Influence of nitrogen ion implantation fluences on surface structure and tribological properties of SiC ceramics in water-lubrication

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ABSTRACT

Nitrogen ions were implanted into SiC ceramics by using ion implantation technology (N⁺-SiC). The surface structure and chemical bonds of N⁺-SiC ceramics were determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and their nanohardness was measured by nanoindenter. The friction and wear properties of the N⁺-SiC tribo-pairs were investigated and compared with those of SiC/SiC tribo-pairs in water using ball-on-disk tribo-meters. The wear tracks on the N⁺-SiC ceramics were observed by non-contact surface profilometer and scanning electron microscope (SEM) and their wear volumes were determined by non-contact surface profilometer. The results show that the N⁺-SiC ceramics were mainly composed of SiC and SiCN phase and Si–N, C–C, C–N bonds were formed in the implantation layer. The highest hardness of 22.3 GPa was obtained as the N⁺-SiC ceramics implanted at 50 keV and 1 × 10¹⁷ ions/cm². With an increase in nitrogen ion fluence, the running-in period of N⁺-SiC/SiC tribo-pairs decreased, and the mean stable friction coefficient decreased from 0.049 to 0.024. The N⁺-SiC ceramics implanted at 50 keV and 5 × 10¹⁷ ions/cm² exhibited the excellent tribological properties in water. In comparison of SiC/SiC ceramic tribo-pairs, the lower friction coefficient and lower wear rate for the N⁺-SiC/SiC tribo-pairs were acquired.

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1. Introduction

If the water-lubrication system can be used to replace the oil-lubrication system in modern machine designs, the problems of environmental pollution and resource shortages will be greatly improved [1]. However, water-lubrication systems present some technical problems for metallic materials, such as lubricity, corrosion and reliability. The recent technical approach to water-lubrication systems is to use engineering ceramics or plastics. Due to insufficient strength and microstructure ageing, engineering plastics could not be applied to water-lubrication systems for longer period of time [2]. Since a very low friction coefficient (<0.002) was found in water-lubricated friction Si₃N₄ sliding against itself with pin-on-disk apparatus [3], Si-based non-oxidation ceramic water-lubrication has already shown the low friction coefficient (<0.05) when the steady-state friction coefficient is obtained) of a-CNₓ coatings deposited on SiC disk, the running-in period (the sliding distance or cycles when the steady-state friction coefficient is obtained) of a-CNₓ/SiC tribo-pair was shorter than that of SiC/SiC tribo-pairs and the wear resistance of SiC ball in water was better than that of SiC/SiC tribo-pair in water [11,12]. When the a-CNₓ coatings slid...
against SiC balls at 5 N and 0.16 m/s in water, the lower friction coefficient of 0.01–0.02 was achieved [13,14], and then the wear mechanism map of the a-CN/SiC tribo-pair in water was established [15]. Under the same frictional conditions, the friction and wear properties of the a-CN/SiC tribo-couple in water are superior to those of the a-C/SiC tribo-pair [14]. Although the above reviews suggest that the a-CN/SiC tribo-pair is the promising candidate for the sliding part in water hydraulic systems, the delamination of the a-CN coatings from SiC substrates was observed at lower sliding speed and higher normal load [15]. As compared with the deposition of surface coatings, the ion implantation was another method to modify the surface characteristics of SiC ceramics. When the SiC ceramic surface was implanted by nitrogen ions, the friction coefficient for N⁺-SiC/steel tribo-pair decreased from 0.60 to 0.20 [16] and the surface hardness of SiC ceramics was enhanced [17]. Thus, it is expected that the running-period of the SiC/SiC tribo-pair was expected to decrease via implanting nitrogen ions into SiC ceramics. However, the friction and wear behavior of N⁺-SiC ceramics has not been investigated in water-lubrication. Thus, the purpose of this paper was to investigate the influence of nitrogen ion implantation fluence on the tribological properties of SiC ceramics in water-lubrication and discuss the wear mechanism of N⁺-SiC ceramics.

