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Wear

Analysis of wear behavior and graphitization of hydrogenated DLC under boundary lubricant with MoDTC

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ABSTRACT

Diamond-like carbon (DLC) with high hardness and low friction has been applied to automotive parts. In this study, the significant wear of hydrogenated DLCs under molybdenum dithio-carbonate (MoDTC)-containing oil was evaluated by a reciprocating sliding tester and the wear has been investigated. Analysis of wear debris collected from oil after a sliding test revealed that DLC wear under MoDTC-containing boundary lubrication are caused by the graphitization, same as in solid lubrication confirmed by previous reports. On the other hand, Mo compounds that are decomposition products of MoDTC harden the surface of counterparts and have the potential of accelerated wear.

1. Introduction

To improve fuel economy and reduce CO_2 emissions, diamond-like carbon (DLC) coated parts have been expanded to be applied to automotive products. Hydrogenated DLCs are amorphous films consisting of carbon and hydrogen with an electronic structure of sp^3 and sp^2, which has low friction and high hardness [1]. However, DLC films were reported to be easily worn away under the lubricant containing molybdenum dithio-carbonate (MoDTC). Mo-DTC as a friction modifier is incorporated into low-viscosity engine oils and forms the decomposition products, self-lubricating MoS_2 sheet and MoO_3 [2]. Shinyoshi et al. evaluated the wear of DLC in engine oil with MoDTC and showed the possibility of a chemical wear mechanism of DLC, which was explained to result in oxidation–reduction reaction between carbon atoms of DLC and molybdenum oxide molecules [3]. In our previous report [4], however, the results of Raman analysis of heat treated DLC samples in vacuum shutting out oxygen less than 10^{-3} Pa showed that MoO_3 has no chemical effect on the graphitization of DLC in the temperature range of 300–800 °C. On the other hand, Jia et al. compared MoDTC with three BN-containing additives and showed that the MoDTC additive had a high wear volume of DLC in spite of lower friction. They concluded that hard molybdenum oxides were formed from MoDTC and destroyed DLC films [5]. The wear of

DLC under solid lubrication is attributed to a transformation from sp^2 to sp^3 in electronic structure of an amorphous matrix, which is referred to as graphitization. Liu et al. indicated that the carbon debris obtained from the friction surface contained a lot of sp^2 coupling and concluded that a wear mechanism of DLC was based on graphitization by heat and pressure [6,7]. Graphitization of DLC has been analyzed by Raman scattering spectroscopy, electron energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) [8–12]. The reports say that hydrogen DLCs are graphitized in a 300–400 °C temperature range under heat treatment [13–17]. Haque et al. proposed that the failure of DLC in MoDTC-containing oil was caused by gradual thinning of the film by polishing wear followed by delamination that is believed to be due to removal of the graphitic layer [18]. That is, the graphitization of DLCs was also confirmed under boundary lubrication.

The wear behavior of DLC in MoDTC-containing oils is a significant problem for product lifetime. In the present work, wear of hydrogenated DLC under boundary lubrication with MoDTC are investigated, especially the presence of graphitization. First, wear volumes of DLC and surface hardness of specimens after sliding are compared between engine oils with/without MoDTC by using a reciprocating sliding tester. Then wear debris from oil residues after sliding are analyzed in detail in order to investigate the change of microstructure of DLC under boundary lubrication condition.

2. Experimental details

Hydrogenated DLC films were prepared with two different hardness, 39 GPa and 25 GPa, by closed-field unbalanced magnetron sputtering. These films were deposited in 1.5 μm amounts on

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carburized chromium molybdenum steel substrates by sputtering a graphite target in argon atmosphere with traces of methane after depositing a chromium carbide interlayer. Since the hydrogen free films formed by sputtering are known to become soft a-C (amorphous carbon structure), relatively-hard a-C:H (hydrogenated amorphous carbon) were prepared in this study [11].

