Tribological properties of a-CNx coatings sliding against SiC balls in ethylene glycol aqueous solution

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ABSTRACT

Amorphous carbon nitride(a-CNx) coatings were deposited on SiC disks by using ion beam assisted deposition, and their bonding structure and hardness were determined using X-ray photoelectron spectroscopy and nano-indenteter, respectively. The contact angles on the surface of the a-CNx coatings were measured with contact angle meter. The friction and wear behaviours of the a-CNx/SiC tribopairs in ethylene glycol aqueous solution were investigated with ball-on-disk tribometer. The results indicated that the a-CNx coatings contained 12at. % nitrogen and their bonding structure consisted of sp2C=N/C=C and sp3C–N bonds. The static contact angles on the a-CNx coatings decreased with the ethylene glycol concentration. The lowest coefficient of friction of 0.019 was acquired as the ethylene glycol concentration was 10vol. %. When the ethylene glycol concentration increased, the specific wear rate of the SiC ball fluctuated in the range of $5.9 \times 10^{-10}$ to $1.1 \times 10^{-9} \text{ mm}^3 \text{ Nm}^{-1}$, while that of a-CNx coatings varied in the range of $3.3 \times 10^{-8}$ to $7.8 \times 10^{-8} \text{ mm}^3 \text{ Nm}^{-1}$.

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INTRODUCTION

To reduce the amount of CO2 evolution and protect the natural environment, water lubrication has already been suggested for replacing oil lubrication in modern machine designs. Water lubrication systems, however, have some tribological problems, such as high friction, high wear and seizures. To overcome the abovementioned problems, it is imperative to develop the new tribo materials to meet the requirements of modern machine designs in water environment. A recent technical approach to this tribological problem is to use high-performance materials such as Si-containing ceramics or engineering plastics. Due to insufficient strength and microstructure ageing, engineering plastics could not be applied.
to water lubrication system for longer period of time. Although the Si₃N₄/Si₃N₄ and SiC/SiC tribo-couples in water all possess low friction coefficient (≤0.01), severe wear is easily observed for the self-mated SiC(Si₃N₄) tribo-pair in water due to the longer running-in period for SiC/SiC tribo pairs in water and the easy occurrence of hydration reaction between SiC(Si₃N₄) and water. An alternative approach is to take advantage of the hard coatings with good lubricity in water environment.

Currently, the water lubrication of carbon-based coatings such as diamond-like carbon and amorphous carbon nitride has recently been concerned. Ronkainen H et al. have indicated that as far as the DLC coatings’ performance in aqueous conditions was concerned, H was detrimental, while Ti or Si was useful whereas Tanaka A et al. reported that the additive elements such as H, Ar, F and Si have no apparent effect on the friction and wear properties of DLC coatings in water. Recently, the a-CNₓ coatings have been found to enhance the wear resistance of SiC ball at lower or higher velocities in water lubrication. When the a-CNₓ coatings slide against SiC or Si₃N₄ balls at 5 N and 0.16 m s⁻¹ in water, the low coefficient of friction of 0.01–0.02 is achieved, and then the wear mechanism maps of the a-CNₓ/SiC(Si₃N₄) tribo pairs in water have been established. Under the same frictional conditions, the friction and wear properties of the a-CNₓ/SiC tribo-couple in water are superior to those of the a-C/SiC tribo-pair. The above reviews indicate that the carbon-based coatings are the very promising candidates of the sliding parts’ coatings in water.

As is known, the ethylene glycol aqueous solution is always used as coolant or hydraulic liquid. However, the friction and wear properties of the a-CNₓ/SiC tribopair in the ethylene glycol aqueous solution have not yet been studied. The aim of this study is to investigate the tribological properties of the a-CNₓ/SiC tribopair in ethylene glycol aqueous solution by using ball-on-disk tribometer at room temperature and discuss the influence of ethylene glycol concentration on the friction and wear behaviours of the a-CNₓ/SiC tribopair.