2. Experimental procedures

The reactive sintered polycrystalline SiC ceramic disks (Ø 30 mm × thickness 4 mm) were supplied by Shanghai Institute of Ceramics, Chinese Academy of Science, and their physical properties were tabulated in Table 1. The SiC ceramics’ surfaces were polished to the average roughness of 44 nm. Prior to ion implantation, the samples were ultrasonically cleaned in ethanol for 10 min. The samples were implanted with nitrogen ions by using a multifunctional ion implantation and deposition apparatus. The samples were placed into chamber, and the working vacuum pressure in the chamber was 1.0 × 10⁻² Pa. The diameter for implanted area was 100 mm. The implantation was carried out at energy of 50 keV at the ions implantation fluence in the range of 1 × 10¹⁷ to 10 × 10¹⁷ ions/cm². During the ion implantation, the beam current was 1.7 mA, and the temperature was 300 °C.

To characterize the microstructure and phases formed upon implantation, the surface phases of the as-implanted SiC ceramics were investigated by using D8-Advance X-ray diffraction (XRD) (Bruker, Germany), and the chemical bonding of the N⁺-SiC ceramics were analyzed by using Thermo ESCALAB 250 X-ray photoelectron spectroscopy (XPS).

The surface roughness of tribomaterials such as SiC balls (Ø 3 mm), SiC disks and the N⁺-SiC disk was measured by using a MicroXAM™ non-contact optical profilometer (ADE Phase-Shift, USA), respectively. To obtain the surface roughness accurately, at least five measurement tests were carried out for each specimen. The mechanical properties of SiC balls were acquired from the balls’ manufacturer, whereas the mechanical properties of the N⁺-SiC ceramics were evaluated using a SA2 nanoindentation hardness tester (MTS, USA) with a Berkovich-type diamond indenter.

The friction tests were performed on a ball-on-disk apparatus which consisted of rotating disk sliding against a stationary ball at 0.20 m/s and 1.8 N. The rubbing surfaces were submerged in distilled water at room temperature. The total sliding distance was 10,000 m. The friction forces were detected by a LMA-A-10N load cell (Kyowa Co. Ltd., Japan). The load cell voltage was measured by a DPM-700B strain amplifier (Kyowa Co. Ltd., Japan) and recorded by NR-110/150 data collection system (Keyence Co. Ltd., Japan) with a compatible personal computer. The diameter of SiC ball’s wear scar under each condition was measured using optical microscope. The cross-section area, A, of wear track on the disk was determined using a MicroXAM™ non-contact optical profilometer (ADE Phase-Shift, USA). Thus, the specific wear rates for balls and disk were calculated using the following equation:

\[ w_{s,b} = \frac{3.14d^4}{64RWL} \]  \hspace{1cm} (1)

\[ w_{s,d} = \frac{2\pi r A}{WL} \]  \hspace{1cm} (2)

where R is the ball radius, d is the diameter of the ball wear scar, r is the disk wear track radius, W is normal load and L is total sliding distance.

<table>
<thead>
<tr>
<th>Name</th>
<th>Density (g/cm³)</th>
<th>Bending strength (GPa)</th>
<th>Compress strength (GPa)</th>
<th>Thermal conductive coefficient, (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>3.12</td>
<td>388</td>
<td>1.93</td>
<td>98.3</td>
</tr>
</tbody>
</table>

Fig. 1. Influence of nitrogen ion implantation fluences on the X-ray patterns of N⁺-SiC ceramics at 50 keV.
distance. Moreover, the wear track on the disk was observe using JEOL-JSM-7001F FE-SEM.

