Ultralow Friction of a Tetrahedral Amorphous Carbon Film Lubricated with an Environmentally Friendly Ester-Based Oil

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The tribological properties of diamond-like carbon (DLC) films that were lubricated with an environmentally friendly ester-based oil were investigated. Sliding tests were performed on two types of DLC films, hydrogenated amorphous carbon (a-C:H) and tetrahedral amorphous carbon (ta-C) films, using a steel cylinder that was in contact with a steel disk coated with either a-C:H or ta-C under boundary lubrication. To compare the tribological properties of ester-based oils and other based oils, Trimethylolpropane (TMP) ester, polypropylene glycol (PPG), and poly-alpha olefin (PAO) were used as the test lubricants. The ta-C film that was lubricated with TMP ester exhibited the ultralow friction coefficient of 0.015; however, the a-C:H film that was lubricated with TMP ester did not exhibit the ultralow friction. On the other hand, results obtained by a quartz-crystal microbalance with dissipation indicated that the adsorption properties of based oils depended on the type of sensor material (carbon or iron) and the type of based oil used in the measurements. Moreover, the frequency change of based oils increased with decreases in the average frictional coefficients of the steel-steel tribopair and the DLC-steel tribopair. Results of surface analysis indicated that TMP ester formed tribofilms on the ta-C surfaces, which exhibited high viscosity and low friction. All these results suggest that the combination of the ta-C film and TMP ester is the new ultra-low-friction and environmentally friendly sliding system.

Keywords: diamond-like carbon, tetrahedral amorphous carbon, hydrogenated amorphous carbon, ester-based oils, quartz-crystal microbalance with dissipation, ultralow friction

1. Introduction

A diamond-like carbon (DLC) film is an amorphous carbon coating that has sp² and sp³ hybridized orbitals and hydrogen. In recent years, DLC films have been widely applied on products because of their excellent tribological properties [1], which depend on the sliding environment. Hydrogenated amorphous carbon (a-C:H) films are of special interest because some of these films exhibit super-low frictional coefficients below 0.01 when they are in contact with ferrous and DLC surfaces under dry conditions, and the coefficients can decrease to 0.001 in hydrogen gas owing to the weak van der Waals interactions of the hydrogen atoms between the sliding surfaces [2,3]. On the other hand, a tetrahedral amorphous carbon (ta-C) film exhibits an ultralow frictional coefficient in the range of 0.02-0.04 under boundary lubrication with glycerol mono-oleate (GMO)-added oils [4-7]. Some researchers proposed that the dangling bonds of carbon atoms on the ta-C film are terminated by the hydroxyl-OH group of GMO, and the formation of a monomolecular layer results in ultralow friction [4-7]. Therefore, the presence of hydrogen or a lubricant with functional groups is essential to the formation of a monomolecular layer with excellent tribological performance on a DLC surface.

On the other hand, most of the commercially available lubricants and many of the additives used to obtain the desired performances are toxic to the environment. Therefore, there has been an increasing demand for “green” lubricants [8]. Among commonly used industrial lubricants, ester-based oils are good alternatives to mineral oils owing to their non-toxic and readily biodegradable nature, as well as good tribological performances [8,9]. Moreover, ester-based oils exhibit better tribological properties than non-polar lubricants on
As mentioned above, the formation of a monomolecular layer on DLC films may yield low-frictional properties under boundary lubrication. Therefore, in order to facilitate easy formation of a monomolecular layer that has low friction with sliding surfaces on a DLC film, it is important to provide lubricants with many functional groups that can easily connect with the carbon atoms on the sliding surfaces. One promising lubricant is ester-based oils. Ester-based oils such as trimethylolpropane (TMP) ester possess high amounts of functional groups such as the hydroxyl-OH and ester-COO- groups. There are several reports of an a-C:H film exhibiting low friction when lubricated with TMP ester [10,11]. However, few studies have focused on the tribological properties of DLC films that are lubricated with ester-based oils and the lubrication mechanism has yet to be clarified.

In the study reported here, the tribological properties of DLC films that were lubricated with environmentally friendly ester-based oils were investigated. Sliding tests were performed using a steel cylinder on a disk that was coated with an a-C:H or ta-C film under boundary lubrication. To compare the tribological properties of ester-based oils and other based oils, TMP ester, polypropylene glycol (PPG) or poly-alpha olefin (PAO) was used as the test lubricant. To reveal the low friction mechanism of DLC films lubricated with ester-based oils, we focused on the relationship between the frictional properties of DLC films and adsorption-decomposition properties of the ester-based oils by using a quartz-crystal microbalance with dissipation (QCM-D) and Fourier-transform infrared spectroscopy (FT-IR). Moreover, surface analyses were carried out using confocal laser scanning microscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