**EXPERIMENTAL DETAILS**

The ion beam assisted deposition (IBAD) machine (Hitachi Ltd, Ibaraki, Japan) was used to deposit the a-CNₓ coatings. Prior to IBAD process, SiC disks (Φ30 mm × t 4 mm) were ultrasonically cleaned in acetone and ethanol for 30 min. A carbon target with purity of 99.99% was put into the electron beam evaporator and a substrate jig with SiC disk was joined to the substrate holder with two screws. Subsequently the vacuum chamber was closed and evacuated to lower than 2.0 × 10⁻⁴ Pa. For further cleaning, the deposited surface was bombarded for 5 min by nitrogen ions generated at an accelerated voltage (a.v.) of 1.0 kV and an accelerated current density (a.c.d.) of 100 μA cm⁻². Later, carbon was heated and evaporated using an electron beam evaporator, and the a-CNₓ coating was synthesised by reaction between carbon vapour and energetic N ions. The energetic nitrogen ions were produced at 1.5 kV (a.v.) and 90 μA cm⁻² (a.c.d.). The evaporation rate of carbon target was 2 nm s⁻¹ via adjusting the carbon vapour emission current. The coating thickness was 0.5 μm. The deposition parameters are listed in Table I.

The coatings’ surface roughness was measured by using Surfcom-1500DX profilometer (Tokyo, Japan). The radius of diamond tip was 2 μm and the contact force between tip and coatings’ surface was 0.75 mN. The tip moving velocity was 0.03 mm s⁻¹ and the amplification ratio of Z-axis was 10000. To obtain the accurate surface roughness, at least five measurement tests were carried out for one specimen. A commercial nano-indentation hardness tester, ENT-1100a, produced by Elionix Co Ltd (Tokyo, Japan) was used to evaluate the nanohardness of the a-CNₓ coatings. Tests were...
performed using a Berkovich-typed diamond indenter. The maximum load was 980 μN. The time for loading and unloading was the same and fixed to 10 s, thus, the loading/unloading rate was 98 μN s⁻¹. The holding time at the maximum load was 1 s. The projected contact area was determined from the tip-shaped polynomial function of the contact depth at maximum indentation load. The reduced elastic modulus is given by \( \frac{1}{E_r} = \frac{(1 - \nu_i^2)}{E_i} + \frac{(1 - \nu_s^2)}{E_s} \) where \( E_i, E_s, \nu_i, \nu_s \) are the elastic modulus and Poisson’s ratio for the indenter and the substrate materials, respectively. For a diamond indenter material, \( E_i \) is 1050 GPa and \( \nu_i \) is 0.1. The Oliver-Pharr method is used to calculate the hardness and reduced modulus values from loading–unloading curves. The results were tabulated in Table II.

The chemical bonding states of the a-CN coatings were investigated by X-ray photoelectron spectroscopy (XPS). The XPS analysis was performed using a Physical Electronics Quantum 2000 Scanning ESCA microprobe (Eden Prairie, Minnesota, USA). The spectrometer was equipped with a hemispherical electron analyser and a 25.1 W AlKα (\( E = 1486.6 \) eV) X-ray source with a 1000 nm beam diameter. The angle between the X-rays and the sample normal was 45°. The pressure in the ion-pumped analysis chamber was blow \( 1.6 \times 10^{-7} \) Pa during data acquisition. The C1s and N1s
spectra were recorded at pass energy of 58.70 eV, respectively. The core-level binding energies (BE) were referenced to the C1s line at 284.8 eV due to adventitious carbon contamination. The binding energy values of the photoelectron peaks were measured with an accuracy of ±0.2 eV.

The surface wetting angle of aqueous solution on the a-CNx coatings was measured with the sessile drops method. A drop of distilled water and ethylene glycol aqueous solution was applied automatically to the a-CNx surface using a micro-pipette in the contact angle meter (SL200B, SOLON TECH, Shanghai, China) at 25 ± 1°C with 67 ± 2% relative humidity. Images of the drop in contact with the a-CNx surface were continuously captured at full video speed. Wetting was measured as contact angle, which is formed by the substrate and the tangent to the surface of the liquid droplet at the contact point.

The friction tests were performed on a ball-on-disk apparatus (Figure 1) which consisted of rotating disk sliding against a stationary ball at 0.15 m s⁻¹ and 3 N. For SiC ball, its diameter and hardness were 8 mm and 22 GPa, respectively. According to the Hertzian contact theory, the maximum contact pressure was 1.15 GPa at the contact area between the a-CNx coating and SiC ball. Prior to each wear test, all samples were ultrasonically cleaned in acetone and ethanol for 30 min. The rubbing surface was submerged in the distilled water and ethylene glycol aqueous solution at room temperature. The total sliding distance was 3500 m. The wear scar diameter of SiC ball under each condition was measured using optical microscope. The cross-section area of wear track on the disk was determined using MicroXAM™ non-contact optical profilometer (ADE Phase-Shift, Tucson, USA). Thus, the specific wear rates for balls and coatings were determined using the following equations:

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

\[
w_{s,b} = \frac{2\pi rA}{WL} \quad (2)
\]

where \(R\) is the ball radius, \(d\) is the diameter of wear scar, \(r\) is the wear track radius, \(W\) is normal load and \(L\) is the sliding distance. The wear test was repeated for three times, and the wear rate in here was the mean value of wear rates thrice. The worn surfaces were observed using an optical microscope.
RESULTS AND DISCUSSION

Chemical bonding structure of a-CN$_x$ coatings

According to XPS analysis, the nitrogen content in the a-CN$_x$ coating was 12at. %. In order to know the chemical bonding configurations of nitrogen doped into the carbon network, the individual C1s and N1s lines were deconvoluted into Gaussian line shapes (Figure 2). As seen in Figure 2, the C1s line was deconvoluted into three peaks at binding energies of 285.1, 286.5 and 288 eV, and the N1s line was deconvoluted into four peaks at binding energies of 398.5, 400.3, 401.5 and 404 eV. Scharf et al.\textsuperscript{15} 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 C1s spectra were attributed to C=C, C=N, C–N and C–O bonds, respectively, while the peaks at 398.6, 400.1 and 402.3 eV for the N1s line were assigned to C–N, C=N and N–O bonds, respectively. In comparison to the abovementioned bonds, the peaks at 285.1, 286.5 and 288 eV in Figure 2a were assigned to C=N/C=C, C–N and C–O bonds, respectively, while the peaks at 398.5, 400.3, 401.5 and 404 eV in Figure 2b were marked as C–N, C=N and N–O bonds, respectively. The appearance of C–O and N–O bonds displayed that the coatings' surface was contaminated by oxygen from air. It was concluded that the sp$^3$ C–N and sp$^2$ C=N/C=C bonds were the major component in the a-CN$_x$ coatings.

Influence of solution concentration on wetting behaviour on a-CNx coatings

Actually, the contact angle measurement is a precise empirical tool to determine the interaction between a liquid (surface tension) and a substrate (surface free energy), but it should be indicated that contact angle is not a property of the liquid or the substrate but the interaction between the two, and that the wet ability in a contact system such as this type is due solely to van der Waals forces. Figure 3 shows the variation of contact angles for ethylene glycol aqueous solution on the a-CN$_x$ coatings with the concentration of ethylene glycol. With an increase in the concentration of ethylene glycol, the contact angles for the ethylene glycol aqueous solution decreased slightly from 79.5° to 60.5°. In

![Figure 2. XPS spectra of C1s and N1s photoelectron peaks for a-CN$_x$ coatings.](image-url)
fact, the carbon nitride coatings are hydrophilic, and the physisorption of the water seems to have a hydrogen-bonded mechanism, i.e. by the formation of hydrogen bonds between the water molecules and the nitrogen atoms of carbon nitride coatings as schematically shown in Figure 4.16 Furthermore, the surface tension of water at 298°K is 0.072 N m\(^{-1}\), higher than that of ethylene glycol (0.048 N m\(^{-1}\)).17 This indicated that the reduction of the contact angle with the solution concentration seemed merely due to the decrease in surface tension of solvent.

**Friction behaviour of a-CN/\textit{SiC} tribopair in aqueous solution with different concentrations**

Figure 5 showed the variation of friction coefficients for the a-CN/\textit{SiC} tribopair in the ethylene glycol aqueous solution at 0.15 m s\(^{-1}\) and 3 N with sliding distance. As seen in Figure 5, in the distilled
water, the coefficient of friction for the a-CN<sub>x</sub>/SiC tribopair was 0.087 initially, and then fluctuated around 0.033 with a little variation with an increase in sliding distance. When the ethylene glycol concentration was 10vol. %, the coefficient of friction of the a-CN<sub>x</sub>/SiC tribopair suddenly decreased from 0.09 to 0.025. After running-in, the coefficient of friction gradually decreased from 0.025 to 0.017 with further sliding. However, as the ethylene glycol concentration increased to 70vol. %, the stable coefficient of friction for the a-CN<sub>x</sub>/SiC tribopair fluctuated in the range of 0.03–0.04.