Sliding tests were performed in the reciprocating cylinder-on-plate tribotester, which controlled the boundary lubrication conditions. The pair specimens were combinations of DLC coating Cr–Mo steel plates of 50 mm × 15 mm × 5 mm and chilled cast iron cylinders of 4 mmφ × 11 mm. In a test, a reciprocating plate contacted the side face of a cylinder in a 30 mm stroke at 16.67 s^{-1} frequency dropping engine oil at 1.0 ml/s. The load was escalated up to 784 N and was kept until the end. The initial temperature of plate surfaces monitored by a radiation thermometer was set at 110 °C by a heater, since temperature in the friction was measured in the range of 100–150 °C. Two synthesized engine oils with/without MoDTC friction modified additive were prepared. Both oils contained ZnDDP as an extreme-pressure additive and CaCO$_3$ as a detergent additive. The initial contact pressure was 822 MPa, calculated from the formula of Hertz contact. Sliding position x, velocity v, and acceleration a are given by

$$x = r \cos(wt - \pi) \quad (-r \le x \le r) \tag{1}$$

$$v = wr \sin(wt - \pi) \quad (-wr \le v \le wr) \tag{2}$$

$$a = w^2 r \cos(wt) \quad (-w^2 r \le a \le w^2 r) \tag{3}$$

where the length of crank $r = 0.015$ m, the angle rate $\omega = 1000$ rpm, and the position of plate center $x = 0$. Friction coefficients were measured by a load cell fixed at the jig of a cylinder, and had the maximum value at the vicinity of sliding edges. A velocity of plates approached zero toward sliding edges at the position of $x = \pm 15$ mm. In this study, the maximum of friction F was monitored during sliding tests. After a sliding test, specimens were degreased by kerosene and acetone, and oil residues were collected from diluted engine oil with hexane by a centrifugal separator.

The surface configurations of sputtering films were measured by a laser displacement meter (LDM) whose cut-off value of 0.25 mm and the film thickness were measured by a calotest equipment. The surface hardness was analyzed by an instrumented indentation tester with reference to ISO14577-1 [19]. The material analysis of sliding products and oil residues was carried out by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) by a 20 keV accelerating voltage and X-ray diffraction (XRD) by a chromium light source radiation with a 0.22896 nm wavelength.

3. Results and discussion

3.1. Wear behavior

Hydrogenated DLCs were significantly worn out under engine oil with MoDTC, while they had high durability without MoDTC. Fig. 1 shows comparison of surface appearance of the plates after 1.8×10^6 cycle tests between oil w/ and w/o MoDTC. A sliding area on a plate is a rectangle of 30 × 11 mm^2 whose position is 1 mm offset from longitudinal center line. In the case of cylinder-on-plate tests, surface pressure is higher at cylinder edges. It was expected that wear of plate materials would start at the corners in a sliding area because of the thin oil film. As shown in Fig. 1a, DLC film in MoDTC-containing oil was abraded and interlayer was exposed at both lower corners of sliding edges. Sliding areas had
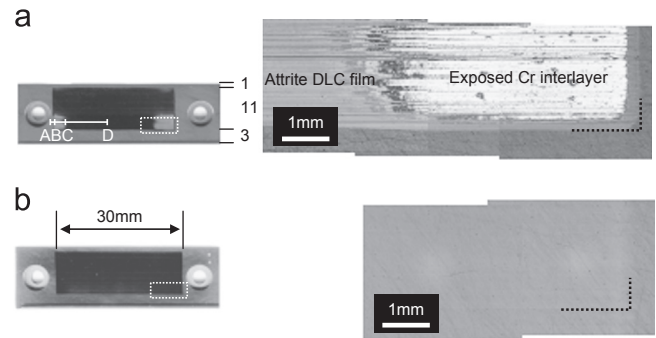

Fig. 1. Comparison of hard DLC surface appearances after 1.8×10^6 cycles sliding test under oil w/ and w/o MoDTC.
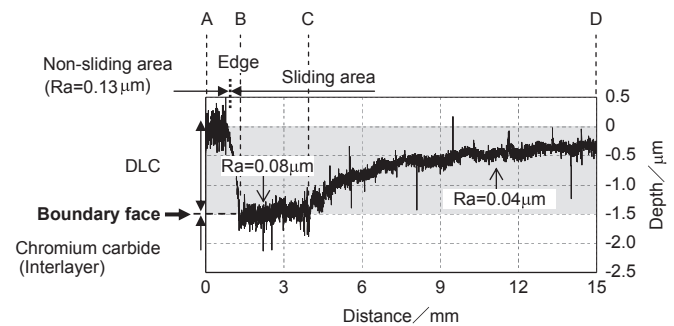

Fig. 2. Wear depth profile of a hard DLC coated plate along a sliding edge after 1.8×10^6 cycles of sliding in engine oil w/MoDTC.

