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Journal of the European Ceramic Society 24 (2004) 219–224

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Tribological properties of silicon nitride ceramics modified by ion implantation

Naoki Nakamura[a,*], Kiyoshi Hirao[b], Yukihiko Yamauchi[b]

[a]*Synergy Ceramics Laboratory, Fine Ceramics Research Association, Shidami Human Science Park, Moriyama-ku, Nagoya, 463-8687 Japan*
[b]*Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology, Shidami Human Science Park, Moriyama-ku, Nagoya, 463-8687, Japan*

Abstract

Surface modification by ion implantation has been carried out in order to improve the tribological properties of gas-pressure sintered silicon nitride ceramics. B^+, N^+, Si^+ or Ti^+ ions were implanted into the silicon nitride ceramics with a fluence of 2×10^{17} ions/cm^2 at an energy of 200 keV. To evaluate the tribological properties of Si_3N_4, Block-on-Ring wear tests were conducted without lubricant, using the ion implanted Si_3N_4 as block specimens and commercially supplied Si_3N_4 as ring specimens. The specific wear rate of the ion-implanted Si_3N_4 could be drastically reduced to a value of 1.6×10^{-9} mm^2/N, accompanied by a decrease in the friction coefficient in the initial stage. According to surface analyses it was considered that the high wear resistance and low friction coefficient are attributed to the amorphization and the increase of surface hardness of the ion implanted layer.

Keywords: Implantation; Si_3N_4; Surfaces; Wear parts; Wear resistance

1. Introduction

Because of their excellent mechanical properties, silicon nitride ceramics have created considerable interest in recent years for their potential application to automobile or power-generating industries.[1–3] Furthermore, silicon nitride ceramics are expected to be frictional materials[4–8] under conditions (e.g. high temperature, corrosion, vacuum, and magnetic fields) where metallic materials cannot be used, because of the superior properties of high strength, heat resistance, corrosion resistance, light weight, and insulation. However, it is necessary to improve the wear resistance of silicon nitride ceramics in order to allow their practical use. Since the mechanical and tribological properties of ceramics are very surface-sensitive, ion implantation is a possible tool to improve the tribological properties,[9–13] because it is possible to implant various kinds of atoms and control the surface structure at the atomic scale (see Fig. 1). The objective of this study is to improve the wear resistance of silicon nitride ceramics by means of ion implantation, whilst retaining the bulk properties earlier described, and to clarify the effect of ion implantation on the tribological properties of silicon nitride ceramics.

2. Experimental

2.1. Fabrication of Si_3N_4

α-Si_3N_4 powder (SN-E10, Ube Industries, Ltd., Japan) was mixed with 5 mass% Y_2O_3 (Shin-Etsu Rare Earth, Ltd., Japan) and 2 mass% Al_2O_3 (AKP-50, Sumitomo Chemical, Ltd., Japan) in ethanol for 2 h by planetary ball milling, followed by drying and pulverizing. The green bodies were then calcined at 800 °C for 2 h under N_2 gas at a flow rate of 1.5 l/min to remove organics. The calcined green bodies were cold isostatically pressed under 500 MPa after mold-pressing, and sintered at 1850 °C for 2 h in N_2 under a pressure of 0.9 MPa in a graphite crucible filled with a 70 mass% Si_3N_4 and 30 mass% BN powder bed. The specimens could be densified to over 97% of theoretical density. The sintered Si_3N_4 was machined into rectangular specimens of 3×4 mm with 1.55 mm thickness, for ion implantation followed by wear test.

* Corresponding author.
E-mail address: nakamura-naoki@aist.go.jp (N. Nakamura).