3. Results and discussion

3.1. Microstructure and chemical bonds of N\(^+\)-SiC ceramics

Fig. 1 shows the influence of nitrogen ion implantation fluences on the X-ray patterns of N\(^+\) implanted SiC ceramics at 50 keV. It is obvious that the surface microstructure of SiC ceramics was composed of SiC and SiCN phases. When the nitrogen ion implantation fluence increased, the diffraction peak intensity of SiCN compound became higher. This indicates that the nitrogen ion reacted with SiC to form SiCN/SiC composite microstructure on the SiC ceramics surface. Figs. 2–4 illustrated wide-scan peaks, Si\(_{2p}\), C\(_{1s}\) and N\(_{1s}\) peaks for XPS spectra at various nitrogen ion implantation fluences. The wide-scan XPS spectra in Figs. 2(a)–4(a) of the N\(^+\) implanted SiC ceramics showed the presence of C, N, Si, and a small amount of O in the implanted layer. The effect of oxygen is neglected because the oxygen peaks centered at 533 eV is very weak and almost disappeared after sputtering with Ar\(^+\) ions. To know the possible chemical bonding configurations of nitrogen doped into the network of silicon carbide, the individual Si\(_{2p}\), C\(_{1s}\) and N\(_{1s}\) lines were deconvoluted into Gaussian line shapes. When the SiC ceramics were implanted by nitrogen ions generated at 50 keV and 1.0 \(\times 10^{17}\) ion/cm\(^2\), the deconvoluted Si\(_{2p}\) spectra of the N\(^+\)-SiC ceramics showed the presence of C, N, Si, and a small amount of O in the implanted layer. The effect of oxygen is neglected because the oxygen peaks centered at 533 eV is very weak and almost disappeared after sputtering with Ar\(^+\) ions.