Influence of solution concentration on tribological behaviour of a-CN<sub>x</sub>/SiC tribopair

As shown in Figure 6a, the mean steady-state coefficient of friction first decreased from 0.033 to 0.019 at 10vol. %, and then fluctuated slightly in the range of 0.030–0.035 with an increase in the ethylene glycol concentration. Actually, when the ethylene glycol concentration increased, the surface tension of the ethylene glycol solutions decreased, while their viscosity increased. It was concluded that the thickness of lubrication film varied with the ethylene glycol concentration, which induced the variation of coefficient of friction. Figure 6b shows the specific wear rate of the a-CN<sub>x</sub>/SiC tribopair in ethylene glycol aqueous solution with different concentrations. When the ethylene glycol concentration increased, the specific wear rates of SiC ball decreased from $11.2 \times 10^{-10}$ mm<sup>3</sup> Nm<sup>-1</sup> to $5.9 \times 10^{-10}$ mm<sup>3</sup> Nm<sup>-1</sup>, whereas the specific wear rate of the a-CN<sub>x</sub> coatings first decreased from $7.8 \times 10^{-8}$ mm<sup>3</sup> Nm<sup>-1</sup> to $3.3 \times 10^{-8}$ mm<sup>3</sup> Nm<sup>-1</sup> as the ethylene glycol concentration was lower than 20vol. %, and then fluctuated in the range of $3.3 \times 10^{-8}$–5.7 $\times 10^{-8}$ mm<sup>3</sup> Nm<sup>-1</sup>. This indicated that ethylene glycol had more influences on the coefficient of friction and wear rate of the a-CN<sub>x</sub>/SiC tribopairs in aqueous solutions.

Influence of ethylene glycol concentration on wear track on a-CN<sub>x</sub> coatings

Figure 7 shows the sectional profiles of wear track on the a-CN<sub>x</sub> coatings as sliding against SiC ball at 0.15 m s<sup>-1</sup> and 3 N in different aqueous solutions. If the a-CN<sub>x</sub> coatings were slid against SiC ball
in the distilled water, the wear track on the a-CN$_x$ coatings became wide and shallow (Figure 7a). Looking at the wear track profiles (Figures 7b–e), the width actually decreased with the ethylene glycol concentration. First it increased for the water case, but then it reduced from 60 to 20 μm, finishing with just a local pits at 70 vol.-% glycol concentration. Figure 8 shows the influence of ethylene glycol concentration on the worn surfaces for SiC ball and a-CN$_x$ coatings. As seen in Figure 8, the diameter of wear scar on the SiC balls increased as the ethylene glycol concentration was lower than 30%, and then decreased slightly with an increase in the ethylene glycol concentration. Furthermore, the worn surface of the SiC balls became smooth and flat besides original voids, and the polished mirror surfaces were observed on the wear tracks of the a-CN$_x$ coatings. This indicated that ethylene glycol was beneficial to lubricating the friction surface and enhancing the wear resistance of the a-CN$_x$ coatings.

**DISCUSSION**

As far as ethylene glycol is concerned, it dissolves in water mutually. If the ethylene glycol was added into distilled water, the lowest coefficient of friction of 0.017 was obtained at 10 vol.-%, and the specific wear rate of SiC balls decreased slightly with increasing the ethylene glycol concentration. Generally, the friction behaviours at contact surface were largely governed by the physical condition of the contacting interface and the chemical interactions between the sliding interfaces and the environment. As the ethylene glycol was added into water, the worn surface of SiC balls became smooth and flat and the wear track surface of the a-CN$_x$ coatings became smooth and bright (Figure 8). This indicated that the tribochemical wear of the a-CN$_x$/SiC tribopair occurred in the ethylene glycol aqueous solution. Since water was saturated with oxygen and oxygen was, therefore, present in the tribocontact, the following equation (1) most likely took place. $\Delta G_f^{298}$ is the Gibbs free energy of formation at 298°K.

$$\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2^{18} \quad \Delta G_f^{298} = -589 \text{ kJ mol}^{-1}$$

Figure 6. Influence of ethylene glycol concentration on the coefficient of friction and specific wear rate for a-CN$_x$/SiC tribopairs in aqueous solutions at 0.15 m s$^{-1}$ and 3 N.
Figure 7. Influence of ethylene glycol concentration on the sectional profiles of wear track on the a-CN$_x$ coatings as sliding against SiC ball in aqueous solution at 0.15 m s$^{-1}$ and 3 N.