uniform contact in the parallel direction of sliding while they did not have in the vertical direction of sliding. Fig. 2 shows a cross sectional profile of wear depth along the line from A to D in Fig. 1a. Arithmetical mean deviations of profile (Ra) at a non-sliding area, exposed interlayer area, and DLC attired area were measured by LDM. The wear surface of DLC of C–D region was slope-shaped as a consequence of abrasion of DLC. The exposed chromium carbide interlayer of the B–C region was worn minimally having a uniform thickness. In addition, the surface roughness of the C–D region was 0.04 μm, lower than the 0.08 μm of B–C. The exposed interlayer in B–C region had many isotropic line marks of the same configuration as the non-sliding region. These marks are traces of polishing streaks introduced to the substrate prior to depositions. On the other hand, the C–D region has a smooth DLC surface without line marks. These results indicate that DLC is more easily worn than chromium carbide under boundary lubrication with MoDTC. The polishing streaks were not observed in a friction surface of DLC, the wear is thought to be progressed on small scale.

Fig. 3 gives the surface hardness of a cylinder after a sliding test. The hardness of MoDTC-containing oil had higher average of 18 GPa and larger deviation than the case of non-MoDTC oil or the as-chilled sample. Fig. 4 shows a SEM image and an EDX-Mo$^{L\alpha1}$ map focused on wear surface of a cylinder after a sliding test in MoDTC-containing oil. The molybdenum-containing product materials were observed along abrasive wear striations, and XPS analysis revealed that these products were MoS$_2$ and molybdenum oxides (MoO$_{2-3}$), which are the decomposition products of MoDTC. The decomposition productions on a cylinder surface cause increasing surface hardness. It was remarkable that the molybdenum compounds were not observed on the DLC surface.

Fig. 5 shows the comparison of wear depth of DLCs (W_{DLC}) and wear volume of cylinders (W_{Steel}) per sliding time between two DLCs with different hardnesses. W_{DLC} was used to measure wear depth at sliding edges. Friction coefficient under MoDTC-containing oil was 0.07 while that under oil without MoDTC was

0.09. Those experimental values did not depend on hardness of DLCs. Hard DLC at 39 GPa has lower W_{DLC} and higher W_{Steel} than soft DLC at 25 GPa, which is explained as a common mechanical wear model. As an effect of addition of MoDTC, W_{DLC} is increased 40–64 times in spite of lower friction and lower W_{Steel}. The MoDTC additive axiomatically influences wear of DLC.

3.2. Analysis of wear debris

To analyze the wear debris from DLC, engine oils after sliding tests were diluted with hexane and centrifuged and their residues were collected. The residues contained metallic solid materials and
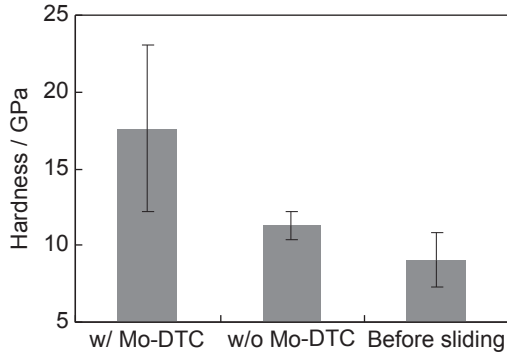

Fig. 3. Comparison of surface hardness of cylinder-specimens.