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doi:10.1016/S0955-2219(03)00243-7

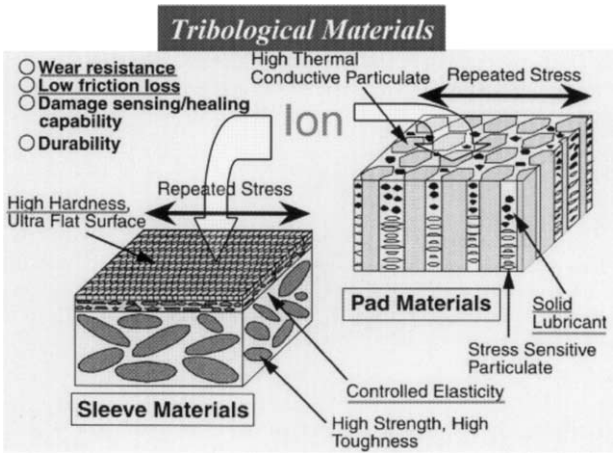

Fig. 1. Expectation of improvement of the wear resistance of Si_3N_4 ceramics for ion implantation.

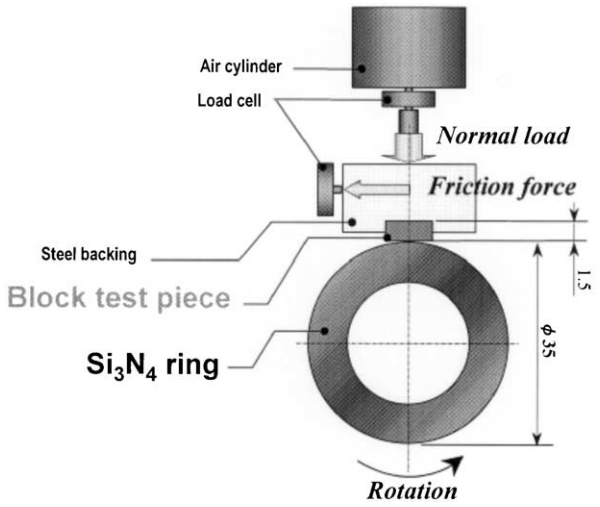

Fig. 3. Schematic view of block-on-ring wear tester.

2.2. Ion implantation to Si_3N_4

Before implantation the specimens were cleaned with acetone in an ultrasonic bath. Boron, nitrogen, silicon or titanium ions were implanted into the mirror finished surfaces of the earlier-described silicon nitride ceramics with a fluence of 2×10^{17} ions/cm^2 at an energy of 200 keV. The ion implantation was carried out using a Freeman-type 400 keV ion implanter at the Ion Engineering Center Corporation, Osaka, Japan. Si_3N_4 specimens were fixed to a 4-inch wafer and set in the vacuum chamber of the ion implanter. The ion source gas was introduced into the arc chamber and then ionized (generating plasma) by thermoelectrons from the filament. BF_3, N_2, SiF_4 and $TiCl_4$ were used as ion sources for B^+, N^+, Si^+ and Ti^+, respectively. Generated ions were accelerated by the application of 30 V on the drawing electrode in front of the ion source, and 200 kV whole acceleration voltage on the acceleration electrode. Only the desired ions were extracted from various ions generated through the analysis electromagnet and slit. Ions were implanted uniformly throughout the whole implantation area in electrostatic scan mode by a beam scan. The expected implantation profiles, shown in Fig. 2, were estimated using the TRIM simulation. The surface-modified nano-structure of the ion implanted Si_3N_4 was evaluated by Nanoindentation and Transmission Electron Microscopy.

2.3. Wear test

A block-on-ring type wear test machine (TRR-100D, Takachiho-Seiki Ltd., Japan) was used for friction and