To know the possible chemical bonding configurations of nitrogen doped into the network of silicon carbide, the individual Si\(_{2p}\), C\(_{1s}\) and N\(_{1s}\) lines were deconvoluted into Gaussian line shapes. The Si\(_{2p}\) core level line in the XPS spectra, there are four peaks at 283.1, 285, 286.7 and 288.3 eV, and the deconvoluted N\(_{1s}\) spectra also displayed the binding energy of 101.9 and 103.25 eV in Fig. 2(b) were assigned to Si–N and Si–O bonds, respectively. As seen in Fig. 2(c) and (d), the deconvoluted C\(_{1s}\) spectra exhibited three peaks at the binding energies of 285.1, 286.8 and 288.9 eV, while the deconvoluted N\(_{1s}\) spectra displayed two peaks at the binding energy of 398.6 and 400.7 eV. Scharf et al. [19] reported that, for the a-CN\(_{0.14}\) coatings, the peaks at binding energies of 284.5, 285.2, 286.5 and 288.6 eV for the deconvoluted C\(_{1s}\) spectra were attributed to C–C, C–N/C–C, C–N, and C–O bonds, respectively, while the peaks at 398.6, 400.1 and 402.3 eV for the N\(_{1s}\) line were assigned to C–N, C–N and N–O bonds, respectively. In comparison of the data of Refs. [20,21], the peaks at 285.1, 286.8 and 288.9 eV in Fig. 2(c) were assigned to C–C/C–C, C–N and C–O bonds, respectively, while the peaks at 398.6 and 400.7 eV in Fig. 3(d) were marked as C–N/N–Si and C–N bonds. If the nitrogen ions implantation was performed at 5.0 \(\times 10^{17}\) ion/cm\(^2\), the Si\(_{2p}\) spectrum can be fitted as three peaks at 101.3, 102.2 and 103.3 eV which are attributed to Si–C, Si–N and Si–O bonds, respectively (Fig. 3(b)). For the C\(_{1s}\) core level line in the XPS spectra, there are four peaks at 283.3, 285, 286.6 and 288.3 eV. It is obvious from Ref. [20] that the binding energies at 283.3 is assigned to Si–C, whereas the binding energies at 285.2, 286.6 and 288.3 eV are related to C–C/C–C, C–N and N–O bonds, respectively. The deconvoluted N\(_{1s}\) spectra displayed three peaks at the binding energy of 398, 400.7 and 402.9 eV, which are attributed to C–N/N–Si, C–N, N–O bonds, respectively. When the SiC ceramics were implanted at 50 keV and 1.0 \(\times 10^{18}\) ion/cm\(^2\), the deconvoluted Si\(_{2p}\) spectra show three peaks at binding energies of 100.9, 101.8 and 102.8 eV which are assigned to Si–C, Si–N and Si–O bonds (Fig. 4(b)). As seen in Fig. 4(c) and (d), the deconvoluted C\(_{1s}\) spectra exhibited four peaks at the binding energies of 283.1, 285, 286.7 and 288.3 eV, and the deconvoluted N\(_{1s}\) spectra also displayed...
four peaks at the binding energy of 397.6, 398.7, 400.4 and 402 eV. As above-mentioned, the peaks at 283.1, 285, 286.7 and 288.3 eV in Fig. 4(c) were assigned to Si–C, C–C/C\textsubscript{N}, C–N and C–O bonds, respectively. For the N\textsubscript{1}s core level line in the XPS spectra, the peak at 397.6 eV is due to the nitrogen in the bulk Si\textsubscript{3}N\textsubscript{4}. The two contributions, which are at 398.7 and 400.4 eV, are observed in a typical CN\textsubscript{x} film. These binding energies of 398.7 and 400.4 eV are due to sp\textsuperscript{3} and sp\textsuperscript{2} bonds between carbon and nitrogen, respectively. The binding energy of 402 eV is due to N–O bonds. The appearance of Si–O, C–O and N–O bonds displayed that the coatings’ surface was contaminated by oxygen from air. To elucidate the influence of nitrogen ion implantation fluence on the surface chemical bonds of the N\textsuperscript{+-}SiC ceramics, the variation of chemical bonds relative percentage with nitrogen ion implantation fluence was illustrated in Fig. 5. With an increase in the nitrogen ion implantation fluence, the relative percentage of chemical bonds such as Si–O, C–O and N–O increased, while that of C–C/C\textsubscript{N} bond decreased. But for Si–N and C–N bonds, their relative percentage fluctuated slightly at the ion implantation fluence lower than 5.0 × 10\textsuperscript{17} ions/cm\textsuperscript{2}, and then increased markedly. But the relative percentage of N–Si/N–C bonds first increased obviously to peak value, then decreased rapidly. Furthermore, it is clear from Fig. 5 that the main chemical bonds on the implantation layer were C–C/C–N, C–N and Si–N bonds. This indicates that the Si–C bonds were broken by the high energetic nitrogen ions during implantation, and then the formation of C–C/C–N, C–N and Si–N bond was occurred simultaneously. If we consider the above-mentioned data, we could conclude that the surface structure of the N\textsuperscript{+-}SiC ceramics has changed from SiC to SiCN/SiC.

### 3.2. Surface roughness and mechanical properties of N\textsuperscript{+-} SiC ceramics

As seen in Table 2, the arithmetic mean roughness R\textsubscript{a} of N\textsuperscript{+-}SiC ceramics was higher than that of unimplanted SiC substrate, and increased from 44 to 53.6 nm as the nitrogen ion implantation fluence lower than 5 × 10\textsuperscript{17} ions/cm\textsuperscript{2}. If the nitrogen ion implantation fluence was 1 × 10\textsuperscript{18} ions/cm\textsuperscript{2}, the surface roughness decreased a little to 49.3 nm. This indicates that the surface self-assembly mechanism for nanoboulder growth occurred. During nitrogen ion implantation, the nucleation and growth of new metastable phase was occurred by ion-beam-enhanced diffusion of N, C and Si across the surface. This would lead the surface roughness increasing. Furthermore, the surface nanohardness of SiC ceramics was 17.7 GPa, while that of N\textsuperscript{+-}SiC at 1 × 10\textsuperscript{17} ions/cm\textsuperscript{2} increased to 22.3 GPa. The results from XPS analysis show that silicon atoms could maintain carbon-to-nitrogen bonds in sp\textsuperscript{3} configuration instead of sp\textsuperscript{2} hybrids as nitrogen ion was implanted into SiC. Thus, nitrogen ion implantation could enhance the surface hardness of SiC ceramics. But it is clear from Table 2 that the surface nanohardness of N\textsuperscript{+-}SiC decreased with an increase in the nitrogen ion implantation.

