Effects of mesh-assisted carbon plasma immersion ion implantation on the surface properties of insulating silicon carbide ceramics

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Plasma immersion ion implantation (PIII) is an effective materials modification and synthesis technique but has seldom been applied to ceramic materials due to the high electrical resistance that reduces the ion bombardment energy and sometimes causes serious electrical arcing in the instrument. Even in cases where PIII is applicable, the surface properties of the implanted insulating materials can be seriously affected due to the low ion energy and materials damage from electrical arcing. In order to enhance the surface and mechanical properties such as wear resistance of ceramic materials used in many industrial applications, surface modification is needed. In this work, we conduct carbon implantation into sintered α-SiC (silicon carbides that are widely used in vacuum ceramic bearings) using mesh-assisted plasma immersion ion implantation to enhance the surface properties. The use of a conducting grid is necessitated by the high electrical resistance that induces a large voltage drop across the substrate when a negative voltage is applied to the back of the specimen. The rough surfaces make direct assessment of the shallow depth profiles difficult and so we directly measure the hardness and surface friction coefficients, both of which are significantly enhanced after implantation. Our data suggest different wear mechanisms for the unimplanted and implanted samples as inferred from the surface topography and wear tracks. © 2004 American Vacuum Society. [DOI: 10.1116/1.1648676]

I. INTRODUCTION

Silicon carbide is composed of tetrahedral covalently bonded carbon and silicon atoms. The alpha form silicon carbide consisting mainly of 6H polytype is of primary interest in industrial applications due to the unique electrical, thermal, structural, and wear characteristics. Silicon carbide possesses high strength, high elastic modulus, excellent thermal shock resistance, superior chemical inertness, and low specific weight and is used in abrasives, refractories, ceramics, and a myriad of high-performance applications. Adjustment of the fabrication processes, contents, and types of additives can alter the bulk mechanical properties of silicon carbide, but in many applications, the surface properties, particularly resistance to wear in hostile working conditions, must be further enhanced. Ion implantation is an effective way to modify the surface properties. Several previous studies have shown that implantation results in surface hardening, enhanced adhesion, mitigation of surface stress, lower surface resistivity, and amorphization. The tribological properties of ceramics have also been shown to be improved after ion implantation and irradiation.

In this work, cathodic arc plasma immersion ion implantation (PIII) was utilized to enhance the surface properties such as friction and wear of α-SiC ceramics. In cathodic arc PIII, the metal plasma drifts toward the source to the negatively biased sample in the vacuum chamber. Since the negatively biased target is immersed in the plasma, electrons are repelled away initially and surrounding ions are accelerated to bombard the exposed surfaces. The biggest advantages of the technique are high throughput and small instrument footprint compared to conventional beam-line ion implantation. However, PIII of insulating materials such as SiC is problematic due to the potential drop across the sample. In the tolerable cases, the ion incident energy is reduced, but if the insulating substrate is thick, the voltage drop can be so severe that there is no implantation. The phenomena can be explained by the capacitance and surface charging effects. Secondary electron emission and positive charge accumulation near the surface give rise to an opposite electric field that deters the incident positive ions. In order to enhance the implantation efficacy and ion energy as well as to reduce electrical arcing, an alternative approach called mesh-assisted PIII employing a conducting grid over the sample is adopted in our experiments. The mechanical properties of the untreated and treated samples are determined.
using Vickers indentation and computer-controlled oscillating ball-on-disc type tribometry. The implanted samples exhibit a large improvement in the wear resistance as well as the friction. Our data suggest different wear mechanisms for the unimplanted and implanted samples as inferred from the surface topography and wear tracks.

II. EXPERIMENT

A silicon carbide-based pressureless sintered ceramic with more than 95% α-phase content was investigated. Before implantation, the samples with dimensions of 30 mm (diameter) and 2.5 mm (thick) were cleaned with ethanol in an ultrasonic bath. Two samples were then silver glued onto a square stainless steel platen for electrical contact to the backside. Before loading the samples into the vacuum chamber, one of the samples was enshrouded by an electrically conducting grid cage that was connected to and had the same potential as the sample stage as shown in Fig. 1. The samples were then positioned approximately 15 cm in front of the exit of the cathodic arc magnetic filter. The base pressure in the vacuum chamber was about $1 \times 10^{-3}$ Pa. The metal plasma source housed a 1 cm diameter carbon cathode and a tungsten mesh anode located about 15 cm away from the cathode. The carbon plasma was generated in the metal vacuum arc plasma source and diffused into the vacuum chamber through a 90° magnetic curved duct with a minor radius of 40 mm and major radius of 100 mm. The magnetic filter was used to reduce macroparticles that formed in the ignition process. An external solenoid around the duct produced an axial magnetic field to confine, focus, and guide the carbon plasma. The main arc current was maintained at around 70 A and the duration was about 200 μs with the repetition rate of 40 Hz. The duct magnetic field was 100 G and the duct dc voltage was 20 V. The plasma stream was extracted along the center of the duct exit and rapidly dispersed to the entire processing chamber with a velocity of about $1-2 \times 10^4$ m/s. The samples stage was pulse biased to $-25$ kV and the pulse duration was 400 μs. The sample voltage was in phase with that of the cathodic arc trigger. A longer sample pulse duration was chosen to ensure pure implantation but the intense plasma stream with a measured implantation current of $\sim 1.7$ A reduced the implantation voltage from 25 to 20 kV as demonstrated in Fig. 2. The implantation time was 100 min.

