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Tribochemical investigation of DLC coating in water using stable isotopic tracers

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Abstract

Tribochemical reaction of DLC coating in water was investigated by using a stable isotopic tracer, ^{18}O labeled water ($H_2{}^{18}O$), to carry out the friction test of DLC coating and 440C ball pair, and using ToF-SIMS to analyze the worn surfaces. The result showed that DLC coating tribochemically reacted with water to form hydrophilic hydroxyl and carboxyl groups on surface, and suggested that the formed hydroxyl mainly combined with the secondary or tertiary carbons on the surface. The surface layer on the counter ball mainly consisted of C from the coating, Cr, Fe from the ball and ^{18}O from water, and was rich in ^{18}OH. It is thought that the hydrophilic groups formed at the interfaces play an important role in low friction and wear behaviors of DLC coating and the counter part in a water environment. Comparing with that obtained from the test in D_2O, the result also suggests that hydrogen/deuterium exchange is easy to occur between the products containing OD on the mated ball and some adsorbates in an ambient air environment.

Keywords: Tribochemistry; Diamond-like carbon; Isotopic tracer; ToF-SIMS

1. Introduction

Diamond-like carbon (DLC) coatings possess high chemical stability and excellent tribological properties in water, such as low friction, high wear resistance, and are attracting great attention for use in water hydraulic systems as solid lubricants [1]. A number of tribological studies carried out in various environments indicate that transfer layer, graphitized tribolayer on the counter parts and chemical interactions at the sliding–contact interfaces are responsible for the tribological behaviors, and the depositing conditions of DLC coatings and the environmental elements affect the tribological properties [2–6]. Recently, a thin tribo-film, which consists of C, O, Cr and Fe, has been observed on the worn counter ball surface tested against a DLC coating in deionized water by transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDS) [7]. This film is thought to be closely related to the tribological properties. On the other hand, no tribo-film has been observed on the worn coating surface. Also, it is lacking in the understanding of the tribo-film on the mated ball surface.

To reveal the formation mechanism of lubrication films at the interfaces of DLC coating and the counter part, we have investigated the tribochemical reactions of DLC coating in water by time of flight secondary-ion mass spectroscopy (ToF-SIMS) analysis of the worn DLC coating and the mated ball surfaces tested in heavy water (D_2O) [8]. The result shows that OD and CD pieces have been formed on the worn coating surface due to the rubbing, even at room temperature. The same result has been also obtained from the test using Si doped DLC (Si-DLC) [9]. However, the source of the oxygen atom remains unclear, because oxygen atom exists not only in water molecule, but also in oxygen molecule dissolved in water and absorbed on the coating and ball surfaces, and in

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some oxides on the surfaces. Additionally, in both the cases of DLC [8] and Si-DLC [9], only a small amount of OD group has been detected from the worn ball surface, whereas OH exists in a large amount. No close relation between the mated ball and D_2O has been confirmed. This result may be due to that the amount of those tribochemical products containing OD group on the mated material is small, or OD group of some tribochemical products has changed to OH due to the hydrogen/deuterium exchange [10,11] with adsorbates after the test. The later one may lead to a misunderstanding of the products on the mated material. Clarifying the source of the oxygen in the products at interfaces and avoiding the possible changes of the products are important in revealing the tribochemical reactions of DLC coating in water. The objective of this work is to distinguish the source of the oxygen in the tribochemical products and to further identify the tribochemical products on the surfaces of DLC coating and the counter material in water more clearly. To do this, ^{18}O labeled water was used as an isotopic tracer to carry out the friction test between DLC coating and 440C ball pair, and the worn surfaces were analyzed by ToF-SIMS.

2. Experimental details

DLC coating was deposited on a silicon wafer substrate by thermal electron excited plasma CVD method. A pulsed-bias was applied to the substrates during depositing. The bias voltage, frequency and duty ratio were -3.0 kV, 1 kHz and 10%, respectively. Toluene (C_7H_8) was used as the carbon source gas. The thickness and the surface roughness Ra of the coating were 1.4 μm and 0.6 nm, respectively. Coatings deposited at the same conditions were employed for characterizations: the hardness was about 16 GPa obtained by nanoindentation method at an indentation depth of 100 nm; the H content was determined by hydrogen forward scattering spectrometry (HFS) and was 24 at.%; the sp^3 content of carbons was 58% determined by near-edge X-ray absorption fine structure (NEXAFS) analysis.