black fine powder. A main element of the solid materials analyzed by XPS was iron, so cast iron debris of a cylinder was found. The oil residue w/MoDTC had much of the fine powder, whose composition was identified as 64 at% carbon, 27 at% oxygen, 4.6 at% calcium and other elements including sulfur, phosphorus, molybdenum and zinc. Fig. 6 shows the XPS-C[1S] spectra of the DLC film and the oil residue w/MoDTC after removal of cast iron debris. The oil residue w/o MoDTC did not have enough fine powder for XPS analysis. The XPS-C[1S] spectrum of the oil residue w/MoDTC has broad peak at 284.50 eV with broadening while DLC film has a peak at 284.82 eV. According to the published literature, in the XPS-C[1S] spectrum with a range of 280–294 eV, C–C single bond and C–H bond such as polymers have the binding energy of 284.85 eV, and graphite with C═C double bonds has 284.50 eV [20]. Carbon to oxygen bonds, for example C–O of 286.6 eV [21], C═O of 287.3 eV [21], and $CaCO_3$ of 289.6 eV [20], have higher binding energy than carbon to carbon bonds. The biding energy of DLC having C–C and C═C bonds is known to change from 284.50 eV to 284.85 eV along with an increasing sp^3 ratio [10]. Those experimental results revealed that as-coated DLC has 284.82 eV as a mixed value of sp^2 and sp^3. In contrast, the oil residue w/MoDTC has biding energy close to 284.5 eV. This result shows that carbon atoms of the oil residue are mainly bonded as a sp^2 electric structure. Fig. 7 shows comparison between XRD spectra of oil residues with and without MoDTC. Both spectra have diffraction lines of $CaCO_3$ crystals indicated by the arrows, but only the spectrum of residue from MoDTC-containing oil displays a halo pattern with a peak at 27°. The halo pattern indicates a lack of long-range order, so the structure could be
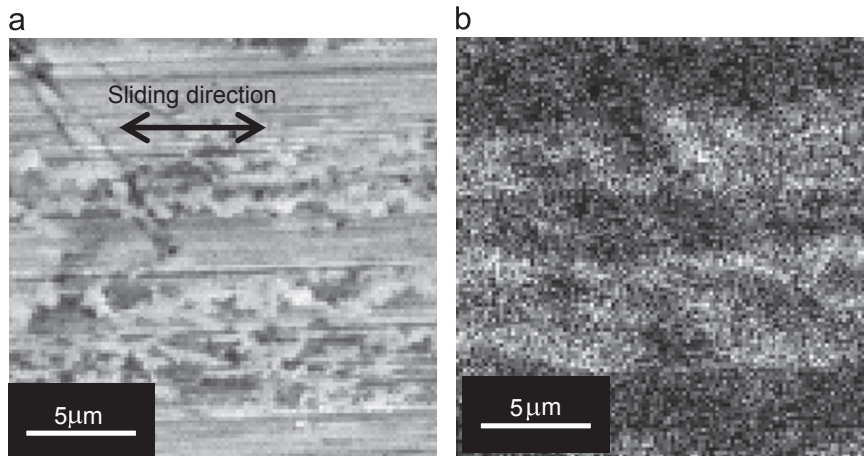

Fig. 4. Observation of a sliding cylinder surface after test in oil w/MoDTC, (a) SEM image, and (b) EDX molybdenum-$L^{\alpha 1}$ map.
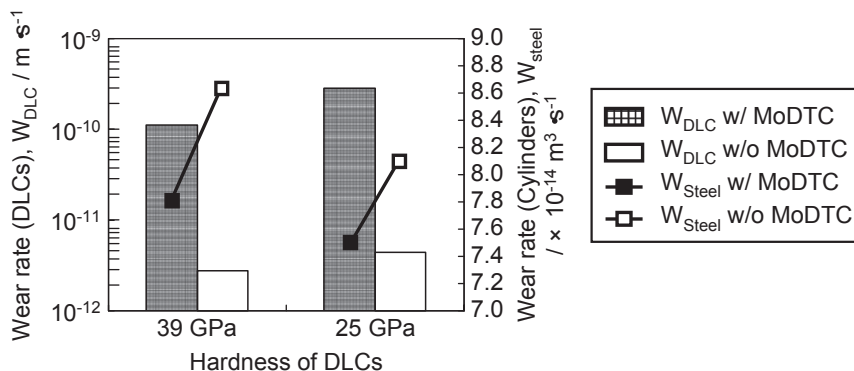