<table>
<thead>
<tr>
<th>Specimens H (GPa)</th>
<th>R\textsubscript{a} (nm)</th>
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<tbody>
<tr>
<td>SiC</td>
<td>17.7 ± 4.4</td>
</tr>
<tr>
<td>50 keV, 1 × 10\textsuperscript{17} ions/cm\textsuperscript{2}</td>
<td>22.3 ± 6.2</td>
</tr>
<tr>
<td>50 keV, 5 × 10\textsuperscript{17} ions/cm\textsuperscript{2}</td>
<td>19 ± 4.8</td>
</tr>
<tr>
<td>50 keV, 1 × 10\textsuperscript{18} ions/cm\textsuperscript{2}</td>
<td>15.4 ± 4.2</td>
</tr>
</tbody>
</table>
Fig. 4. XPS spectra of wide scan peak (a), Si2p photoelectron peaks (b), C1s photoelectron peaks (c) and N1s photoelectron peaks (d) for SiC ceramics implanted with N\(^+\) ions at 50 keV and 1.0 \(\times\) 10\(^{18}\) ion/cm\(^2\).

Fig. 5. Influence of ion implantation fluences on the chemical bonds’ relative percentage of N\(^+\)-SiC ceramics.
et al. [17] have reported the phenomenon results from the formation of bubbles below the Si–C–N compound with high ion fluence.

3.3. Sliding friction and wear properties of N⁺-SiC ceramics in water

Fig. 6(a) showed the variation of friction coefficients for the N⁺-SiC/SiC tribo-pairs in water at 0.20 m/s with sliding distance at various ion implantation fluence. As seen in Fig. 6(a), the initial friction coefficient for the N⁺-SiC/SiC tribo-pair was 0.26 or so, a little higher than that of the SiC/SiC tribo-pair. For the SiC/SiC tribo-pair, the friction coefficient first decreased gradually from a higher initial value (0.25) to 0.049 as the running-in period was shorter than 5000 m. With further sliding, the friction coefficient fluctuated around 0.047 with a little variation. When the nitrogen ion implantation fluence was \(10^{17}\) ions/cm², the friction coefficient of the N⁺-SiC/SiC tribo-pairs first decreased linearly from 0.255 to 0.036 with sliding distance shorter than 4500 m, and then varied around 0.035 with further sliding. If SiC ceramic was implanted by nitrogen ion at \(5 \times 10^{17}\) ions/cm², the friction coefficient first decreased rapidly from 0.27 to 0.04 at the running-in period shorter than 1520 m. Then, the friction coefficient decreased slightly from 0.04 to 0.018 with an increase in sliding distance. As the nitrogen ion fluence was \(10^{18}\) ions/cm², the friction coefficient of the N⁺-SiC/SiC tribo-pairs first decreased suddenly from 0.26 to 0.03 as the running-in period shorter than 3000 m, and then fluctuated around 0.025 with further sliding. Fig. 6(b) exhibited the influence of nitrogen ion implantation fluence on the mean stable friction coefficient \(\mu_m\) after running-in in water. When the ion fluence was lower than \(5 \times 10^{17}\) ions/cm², the mean steady-state friction coefficients decreased markedly from 0.049 to 0.024. Whereas the mean steady-state friction coefficients varied a little in the range of 0.24–0.025 as the ion fluence higher than \(5 \times 10^{17}\) ions/cm². The above-mentioned results indicated that the nitrogen ion implantation could shorten the running-in period of SiC/SiC tribo-pairs and improve the water-lubricated characteristics of self-mated SiC tribo-pairs.