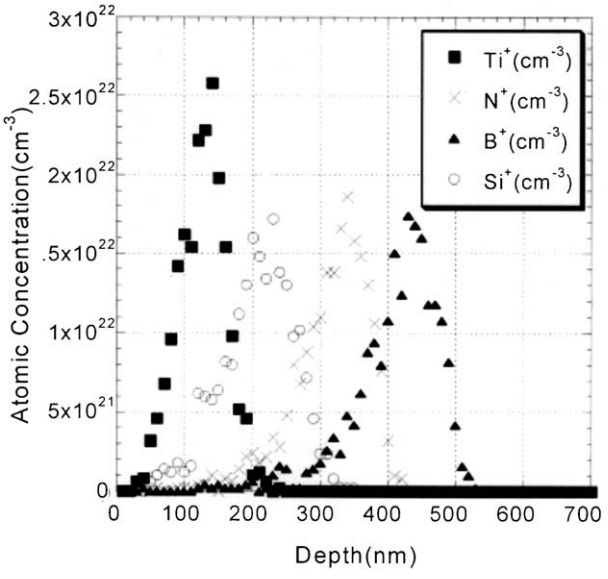

Fig. 2. Ion implantation profiles predicted by TRIM simulation.

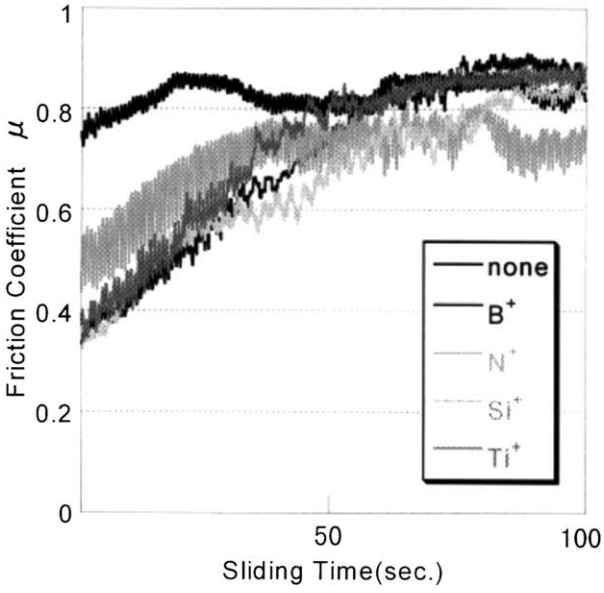

Fig. 4. Friction coefficient in the initial stage for Si_3N_4 unimplanted and implanted with 200 keV ions.

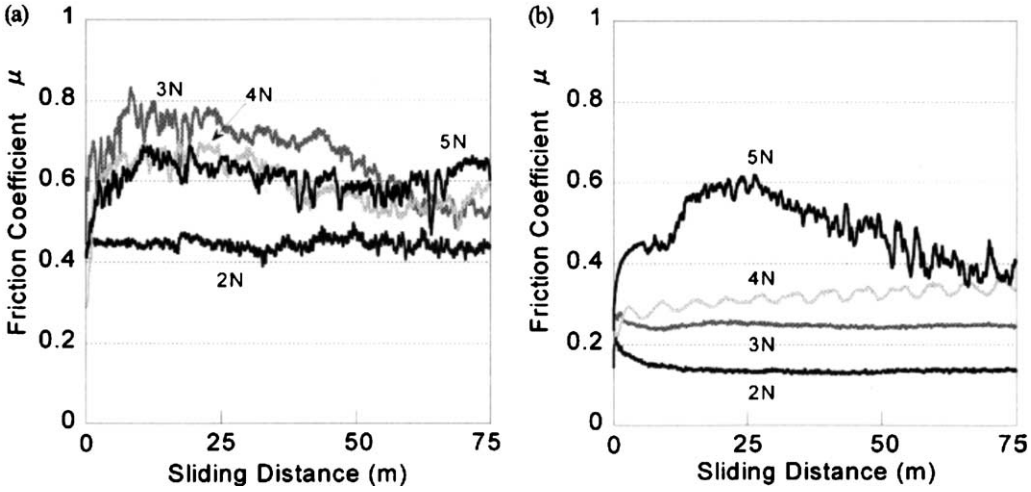

Fig. 5. Friction coefficient of Si_3N_4 at a load of 2, 3, 4, 5 N: (a) unimplanted, (b) Si^+-implanted.

