6, that Nano-Si$_3$N$_4$ + 5 wt % of Nano BN possesses higher hardness, as compared to composite of micro-sized Si$_3$N$_4$ + 5 wt % of BN. The higher values of hardness in the case of Nano-Si$_3$N$_4$ + 5 wt % of Nano-BN is attributed to the fact that hardness of fine-grained ceramics generally increases with decreasing grain size, e.g., due to Hall-Petch type effects on the associated plastic flow Quinn et al. (2006), Xu et al. (2006), Xu et al. (2007) and Wani (2009).

The indentation time tests were carried out to determine the influence of indentation time on hardness value (HV and HK). These indentation tests were performed on specific Si$_3$N$_4$ ceramics and its composites, viz., Nano-Si$_3$N$_4$ + Nano-BN, Si$_3$N$_4$ + TiN and Si$_3$N$_4$ + Y$_2$O$_3$. The influence of indentation time (6 seconds-12 seconds) on HV and HK is shown in Figure 7 and 8. Figure 7, indicates the influence of indentation time (6 seconds - 12 seconds) on HV and HK at constant indentation load of 0.3 Kg, where as, the influence of indentation time (6 seconds-12 seconds) on HV and HK at constant indentation load of 0.5 Kg is shown in Figure 8. As can be seen in Figure 7 and 8, the hardness HV and HK decreases with the increase in indentation time (6 seconds - 12 seconds), however, the decrease in the values of hardness is small for indentation time of (8 seconds - 12 seconds).
As mentioned in previous section that indentation (Vickers and Knoop) were observed under optical microscope at 50 and 100 magnification. Indentation images on the surfaces of Si$_3$N$_4$ ceramics and its composites are shown in Figures 9-11. Indentation images on the surface of Si$_3$N$_4$ ceramic sintered with Y$_2$O$_3$ are shown in Figure 9. Figure 9 (a, b and c), indicates the indentation image of Vickers indenter at 0.5 Kg, 1.0 Kg and 2.0 Kg, respectively. Where as, Figure 9 (d and e), indicates the images of Knoop indenter at 0.5 Kg and 1.0 Kg, respectively. Figure 10, shows indentation images on the surface of Si$_3$N$_4$ + 30 wt % TiN. Indentation images on the surface of Si$_3$N$_4$ + TiN at 1.0 Kg and 2.0 Kg are shown in Figure 10 (a and b), respectively. Where as, Figure 10 (c and d) shows Knoop indentation images on the surface of Si$_3$N$_4$ + TiN at 0.5 Kg and 1.0 Kg, respectively. Indentation images on the surface of Nano-Si$_3$N$_4$ + 5 wt % of Nano BN are shown in Figure 11. Indentation image on Nano composite at 0.5 Kg, 1.0 Kg and 2.0 Kg are shown in Figure 11 (a, b and c), respectively. Knoop indentation image of Nano composite is shown in Figure 11 (d and e) at 0.5 Kg and 1.0 Kg. As can be seen in Figure 10 (c) and Figure 11 (c), the cracks are developed at the edges of Vickers indenter at indentation load of 2 kg in the case of Si$_3$N$_4$ + 30 wt %TiN and Nano-Si$_3$N$_4$ + Nano-BN, respectively. This is marked by an arrow in Figure 10(c) and Figure 11 (c). The hardness values obtained are given in table 1.

Fracture toughness of ceramic composites was obtained by measuring crack length at the edges. Indentation fracture toughness is calculated, in terms, of toughness parameter (TP) relationship given in the reference, Jones et al. (2001).

\[
TP = 10.282 \times 10^{-0.4} E^{0.6} P^{0.7} a^{-1.5} (c'/a)^{1.5} \text{ MPa m}^{1/2},
\]

where E = Elastic Modulus (GPa), P = indentation load (N), c' = \(\frac{1}{2}\) total crack length (µm) and a = diagonal length (µm).

Fracture toughness value of 8.0 MPa m$^{1/2}$ and 7.0 MPa m$^{1/2}$ were obtained for Si$_3$N$_4$ + Y$_2$O$_3$ and Si$_3$N$_4$ + MgO, respectively. Where as, fracture toughness value of 9.00 MPa m$^{1/2}$ and 8.0 MPa m$^{1/2}$ were obtained for Si$_3$N$_4$ + 30 wt %TiN and Si$_3$N$_4$ + 10 wt % TiC, respectively. In the case, Si$_3$N$_4$ + 5 wt % BN and micro-sized Si$_3$N$_4$ + 5 wt % of BN, fracture toughness value of 11.0 MPa m$^{1/2}$ and 8.17 MPa m$^{1/2}$ were obtained for Nano sized Si$_3$N$_4$ + 5 wt % BN and micro-sized Si$_3$N$_4$ + 5 wt % of BN, respectively. Nano-sized Si$_3$N$_4$ /BN composite possess highest fracture toughness value, as compared to other Si$_3$N$_4$ ceramics and its composites.
4. CONCLUSION

Silicon nitride ceramics and its composites were developed using hot pressing and Spark Plasma Sintering methods. Microhardness values (HV and HK) of Si₃N₄ and its composites were studied, using Vickers and Knoop indentation methods. Fracture toughness values of Si₃N₄ and its composites were also determined on the basis of Vickers...
indentation methodology. Microhardness values of Si3N4 ceramic is highly influenced by the presence of sintering additives. Si3N4 ceramic sintered with Y2O3 possesses higher microhardness values (HV and HK), as compared to Si3N4 ceramic sintered with MgO. Microhardness values (HV and HK) of Si3N4 ceramic composite of TiN, as compared to Si3N4 ceramic composite of TiC. Nano-Si3N4 / Nano-BN composite possesses higher values of Vickers and Knoop hardness, as compared to micro-sized Si3N4 / BN composite. Nano-Si3N4 / Nano-BN composite possesses microhardness values (HV and HK), as compared to Si3N4 +Y2O3, Si3N4 +MgO, Si3N4 +TiC, Si3N4 +TiN and micro-sized Si3N4 + BN ceramics. Nano-Si3N4 / Nano-BN composite possesses highest fracture toughness (11.0 MPa m^1/2 ), as compared to Si3N4 ceramics of ( Y2O3 and MgO) and Si3N4 ceramic composites of BN, TiC and TiN.

REFERENCES


AUTHORS PROFILE

M F Wani is working as Professor in Mechanical Engineering Department, and Dean at National Institute of Technology Srinagar. He is having research and teaching experience of 25 years in the field of tribology of advanced ceramics, life cycle assessment and life cycle design of mechanical systems.
**Dr Zulfiqar Khan** (CEng, MIMechE) is Associate Dean Research and Enterprise in the School of Design, Engineering & Computing and Co-Director Sustainable Design Research Centre Bournemouth University. Dr Khan’s research interests are Tribology and sustainable design.

**Professor Mark Hadfield** is Deputy Dean Research and Enterprise in the School of Design, Engineering & Computing and Director Sustainable Design Research Centre Bournemouth University. He is involved in various national and international collaborative research projects as lead investigator. His research interests are Tribology and Design.