3.4. Observation of worn surface on disk at various ion fluences

Fig. 7. Influence of ion implantation fluences on wear rates of N⁺-SiC ceramics/SiC tribo-pairs in water.

At a constant sliding speed of 0.20 m/s, the variation of the specific wear rates for tribomaterials with ion implantation fluence was illustrated in Fig. 7. It is clear that the specific wear rates of SiC balls first decreased markedly from \(1.5 \times 10^{-6}\) to \(0.25 \times 10^{-6}\) mm³/Nm at \(5 \times 10^{17}\) ions/cm², then increased slightly to \(0.66 \times 10^{-6}\) mm³/Nm. This indicated that the N⁺-SiC ceramics implanted at 50 keV and \(5 \times 10^{17}\) ions/cm² exhibited the excellent tribological properties in water. The friction and wear behavior difference between the SiC/SiC and the N⁺-SiC/SiC tribo-pairs indicated that the nitrogen incorporation had some influences on the wear mechanism of SiC ceramics in water.
SiC ceramics at $1 \times 10^{17}$ ions/cm$^2$, the wear track surface exhibited smooth surface and some pits besides some original voids (Fig. 9(b)), which was similar to that of SiC (Fig. 9(b)). When the ion fluence increased to $5 \times 10^{17}$ ions/cm$^2$, there were many original scratch lines on the smooth wear track surface, and the shallower grooves and pits were observed (Fig. 9(c)). If SiC ceramics implanted by nitrogen ions were performed at $1 \times 10^{18}$ ions/cm$^2$, the wear tracks displayed many deeper grooves and larger size voids on the surface (Fig. 9(d)). This indicated the wear mechanism was mix of mechanical wear and tribochemical wear and the nitrogen ion implantation fluence would influence the ratio of between mechanical wear and tribochemical wear.

Fig. 8. Influence of ion implantation fluences on three-dimensional and sectional morphologies of wear track on N+-SiC ceramics: (a) and (b) SiC, (c) and (d) $1 \times 10^{17}$ ions/cm$^2$, (e) and (f) $5.0 \times 10^{17}$ ions/cm$^2$, (g) and (h) $1.0 \times 10^{18}$ ions/cm$^2$. 
3.5. Discussion

From a tribological standpoint, one can argue that the extent of friction between two sliding surfaces is largely governed by the physical condition of the contacting interface and the extent of chemical interactions between the sliding interfaces and the environment. Physically, rough surfaces can create higher plowing and hence high friction. As seen in Table 2 and Fig. 6(a), the surface roughness of N+-SiC ceramics was higher than that of SiC disk. Thus, the initial friction coefficient of N+-SiC/SiC tribo-pair was higher than that of SiC/SiC tribo-pair. As the surface roughness diminished through running-in wear, the friction coefficient for two kinds of tribo-pairs decreased.