wear testing. The experimental setup used is illustrated in Fig. 3. Test samples described in Sections 2.1 and 2.2 were used for the block side and commercially supplied Si_3N_4 (SN235P, Kyocera, Japan) was used for the ring test piece. To eliminate the contribution of lubricant, wear tests were conducted under dry conditions in air. Temperature and humidity were kept constant at 25±3 °C, 25±2% relative humidity, respectively. Sliding conditions were set at 0.15 m/s sliding speed, 2–5 N normal load, and 75 m sliding distance. The friction coefficient was recorded by monitoring the load and friction during the sliding test in real time using two sets of load cells. The wear volume was calculated by section analysis (analysis of nine lines) of the wear tracks, which were generated by the block-on-ring wear test, using a surface roughness tester (SV-624, Mitsutoyo, Japan). The specific wear rate (mm^2/N) was obtained by dividing the wear volume (mm^3) by the product of load (N) × sliding distance (mm).

3. Results and discussion

3.1. Influence of ion implantation on the tribological properties of Si_3N_4

Fig. 4 illustrates the variation of friction coefficient μ in the initial stage. For the unimplanted specimen, μ showed a large value of 0.8 over the whole sliding time range measured, even in the initial stage of the wear test. On the other hand, for the ion-implanted specimens, μ showed a low value of 0.4 in the initial stage and a gradual increase with increase of sliding time. Fig. 5 shows variation of friction coefficients under different loads of 2, 3, 4 and 5 N. For the unimplanted Si_3N_4, there was little difference in the friction coefficient, μ, under 3, 4, 5 N load. On the contrary, for the Si^+-implanted specimens, there was an obvious dependence on normal load, that is to say, decreasing friction coefficient with lower normal load. Fig. 6 summarizes the specific wear rates for the Si_3N_4 specimens in relationship to the ion species. Remarkable reduction of the specific wear rate was realized for each specimen of the ion-implanted Si_3N_4. For example, the specific wear rate of Si^+-implanted specimen was reduced to a value of 1.64×10^{-9} mm^2/N, equal to a quarter of the unimplanted one. The specific wear rate of ion-implanted Si_3N_4 showed ion species dependence, with the specific wear rate decreasing in the order of $B^+ > N^+ > Ti^+ > Si^+$. These ion species dependence is explained in terms of the implantation depth (see Fig. 2). The implanted layer prevented wear from progressing, and the shallower the implantation depth, the better is the wear resistance for B^+-, N^+-,

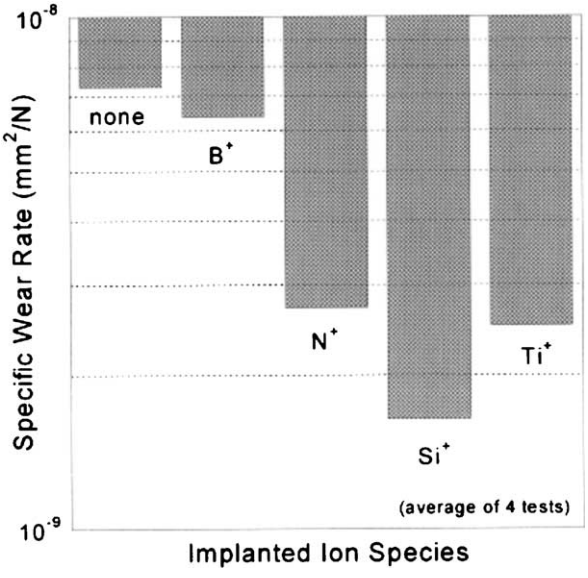

Fig. 6. Specific wear rates for unimplanted and implanted Si_3N_4.