Friction test was carried out by a ball-on-disk type reciprocating tribometer at room temperature under the following conditions: load 10 N; frequency of vibration 1 Hz; amplitude 7 mm; sliding time 60 min. A 440C steel ball with a diameter of 6.35 mm was used. The main composition of 440C steel was Cr 16–18%, C 1%, Si <1%, Mn <1%, Ni <0.6%, and the balance was Fe. ^{18}O labeled water (water-^{18}O, $H_2{}^{18}O$, $\geq$98 at.% ^{18}O) was used in the test. Before test, the DLC coating and the ball specimens were cleaned ultrasonically for 5 min firstly in acetone, and then in petroleum ether. The friction coefficient was measured continuously by a load cell. The specific wear rate of the DLC coating was measured by an optical interferometer, and that of the ball was calculated from the diameter of the scar on the ball assuming the wear scar was flat. After the test, both frictional surfaces of the coating and the mated ball were analyzed by ToF-SIMS in a 180 μm square of analysis area. Ga^+ was used as a primary ion, and both positive and negative secondary-ions were detected.

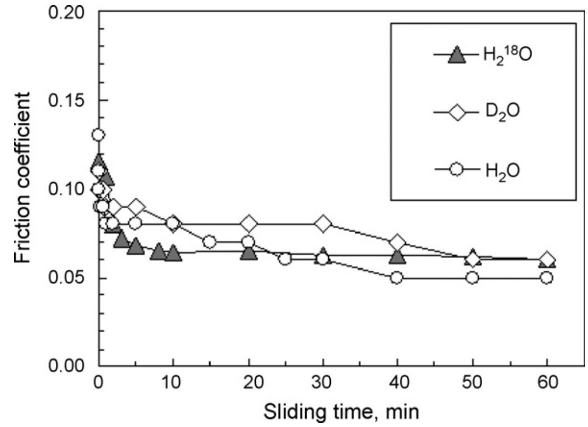

Fig. 1. Variation of friction coefficients as a function of sliding time tested in H_2O, D_2O [8] and $H_2{}^{18}O$.

3. Results and discussion

3.1. Tribological behaviors

Fig. 1 shows the variation of friction coefficient with sliding time tested in $H_2{}^{18}O$. For comparison, the results obtained from the tests carried out in D_2O and ion-exchanged water (H_2O) [8] are also given. The friction behavior of DLC coating and 440C ball pair in $H_2{}^{18}O$ is similar to that in D_2O and H_2O: the friction coefficient decreased at the beginning of the sliding, and then came to a stable and low value, around 0.06. The specific wear rates of the DLC coating and the mated ball in $H_2{}^{18}O$ were 2.2×10^{-8} and 2.3×10^{-8} mm^3/Nm, respectively, and were in the same level as those in D_2O and in H_2O [8]. No significant difference was confirmed in the friction and wear behaviors indicating that by using stable isotope labeled water, the tribological properties of the DLC coating and the ball were not changed.

3.2. ToF-SIMS mass spectra

Fig. 2 shows the ToF-SIMS spectra of negative ions obtained from the inside and outside surfaces of the wear scar on the DLC coating, and the worn surface of the mated ball in $H_2{}^{18}O$. Compared with the outside surface, two strong peaks were detected at m/z 18.00 and 19.01 from the inside surface of the wear scar on the coating. The same peaks were also observed in the spectrum of the worn ball surface. These two peaks can be assigned to ^{18}O (17.999 amu) and ^{18}OH (19.007 amu), respectively. This result is in agreement with those obtained in our previous works, i.e., these peaks were not confirmed by the spectrum of the worn DLC surface tested in H_2O, and the peak corresponding to OD (18.009 amu) was detected at m/z 18.01 from the worn DLC [8] and Si-DLC [9] surfaces tested in D_2O. It is clear that water molecule is an important source of the hydroxyl group tribochemically formed at the interfaces of the DLC coating and the counter ball.

Fig. 3 shows the spectra around m/z 42 and 43 of negative ions obtained from the worn DLC coating surfaces tested in $H_2{}^{18}O$ and D_2O. A fragment ion with a m/z of 43.008 was