From equation (1), it is clear that the formation of SiO$_2$ film that evolved from SiC occurred on the friction surface.$^{2,3,18}$ The oxides could be hydrated by association with an undetermined amount of water molecules to form SiO$_2$·$x$H$_2$O gels. Such films have been described specifically in the wear experiments of SiC/SiC tribo-couples running in moist air.$^1$ For SiO$_2$, a subsequent dissolution reaction in the tribo-contact would also be expected to occur:
If ethylene glycol was added into water, SiO$_2$ would be reacted with alcohol and convertible into silicon esters, which were soluble in glycol by esterification occurring between SiO$_2$ and glycol:

$$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4$$

$$\Delta G_f^{298} = -237 \text{ kJ mol}^{-1}$$

(4)

Figure 8. Optical micrographs of worn surface on balls and disks in different ethylene glycol concentration aqueous solution.
This esterification proceeded by dissociative chemisorptions of ethylene glycol on SiO$_2$. Hibi et al.\textsuperscript{19} indicated that lower alcohol could easily approach a silicon atom during nucleophilic substitution and tribochemical wear was appreciable. As seen in Figure 3, the contact angles decreased with the content of ethylene glycol. This indicates that the surface tension of the solvent decreased. In fact, the viscosity of the solvent increased with the ethylene glycol concentration. If the ethylene glycol aqueous solution existed at the contact area as lubricant, the thickness of lubrication film increased with the ethylene glycol concentration. Actually, the lubrication mechanism of ceramics in aqueous solution was governed by the tribo-chemical reaction between tribomaterials and lubricant. If the tribo-chemical reaction occurred easily and the friction surface became smooth and flat, the lubrication mechanism was mix or hydrodynamic lubrication.\textsuperscript{2} Moreover, the amorphous carbon nitride coatings were hydrophilic, and the surface physisorption seemed to have a hydrogen-bonded mechanism by formation of hydrogen bonds between OH and nitrogen atoms.\textsuperscript{16} During sliding friction, the nitrogen atoms were removed easily form the a-CN$_x$ coating by reaction with OH in aqueous solution, which induced the a-CN$_x$ coating surface structure transformation. Zhou et al.\textsuperscript{12} have reported that the surface nitrogen concentration on the wear track for the a-CN$_x$ coating decreased and the intensity ratio between sp$^2$C=N/C=C and sp$^3$C–N on the wear track for the a-CN$_x$ coatings increased after sliding against SiC ball in water. This indicated that the surface structure of the a-CN$_x$ coating was transferred as rich sp$^2$C=N/C=C bonds. Matta et al.\textsuperscript{20} have studied the tribochemistry of at-C coatings in the OH-containing lubricants, and indicated that the low friction stripfilm was formed during friction by: (i) the hydroxylation of the top surface of the at-C coatings, and (ii) the formation of a low energy van der Waals interaction between the OH-terminated carbon film surface and the OH-terminated lubricant. Tanoak et al.\textsuperscript{7} have reported that the structure of transferred material was different from that of original DLC film and similar to that of polymer-like carbon, which was softer in comparison to DLC film. This indicated that the soft materials were easily formed on the a-C based coatings as sliding in aqueous solution. The tribofilms with low shear strength were responsible for the decrease of coefficient of friction and wear rate for the mating balls. This indicated that the wear mechanism of a-CN$_x$ coating/SiC ball was related to the formation of tribofilm with rich sp$^2$C=N/C=C bonds on the friction surface of the a-CN$_x$ coatings.

**CONCLUSIONS**

The friction and wear properties of the a-CN$_x$ coatings sliding against SiC ball in ethylene glycol aqueous solution have been investigated. The main results can be summarised as:

- The sp$^2$C=N/C=C and sp$^3$C–N bonds were the major component in the a-CN$_x$ coatings.
- The static contact angles on the a-CN$_x$ coatings decreased with an increase in the concentration of ethylene glycol.
- The mean steady-state coefficient of friction first decreased from 0.033 to 0.019 at 10vol. %, and then fluctuated slightly in the range of 0.030–0.035 with an increase in the ethylene glycol concentration.
- The specific wear rates of SiC ball fluctuated in the range of $1.1 \times 10^{-9}$ to $0.6 \times 10^{-9}$ mm$^3$ Nm$^{-1}$, while those of the a-CN$_x$ coatings varied in the range of $3.3 \times 10^{-8}$–$7.8 \times 10^{-8}$ mm$^3$ Nm$^{-1}$ with increasing the ethylene glycol concentration.
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