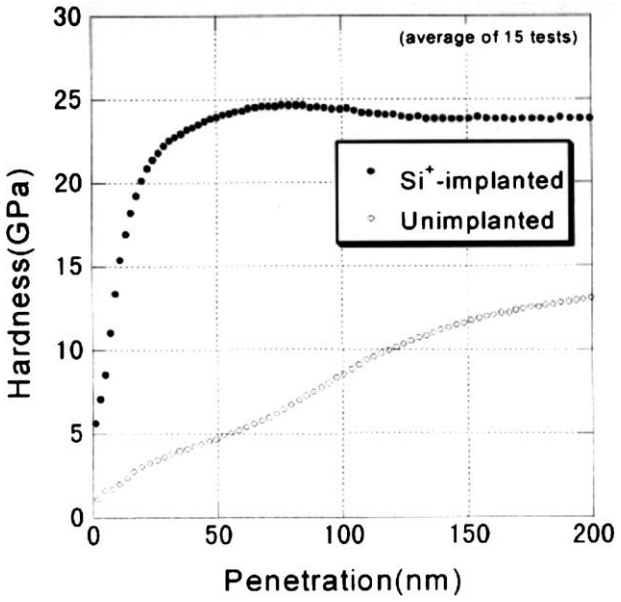

Fig. 7. Surface hardness of unimplanted and implanted Si_3N_4 evaluated by Nanoindentation.

Si^+-implanted specimens because most of the implanted ions are located at the near surface region. As for the Ti^+-implanted specimen, the peak value of implanted atomic concentration is higher than the other ion species and the atomic radius is also largest (Ti: 1.45Å, B: 0.9 Å, N: 0.75 Å, Si: 1.15 Å), which may have broken the Si–N bond, leading to less wear resistance compared with Si^+ case.

3.2. Structural investigation of ion-implanted Si_3N_4

In order to clarify the effect of ion implantation on the tribological properties of Si_3N_4, Nanoindentation method was used for measuring surface hardness and cross-sectional TEM was used for observing the microstructure of surface-modified Si_3N_4. The nanoindentation was carried out using a nanoindenter (Nano Indenter XP, MTS Systems Corporation, USA). The surface hardness is plotted against the penetration depth in Fig. 7. It can be clearly seen that the Si^+-implanted surface is harder than the unimplanted surface. For the unimplanted Si_3N_4, the hardness increases gradually up to a penetration depth of 200 nm. In contrast, for the Si^+-implanted Si_3N_4, the hardness shows a sharp rise just near the surface, followed by saturation state at around 50 nm. The hardness of Si^+-implanted Si_3N_4 increases by 80% to 23.5 GPa compared with the unimplanted Si_3N_4 at 200 nm. In general, the hardness of a material increases with decreasing the interatomic distance, so the hardness increase is considered to be due to the densification caused by ion implantation, resulting in the low friction and high wear resistance.

A cross-sectional TEM (H-9000UHR III, Hitachi, Japan) micrograph of Si^+-implanted Si_3N_4 is shown in Fig. 8. Directly at the surface a 350 nm wide gray band is visible in the Si^+-implanted Si_3N_4, while no such band was observed in the unimplanted Si_3N_4. The electron diffraction patterns in Fig. 8(b) are from the locations indicated by the arrows. The observed broad