Moreover, chemical interactions between two sliding surfaces and water can play more important role in the friction and wear behavior of N+-SiC ceramics in water. The large difference in friction and wear behaviors between N+-SiC/SiC and SiC/SiC system suggested that their lubrication and wear mechanism be different. It is clear that the difference of running-in period between SiC and N+-SiC could be attributed to their energy gap difference [22]. The smaller the energy gap between both reagents, i.e. the higher the reaction rate is. As seen in Figs. 2–5, it is obvious that the network of sp2-bonded C and Si linked by threefold-coordinated N atoms was formed by nitrogen ion implantation, and the concentration of Si–N bonds increased on the surface of N+-SiC ceramics [17]. Although the energy gap of SiC and Si(C)3N4 is small compared with water, the difference of energy gap between Si(C)3N4 and water is 3.0 (1.25) eV but that between SiC and water is 5.2, so the reaction rate between Si(C)3N4 and water is higher than that between SiC and water [11]. This indicated that the nitrogen ion implantation would have more acceleration effects on the tribocohemical reaction during sliding in water. For the SiC(N+)/SiC tribo-couples in water, the wear rate of N+-SiC ceramic was lower than that of SiC ceramic. This indicated that the tribocohemical reaction of N+-SiC in water occurred easily. Thermodynamic calculations of the phase equilibrium within the interface showed that water did not react with SiC or Si3N4 in the presence of oxygen. Since the water was saturated with oxygen and oxygen was therefore present in the tribo-contact, the following Eqs. (3) and (4) most likely took place. $\Delta G_f^{298}$ is the Gibbs free energy of formation at 298 K.

$$\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2, \quad \Delta G_f^{298} = -589 \text{ kJ/mol} \tag{3}$$

$$\text{Si}_3\text{N}_4 + 3\text{O}_2 \rightarrow 3\text{SiO}_2 + 2\text{N}_2, \quad \Delta G_f^{298} = -1779.4 \text{ kJ/mol} \tag{4}$$

From Eqs. (3) and (4), it is clear that the formation of SiO2 film which evolved from Si3N4 was expected to be more rapid than SiC tribo-pairs. The oxides could be hydrated by association with an undetermined amount of water molecules to form SiO2-h2O gels. Such films have been described specifically in the wear experiments of SiC/SiC and Si3N4/Si3N4 tribo-couples running-in moist air [3]. For SiO2, a subsequent dissolution reaction in the tribo-contact would also be expected to occur:

$$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4, \quad \Delta G_f^{298} = -237 \text{ kJ/mol} \tag{5}$$

If the hydration reaction between Si3N4 or SiC ceramic and water occurred directly, we could calculate from Eqs. (6) and (7) that silicon nitride was more easily hydrated than silicon carbide.

$$\text{SiC} + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + \text{CH}_4, \quad \Delta G_f^{298} = -598.91 \text{ kJ/mol} \tag{6}$$

$$\text{Si}_3\text{N}_4 + 12\text{H}_2\text{O} \rightarrow 3\text{Si(OH)}_4 + 4\text{NH}_3, \quad \Delta G_f^{298} = -1268.72 \text{ kJ/mol} \tag{7}$$

where $\Delta G_f^{298}$ is the reaction Gibbs free energy of formation at 298 K. From Eqs. (4) and (6), we could conclude that silicon nitride was more easily hydrated than silicon carbide. This indicates that the tribocohemical wear easily occurred for N+-SiC, which caused the running-in period of N+-SiC/SiC tribo-pairs being lower than
that of self-mated SiC tribo-pairs. Thus, the N⁺-SiC/SiC tribo-pairs exhibited the lower fiction coefficient and lower wear rate in water-lubrication.

4. Conclusions

The influences of nitrogen ions implantation fluence on the friction and wear property of SiC ceramics in water have already been investigated in detail. The main results could be summarized as:

1. The N⁺-SiC ceramics were mainly composed of SiC and SiCN phase, and Si–C, Si–N and C–N bonds were formed. The highest hardness of 22.3 GPa was obtained as SiC implanted at nitrogen ions fluence of $1 \times 10^{17}$ ions/cm².
2. With an increase in nitrogen ion fluence, the running-in period of N⁺-SiC/SiC tribo-pairs decreased, and the mean stable friction coefficient decreased from 0.049 to 0.024.
3. The specific wear rate of tribomaterials for N⁺-SiC/SiC tribo-pairs first decreased to minimum vale, and then increased a little with the nitrogen ion fluence increasing. The N⁺-SiC ceramics implanted at 50 keV and $5 \times 10^{17}$ ions/cm² exhibited the excellent tribological properties in water.

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References