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Sliding friction and wear property of a-C and a-CN$_x$ coatings against SiC balls in water

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Abstract

The amorphous carbon coatings with and without nitrogen ion incorporation (a-CN$_x$ and a-C) were deposited on Si (100) wafers and SiC disks by using ion beam assisted deposition, and their composition, structure and chemical bonding were characterized by using Auger electronic spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. The friction and wear properties of the a-CN$_x$ coatings sliding against SiC ball in water were investigated and compared with those of the a-C coatings. The worn surfaces of the a-CN$_x$ coatings were observed by scanning electron microscopy and analyzed by XPS. The micro-analysis results showed that the a-CN$_x$ coatings contained 12 at.% nitrogen and the sp^3 fraction in the a-CN$_x$ coatings was lower than that in the a-C coatings. There were two kinds of N 1s bonding states such as sp^{2}C=N and sp^{3}C–N in the a-CN$_x$ coatings. The nanohardness of the a-CN$_x$ coatings was 29 GPa, lower than that of the a-C coatings (34 GPa). The tribological tests in water showed the friction coefficients of the a-CN$_x$/SiC tribo-pair were in the range of 0.02–0.05, smaller than those of the a-C/SiC tribopair (0.03–0.07), and the specific wear rates of the a-C coating and SiC ball in the a-C/SiC tribo-pair were slight larger than those in the a-CN$_x$/SiC tribopair. The XPS analysis on the a-CN$_x$ coatings' wear track showed that the surface nitrogen concentration of the a-CN$_x$ on the wear track decreased. This indicated that the nitrogen removal would change the wear track surface structure, and then improve the tribological properties of the a-CN$_x$ coatings in water.

Keywords: Carbon coatings; Carbon nitride coatings; Nanohardness; Friction; Wear; Water lubrication

1. Introduction

Due to high hardness, low friction coefficient, good chemical inertness and good biocompatibility, the amorphous carbon (a-C) and carbon nitride (a-CN$_x$) coatings are of great interests for a lot of tribological applications. However, their tribological properties are very sensitive to the environment factors [1,2] and dependent on the deposition method and conditions. Generally, the hydrogen-free diamond-like carbon (DLC) coatings produced by cathodic-arc deposition or pulsed laser deposition consist of pure carbon with very high sp^3 bonding. They are very hard and exhibit the friction coefficient of 0.05–0.1 in unlubricated sliding against steel under ambient environment [3]. Whereas the hydrogenated DLC coatings showed low friction coefficient in inert atmospheres and in vacuum [4–6]. Recently, the a-CN$_x$ coatings have already been proven to possess the low friction coefficient of 0.007 only in dry N$_2$ gas [7,8]. Furthermore, their friction coefficients increased with an increase in the relative humidity [9,10]. But now, the development of carbon-based coatings, with good tribological properties in water, has been expected in connection with environmental problems and biotechnology. For example, in modern machines' design, water-lubrication has already been suggested replacing the oil-lubrication to eliminate the oil pollution and save the energy sources. For biotechnology, wear debris produced from movement of joints can lead to wear-induced biodegradation [11]. To lengthen the service life of joints, carbon-based coatings have already been noted as protective coatings for biomedical applications due to their good biocompatibility, such as the

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absence of inflammatory responses in vitro when assessed by mouse peritoneal macrophages [12] and the absence of histopathological changes in vivo when implanted in animal bone [13]. Thus, the water lubrication of carbon-based coatings, such as DLC [14–21] and a-CN_x coatings [22–26], have recently been concerned.