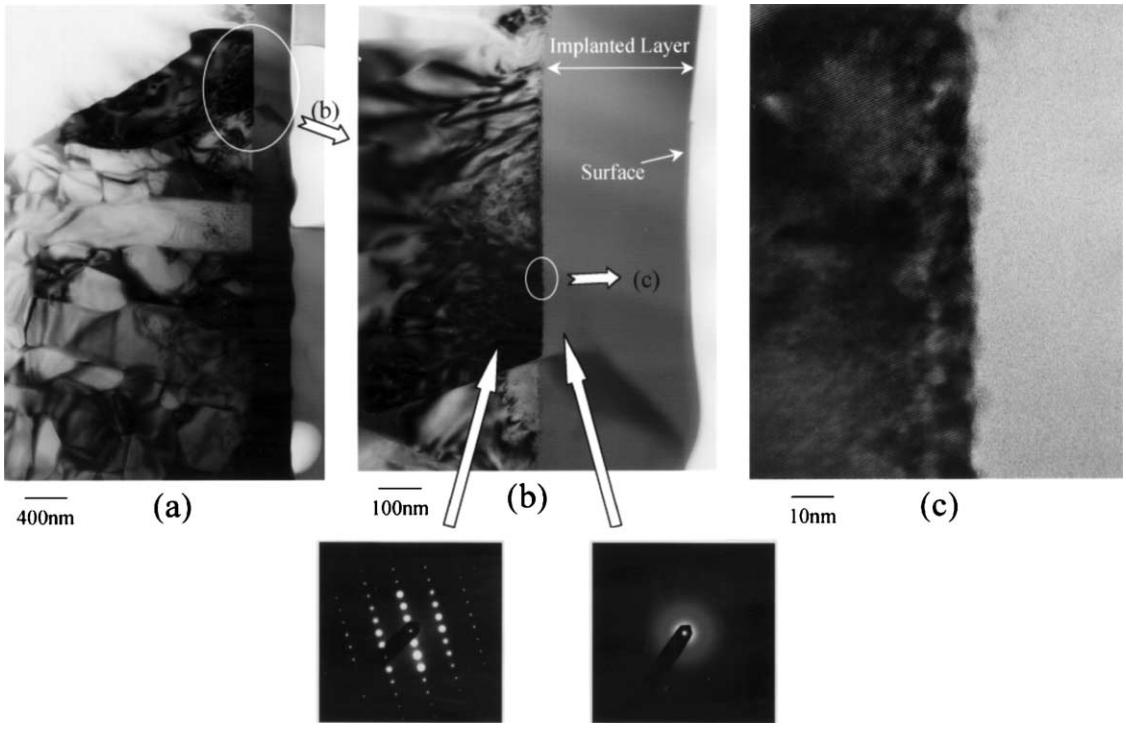

Fig. 8. Cross-sectional TEM micrographs of the Si^+ implanted Si_3N_4 with electron diffraction patterns.