Since the SiC surface is quite rough, with the root-mean-square value of $\sim 40$ nm as determined by surface profilometry, and the implant projected range is only several tens of nanometers, the implant depth profile was not acquired. We have already experimentally demonstrated that the ion energy could be improved significantly using mesh-assisted PIII, and so in this work, we directly focused on the more relevant materials properties instead. The surface hardness of the implanted samples was measured by Vickers indentation under a load of 500 g. Each value of the surface hardness represents the mean of at least 20 measurements. For the indentation tests, the depth of the indentation approached or exceeded the carbon ion implantation range ($R_p$ of 50 nm and $\sigma$ of 20 nm for 25 keV carbon ions) estimated from TRIM. Here, it should be noted that the implantation affected zone can be on the order of several hundred nanometers. The friction coefficients were measured using a computer-controlled oscillating ball-on-disc scratch tester equipped with a 5 mm chromium steel ball. The wear tests were conducted in air under a load of 10 N with a rotation diameter of 10 mm and sliding speed of 114 rpm. The microstructure of the tested surface was evaluated using optical microscopy and secondary electron microscopy (SEM) and surface profilometry was employed to determine the width of the wear tracks. At least three measurements were conducted to produce the average values reported in this article.

III. RESULTS AND DISCUSSIONS

In the conventional PIII process, the voltage drop across the poorly conducting SiC ceramic samples result in shallow implantation depth and in the worst case, no implantation. In our work, a conducting grid is used to enhance the implantation energy and efficacy. The purposes of the grid are to more effectively accelerate the ions from the plasma, reduce the capacitance effects on the sample, build up an equipotential space between the grid and insulator surface, and retract secondary electrons generated by ion bombardment thereby reducing surface charging. The discharging phenomena on the ceramic surface can be directly observed from the tail of implantation current as shown in Fig. 2. The surface poten-
tial of the samples can be derived from the setup geometry and plasma physics. Charges will accumulate on the insulator surface during implantation and the effective surface potential is given by

$$\xi_{(t)} = \xi_o - \Delta \xi_{(t)},$$

(1)

where $\xi_o$ is the applied pulse potential and $\Delta \xi_{(t)}$ is the potential difference between the sample and holder. The potential difference critically depends on the accumulated charges, relative dielectric property, and thickness of the material. At the same time, the amount of charges deposited on the surface is related to the plasma parameters. In a drifting plasma from a cathodic vacuum arc plasma source, the drifting ion velocity that is higher than the directed ion velocity in stationary plasma and the ion density significantly affect the collected ion current as well as the ion sheath dimension and shape.\(^{20}\) The effective surface potential becomes

$$\xi_{(t)} = \xi_o - \frac{e n_i d}{\epsilon_o \epsilon_r} \gamma(s + \mu_d t),$$

(2)

where $e$ is the electron charge, $n_i$ is the ion density, $d$ is the sample thickness, $\epsilon_o$ and $\epsilon_r$ is the vacuum and relative permittivity of the dielectric material, respectively, $\gamma$ is the secondary electron coefficient that depends on the bombardment energy of the incident ions, $\mu_d$ is the ion drifting velocity, $t$ is the treatment duration time, and $s$ is the sheath thickness which is interrelated to the potential and can be expressed as

$$s = A \frac{\lambda_{De} \xi_{(t)}^{3/4}}{\mu_d^{1/2} T_e^{1/2}},$$

(3)

where $A = 2/3(2 e/M)^{1/4}$, $\lambda_{De}$ is the Debye length, and $T_e$ is the electron temperature. As mentioned earlier, the plasma is extracted thought a curved duct with a high drifting ion velocity and the ion density in the processing chamber is typically $\sim 10^{10} \text{cm}^{-3}$ but it is somewhat determined by the transport and diffusion efficiency of the plasma in the duct. Since our samples have poor electrical conductance, the surface potential is naturally reduced during the pulse. Once the surface potential decreases, the potential-dependent ion sheath shrinks back simultaneously while charges continue to be deposited and accumulated on the surface. If the amount of the accumulated charge becomes big, a zero potential or serious arcing occurs on the sample surface. In our experiments, the accelerating voltage is provided by the grid which sits at a small distance above the sample. The grid also serves another important purpose in that it reflects the secondary electrons emitted from the sample surface back to the sample. Electrical arcing was observed to be absent in our experiments and as inferred from the results to be discussed in the paragraph, the implantation efficacy has been improved using the mesh-assisted approach.