2. Materials and experimental details

2.1. Materials and lubricants

A steel bearing disk (diameter φ = 24 mm; thickness t = 7.9 mm; American Iron and Steel Institute (AISI) steel grade: 52100; hardness: 700 HV) with and without a ta-C or a-C:H coating and a bearing steel cylinder (φ = 6 mm; length l = 8 mm; AISI 52100 with a hardness of 700 HV) were used as the test specimens. In this study, the ta-C and a-C:H films were commercial coatings produced by ITF Co. (Kyoto, Japan) using an arc ion plating (AIP) process and by KYB Co. (Tokyo, Japan) using unbalanced magnetron sputtering (UBMS), respectively. The physical properties of these films were measured using a tribo-indenter (Ti950, Hysitron, US), a coating-thickness analyzer (Calotest, Anton Paar Tritec SA, Switzerland), and elastic recoil detection analysis (ERDA). The properties of these films are listed in Table 1.

Three types of VG46 lubricants-PAO, PPG (n-butanol-initiated), and TMP ester of oleic acid-were used in the sliding tests. The average molecular weights of PAO, PPG and TMP are approximately 600, 1060-1120 and 928, respectively. The structure of each ester-based oil is shown in Fig. 1.

2.2. Friction test conditions

The tribological properties were evaluated using a reciprocating-type cylinder-on-disk tribotester (SRV4, Optimol, Germany). Figure 2 presents a schematic of the SRV tribotester. The friction tests were performed on disk-cylinder tribopairs of an uncoated steel disk and uncoated steel cylinder (steel-steel), an a-C:H-coated steel disk and uncoated steel cylinder (a-C:H-steel), and a ta-C-coated steel disk and uncoated steel cylinder (ta-C-steel). The sliding conditions were as follows: a load of 50 N (corresponding to a maximum initial Hertzian contact pressure of 340 MPa), frequency of 50 Hz, temperature of 80°C, stroke of 1.0 mm, mean sliding speed of 1.0 m/s, 90 μL of lubricant, and test duration of 1800 s. The friction tests were carried out under the boundary lubrication regime, which was estimated by the lambda ratio defined in the literature [12]. The calculated lambda ratio was 0.57 for the test conditions at the ta-C-steel contact that was lubricated with TMP.

2.3. QCM-D measurements

The adsorption properties of the three based oils

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>AIP</th>
<th>UBMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Roughness Rₐ [μm]</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>Film thickness [μm]</td>
<td>1.0</td>
<td>0.65</td>
</tr>
<tr>
<td>Hardness [GPa]</td>
<td>73</td>
<td>10</td>
</tr>
<tr>
<td>Elastic modulus [GPa]</td>
<td>650</td>
<td>92</td>
</tr>
<tr>
<td>Hydrogen content [at.%]</td>
<td>&lt;1.0</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 1 Properties of DLC films
were evaluated by the QCM-D (Q-Sense, Sweden). In general, any increase in the mass \((m)\) on the quartz surface changes the resonance frequency \((f)\). The change in resonance frequency \((\Delta f)\) can be directly related to the added mass of the adsorbed layer \((\Delta m)\) when adsorbed molecular are attached to the quartz surface. This relationship is linear as long as the added mass is rigid, firmly attached to the surface, and small compared with that of the crystal. Equation (1) was derived and is known as the Sauerbrey relation [13].

\[
\Delta m = -\frac{\rho_q \Delta f}{n f_0^2}
\]

(1)

where \(\rho_q\) is the specific density of quartz, \(t_q\) is the thickness of the quartz crystal, \(f_0\) is the fundamental resonance frequency, and \(n\) is the harmonic number \((n = 3\) in this study). In this study, the adsorption properties of ester-based oils were evaluated by measuring the changes in resonance frequency \((\Delta f)\) of quartz-crystal sensors [13].

In addition, the viscoelastic properties of the adsorbed film were evaluated by measuring the dissipation factor \((D)\), which is the inverse of the \(Q\) factor and defined by

\[
D = \frac{1}{Q} = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}
\]

(2)

where \(E_{\text{dissipated}}\) is the energy dissipated during one period of oscillation, and \(E_{\text{stored}}\) is the energy stored in the oscillating system. During the measurement, the driving power to the piezoelectric oscillator was switched on and off. The resonance frequency was measured when the oscillator was on. When it was turned off, the amplitude of oscillation, \(A\), decayed as an exponentially damped sinusoidal function:

\[
A(t) = A_0 e^{(-t/\tau)} \sin(\omega t + \phi) + C
\]

(3)

where \(s\) is the decay time, \(x\) is the angular frequency at resonance, \(\omega\) is the phase angle, and the constant \(c\) is the DC offset. The dissipation factor is related to the decay time through

\[
D = \frac{1}{\pi f \tau}
\]

(4)

The dissipation changed with the density and viscosity of the solution according to Eq. (4). It was also affected by the properties of the adsorbed layer [13].