Fig. 5. Effect of MoDTC on wear depth of DLC film and wear volume of cylinder-specimen.
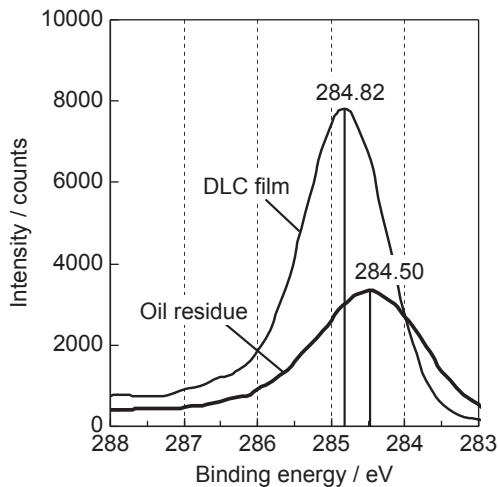
Fig. 6. Comparison of X-ray photoemission spectra of oil residue and as-deposited DLC.
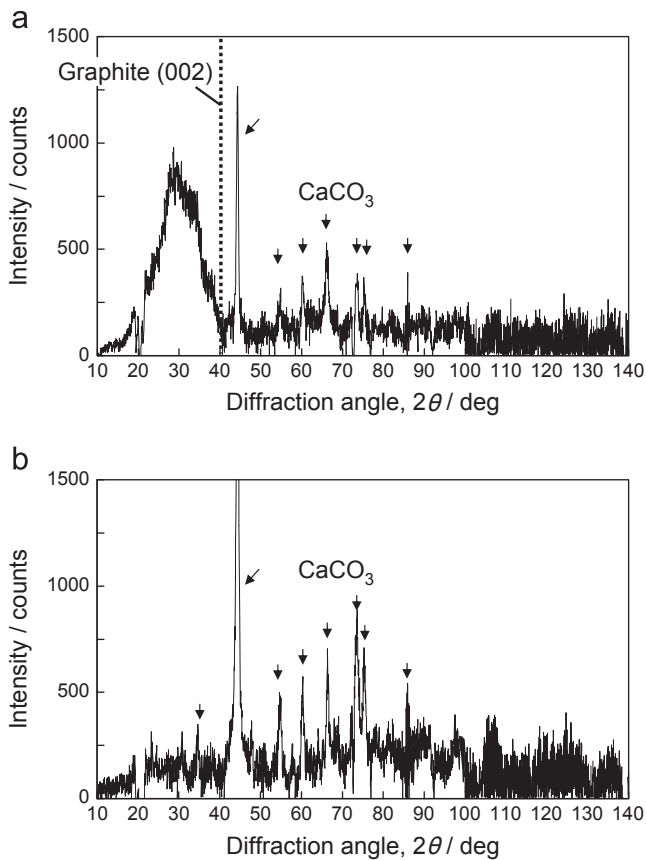

Fig. 7. X-ray diffraction spectra of residue from oil w/ and w/o MoDTC, arrow shows $CaCO_3$.

amorphous or solidified polymer. If the oil residue is the solidified engine oil elements, the halo peak at 27° in XRD spectrum should be observed in both oil residue and carbon to oxide bonds should be emphasized in XPS-C^{1S} spectrum of the oil residue. This hypothesis does not accord with the experimental results. Hence the residue from MoDTC-containing oil is determined as the wear debris of DLC with an amorphous structure dominated by sp^2 bonds. The XRD pattern of a graphite crystal of hcc has a diffraction line of (002) plane at 40.0° in the case of chromium light source with a 0.22896 nm wavelength. The halo with a peak

at 27° is thought to be based on (002) plane of graphitic structure that shifts toward lower angle from 40.0°, or the microstructure changes into lower atomic density.

In this study, the wear debris of DLC under boundary lubrication was successfully collected from the residue of MoDTC-containing oil. The amorphous microstructure of the debris was found to have lower atomic density and more sp^2 bonds than the original DLC. In other words, the graphitization of DLC was confirmed in the sliding test.

3.3. Discussion

The wear debris of DLC collected from oil residue with MoDTC were confirmed to be dramatically transformed into a brittle microstructure that had an almost sp^2 electronic structure. Based on the result, the wear of DLC films under boundary lubrication with MoDTC are explained by graphitization as same as the case of solid lubrication reported previously [6,7]. The wear tests under boundary lubrication also showed that the MoDTC additive axiomatically accelerates the wear of DLC. The molybdenum oxide and sulfide were formed on the counterparts, so they hardened the surfaces. MoDTC additive is considered to facilitate the mechanical wear of brittle graphitized DLC by producing the hard molybdenum compounds on the counterpart surface. Further studies are necessary to confirm the potential of chemical wear by oxide or sulfide.

4. Conclusion

The reciprocating cylinder-on-plate slide tests with DLC under boundary lubrication including MoDTC were carried out, and the following were found. DLCs are dramatically worn under MoDTC-containing oil in spite of lower friction compared to oil without MoDTC. Hard molybdenum compounds, including MoS_2 and molybdenum oxides, were observed on the surface of counterparts. The microstructure of wear debris of DLC was also analyzed, which had mainly sp^2 bonds. Wear of DLC under boundary lubricant with MoDTC is thought to result from graphitization.

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