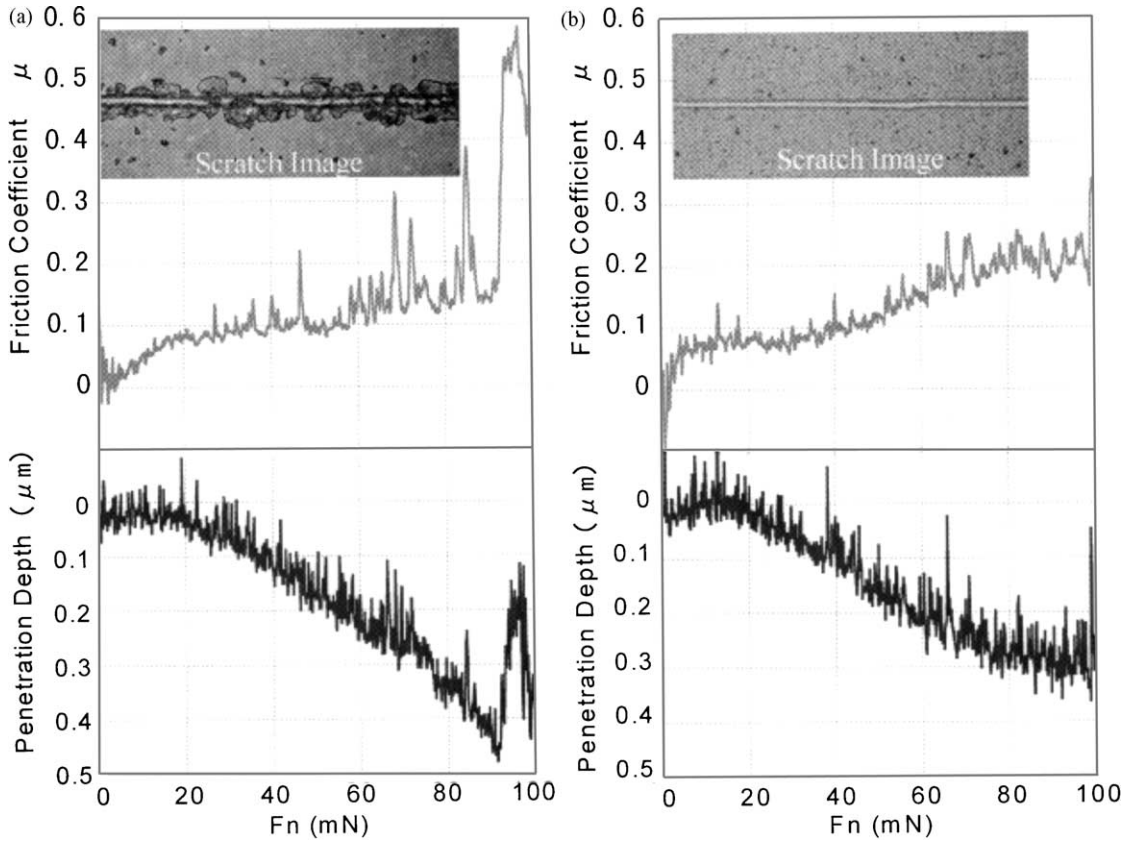

Fig. 9. Results of the scratch tests for unimplanted and Si^+-implanted Si_3N_4; (a) unimplanted, (b) Si^+-implanted.

fringes indicate that the gray region is amorphous. The depth of the amorhized region is in fairly good agreement with the ion-implanted region predicted by TRIM (see Fig. 2). Thus, the tribological properties of silicon nitride ceramics are considered to be strongly affected by the surface amorphization. Based on the earlier results, it is considered that the high wear resistance and low friction of the ion implanted Si_3N_4 are attributed to the increase of surface hardness, the surface shear stress relaxation and the prevention of grain boundary related crack initiation due to the surface amorphization.

In order to prove this wear mechanism, nano-scratch test was conducted using a scratch tester (Nano-Scratch Tester, CSM Instruments, Switzerland). A spherical diamond indenter of radius 2 μm was used with a loading rate of 140 mN/min. The results presented in Fig. 9 show progressive load measurements over the range 0–100 mN on the surfaces of the unimplanted and Si^+-implanted Si_3N_4. For the unimplanted specimen, friction coefficient fluctuated on a large scale, followed by a sharp rise to 0.5 at 90 mN, which is identified as chipping after the optical microscope observation. On the other hand, the friction coefficient of the Si^+-implanted specimen showed less fluctuations and lower values over the whole range of normal force, without chipping as is shown in the optical micrograph. Thus, the nano-scratch results are consistent with the wear mechanism speculated earlier.

4. Conclusion

Surface modification by ion implantation has been carried out in order to improve the tribological properties of Si_3N_4. B^+,N^+,Si^+ or Ti^+ ions were implanted into the mirror-finished surface of silicon nitride ceramics with a fluence of 2×10^{17} ions/cm^2 at an energy of 200 keV. The wear behavior of the ion-implanted Si_3N_4 was evaluated using a block-on-ring wear tester, and related to the effect of surface modification by ion implantation. Both the friction coefficient and the specific wear rate were reduced by ion implantation. The specific wear rate of Si^+-implanted specimen, which showed the greatest improvement, was reduced to a value of 1.64×10^{-9} mm^2/N, equal to a quarter of the unimplanted one. According to surface analyses, the high wear resistance and low friction coefficient were attributed to the surface amorphization and the increase of surface hardness of the ion implanted layer.

Acknowledgements

This work has been supported by METI, Japan, as part of the Synergy Ceramics Project. Part of the work has been supported by NEDO. The authors are members of the Joint Research Consortium of Synergy Ceramics.

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