For the role of H, Ar, F, Si and Ti on the tribological properties of the DLC coatings in water, Ronkasinen et al. [14,16] indicated that, as far as the DLC coatings' performance in aqueous conditions was concerned, H was detrimental, while Ti or Si was useful. However, Tanaka et al. [18–20] reported that the additive elements such as H, Ar, F, and Si had no apparent effect on the friction and wear properties of DLC coatings in water. Recently, the a-CN_x coatings have been found to enhance the wear resistance of SiC ball at lower or higher velocities in water lubrication [22–25], and then the wear-mechanism map of the a-CN_x/SiC tribopair in water has already been developed [25]. At 5 N and 160 mm/s in water, the lower friction coefficients of 0.01–0.02 were obtained as the a-CN_x coatings slid against SiC and Si_3N_4 balls, while the higher friction coefficients of 0.07–0.10 were obtained as the a-CN_x coatings slid against Al_2O_3, SUS440C and SUJ2 balls [26]. The above review on the a-C and the a-CN_x coatings' water lubrication indicates that the carbon-based coatings are the very promising candidates of the sliding parts' coatings in water. However, the friction and wear property of the a-C coatings with or without nitrogen ions incorporation in water lubrication under the same testing conditions has not yet been performed in detail. Moreover, the role of nitrogen on the tribological behavior of carbon coatings in water lubrication was not clear. Therefore, the aim was to understand the influence of nitrogen on the structure, hardness and tribological properties of the a-C coatings in water.

2. Experimental procedures

2.1. Deposition of a-C and a-CN_x coatings

The ion beam assisted deposition (IBAD) machine (Hitachi Ltd., Japan ,as seen in Ref. [23–25]) was used to deposit the amorphous carbon-based coatings. Prior to IBAD process, SiC disks (φ 30 mm × t 4 mm) and Si(100) wafers 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 substrate (SiC or Si wafer) was installed on the substrate holder with two screws, and then the vacuum chamber was subsequently 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 evaporated with an electron beam evaporator, and the a-C coating was deposited by using carbon vapor directly, while the a-CN_x coating was synthesized by mixing carbon vapor and energetic N ions. For a-CN_x coatings, 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, which was controlled by adjusting the carbon vapor emission current. The coatings' thickness was about 0.5 μm.

2.2. Microstructure, chemical bonding state and composition analysis of a-C and a-CN_x coatings

Due to the very high sensitivity of Raman spectroscopy to the various carbon structures, the microstructure of the a-C and α-CN_x coatings was investigated by Raman spectroscopy. The Raman spectroscope with the Ar ion laser (12 mA) was used to characterize the surface structure. The reference laser wavelength was 514.5 nm. The scanning solution was 1 cm^{-1}. The single monochromator and microscope mode with normal incidence was used. Rayleigh scattering was eliminated by the use of two high performance notch filters. The laser spot size was approximately 1 μm, and the acquisition time was 500 s.

The chemical bonding states of the a-C and a-CN_x coatings were investigated by X-ray photoelectron spectroscopy (XPS). The XPS analysis was performed using a Physical Electronics Quantum 2000 Scanning ESCA microprobe. The spectrometer was equipped with a hemispherical electron analyzer and a 25.1 W AlK_α (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 1.6×10^{-7} Pa during data acquisition. The C 1s and N 1s regions were recorded at a pass energy of 58.70 eV. The core-level binding energies (BE) were referenced to the C 1s 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.

Besides Auger electron spectroscopy (AES) analysis, the surface atomic composition of the a-CN_x coatings could be also derived by applying Multipack Spectrum, a software package developed by Physical Electronics for interpreting XPS data acquired on their instruments. The software facilitated data analysis by means of two pre-processing steps: (1) the Savitzky-Golay smoothing algorithm, based on a 7-point running average, suitably modified for end points, was applied to reduce spectral noise, and (2) a Shirley, integrated background correction was obtained by successive iterations to minimize interface caused by the inelastic scattering of low energy electrons. The pre-processed data in each element region was then integrated to obtain peak areas, which when multiplied by sensitivity factors, provided surface atom densities. The results were then normalized to obtain units of surface atom percent. After the experimental curve was fitted with Gaussian lines, the eigen spectra numbers of chemical states were also determined by using the Multipack Spectrum software.

2.3. Surface roughness and mechanical properties of a-C and a-CN_x coatings

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 and the amplification ratio of Z-axis was 10,000. To