After ion irradiation, both the implanted samples (with and without the grid) demonstrate an increase in microhardness of around 40 to 60% as shown in Fig. 3. McHargue and Williams reported that Cr implantation into SiC could cause amorphization under high implantation energy (260 keV) and high ion fluences resulting in low surface hardness.\(^{21}\) However, some other studies have shown that surface hardness is related to the implantation dose.\(^{5,22}\) In our study, since the smaller carbon atoms at a relatively small bombardment energy are not likely to cause significant amorphization, the

![Fig. 3. Surface microhardness of the unimplanted and implanted samples acquired by Vicker indentation.](image)

![Fig. 4. Friction coefficients as a function of sliding time measured from the unimplanted and implanted samples.](image)

![Fig. 5. Wear tracks of the samples: (a) unimplanted, (b) implanted without the conducting grid, and (c) implanted with the conducting grid.](image)
observed increase in the surface hardness may be due to implantation induced defects (compressive stress)\(^5\) and dislocation effects. The sample implanted using the grid exhibits the highest hardness thereby indicating higher implantation energy is beneficial. At higher energy, the carbon ions penetrate deeper and the implanted zone is thicker. Adding a large number of carbon atoms into the SiC grains results in a volume change and it is believed that dislocation may build up along the ion cascade paths and point defects cause hardening. Our results suggest that the dislocation effects may only take place in the samples implanted using the grid because a large enough implantation energy is not achievable otherwise.

Figure 4 depicts the friction coefficients \(\mu\) of the unimplanted and implanted samples. During the wear test, two sliding states are observed. In the initial run-in period, there are a considerable number of asperity collisions because of the roughness of the surface and higher friction coefficients are recorded. Afterward, the friction coefficient diminishes to \(\approx 0.31\) for the unimplanted sample and \(\approx 0.2\) and \(\approx 0.19\) for the sample implanted without and with the grid, respectively. The values remain constant until the end of the wear test. Again the best results are obtained from the sample that has undergone mesh-assisted PIII. It should be noted that more work is being conducted in our laboratory to confirm the effects by varying the treatment conditions. Figures 5 and 6 display the wear tracks and the cross-sectional profiles of the wear tracks of the unimplanted and implanted samples. The unimplanted sample shows a deep and wide wear groove, whereas the implanted samples exhibit a similar groove width but a slightly different depths.

In order to better understand the wear behaviors of the unimplanted and implanted samples, the wear tracks are evaluated using scanning electron microscopy (SEM) and the micrographs are displayed in Fig. 7. The results suggest that the wear modes of the samples are quite dissimilar. For the unimplanted sample in Fig. 7(a), the ceramic surface seems to be scratched away and the surface inside the track has been flattened after the ball-on-disc test. The size and num-

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**Figure 6.** Wear track line scan.

**Figure 7.** SEM micrographs of the scratched and unscratched surface of the samples. The dotted line indicates the boundary of the wear tracks: (a) unimplanted, (b) implanted without the conducting grid, and (c) implanted with the conducting grid.
number of pores on the scratched surface are smaller than those on the unscratched surface. It is not surprising that wear debris are flattened after sliding and this is the reason why the surface shows smaller and less numerous pores since spalling may fill the pores and reconstruction may ensue. In general, microabrasion and microfracture occur during the sliding test. For the sample implanted without the grid [Fig. 7(b)], surface flattening is also observed after the grinding test. Moreover, materials are abraded from the steel ball and a certain amount sticks onto the surface but the size of the “lifted-off” objects is quite small and some of the ceramic surface has also been removed. On the contrary, for the sample implanted with the grid [Fig. 7(c)], large debris lifted off from the ball can be found on the track, and energy dispersive x-ray analysis reveals the presence of Fe on the scratched surface but not on the unscratched surface. Our data thus indicate that debris from the steel ball adhere onto the track surface during the test.

Based on the empirical results, it appears that there are different modes of wear due to the dissimilar surface nature such as compressive stress induced by implantation. After carbon implantation, the surface hardness is enhanced and the wear resistance is increased since the friction coefficient is partially related to the surface hardness. The unimplanted sample with the lowest hardness shows the widest and deepest wear grooves thereby indicating an abrasive mechanism. For the sample implanted without the conducting grid, the carbon ions only receive a low energy and deposition is more likely on the surface thereby forming a thin layer. In comparison, the carbon ions are accelerated to high bombardment energy into the sample covered with the grid. Both implanted samples exhibit improvement in the surface hardness and friction but due to a different mechanism. The results acquired from the sample implanted without the grid suggests mainly abrasive wear combined with some adhesive wear indicated by the fine debris on the track surface from the steel ball. The results obtained from the sample implanted with the grid suggest a predominantly adhesive mechanism since a large amount of debris abraded from the steel ball land on the wear track. The difference in the wear mechanism and improved wear behavior can be attributed to the enhancement in the implantation energy with the use of the conducting grid.

IV. CONCLUSION

The hardness and tribological properties of carbon plasma implanted SiC ceramics are enhanced. The improvement is more substantial when the mesh-assisted approach is adopted. There is 40 to 60% improvement in the surface hardness and the friction coefficients are dramatically reduced from $\mu = 0.31$ to 0.19 after carbon PIII. Our results suggest that the degree of enhancement depends on the implantation energy and the wear resistance mechanism is different for the treated samples. When mesh-assisted PIII is adopted, the ion energy increases and the wear mechanism changes from predominantly abrasive to adhesive.

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