To clarify the effects of materials on adsorption properties of the based oils, iron- and carbon-coating sensors with a fundamental frequency of 5 MHz \((\varphi = 14\) mm and \(t = 0.3\) mm) were used in this study. Before the measurements, the sensors were rinsed in an acetone-benzine mixture. The lubricants used in the QCM measurements were \(n\)-hexadecane and \(n\)-hexadecane-added TMP, PPG, and PAO \((10\) mass\%). These measurements were carried out at an oil temperature of 60°C for the third overtone \((5\) MHz). The QCM-D measurements proceeded in three stages: (A) flowing of \(n\)-hexadecane to stabilize the signals in a liquid environment; (B) \(10\) mass\% of \(n\)-hexadecane was added to the ester-based oil and left to incubate for a specified period; (C) rinsing with \(n\)-hexadecane to remove the physically adsorbed layer. In this study, the change in frequency after rinsing with \(n\)-hexadecane is defined as the amount of chemically adsorbed lubricant.

2.4. Surface and lubricant analyses

After the friction test, the disks were rinsed in \(n\)-hexane. The wear volume loss of pin specimens was calculated by measuring the width and the length of wear tracks. On the other hand, the wear volume loss of disk specimens by measuring the length of wear tracks and the area of cross sectional profiles on the middle of wear tracks. Confocal laser scanning microscopy (VK-X150, Keyence, Japan) was used to measure the width and length of wear tracks and the area of cross sectional profiles on the middle of wear tracks.

Surface analyses were conducted on the wear tracks using XPS (VG Scientific Theta Probe, Thermo Fisher Scientific, USA) with an Al Kα X-ray source, scan area with \(\varphi = 400\) μm, and take out angle of 45°, and AFM (NanosNav Real, SII, Japan) with commercial cantilevers made of silicon with an integrated pyramidal tip (approximate tip radius of 10 nm) (SI-DF20, Olympus, Japan).

The decomposition of TMP ester after the friction test was investigated by FT-IR (FT-IR-6100, Jasco, Japan) using the attenuated total reflection (ATR) method. All measurements were recorded in the frequency range of 400-4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\).

3. Results and discussion

3.1. Frictional and wear properties

The coefficients of friction of the DLC-steel and the steel-steel tribopairs that were lubricated with PAO, PPG, and TMP ester are shown in Fig. 3(a-c), respectively, as functions of the sliding time. The average frictional coefficients \((\text{calculated over the last 600 s of the test period})\) at all contacts with each lubricant are shown in Fig. 4.

For the steel-steel tribopair, lubrication with TMP ester yielded the lowest friction coefficient followed by lubrication with PAO and PPG, as shown in Fig. 3(a) and Fig. 4. Polar lubricants normally exhibit better tribological properties than non-polar lubricants on ferrous surfaces [10]. However, it should be noted that lubrication with PAO yielded lower friction than PPG at the steel-steel contact. The behavior will be discussed with the results of QCM-D. As shown in Fig. 3(b) and Fig. 4, the friction coefficient gradually decreased from 0.1 to 0.05 during the initial 600 s of the test period for the ta-C-steel tribopair lubricated with PAO. However, the friction coefficient dramatically increased from 0.05 to 0.13 after the initial period. On the other hand, the ta-C-steel tribopair exhibited low friction coefficients of 0.04 and 0.015 when lubricated with PPG and TMP ester, respectively. In particular, the ultralow friction
phenomena appeared for the lubrication with TMP ester. Just like the ta-C-steel tribopair, the a-C:H-steel tribopair exhibited the lowest friction when lubricated with TMP ester, followed by lubrication with PPG and PAO, as shown in Fig. 3(c) and Fig. 4. However, the ultralow friction phenomenon was not observed for the a-C:H-steel tribopair. Therefore, the type of DLC film played an important role in the ultralow friction phenomenon when ester-based oils were used as lubricants.

Figure 5(a,b) shows images of wear tracks on the disks and cylinders after the friction tests. For the DLC-coated disks, the steel substrate was hardly visible on all wear tracks except the case of PAO-lubrication for the ta-C-steel tribopair, demonstrating that the DLC-steel contacts remained throughout the friction test except the case of PAO-lubrication for the ta-C-steel tribopair. On the other hand, the steel substrate was partially observed on the wear track of the ta-C film that was lubricated with PAO. This was the reason lubrication with PAO at the ta-C-steel contact yielded high friction (Fig. 3(c)).

The wear volumes of the disk and the cylinder at the DLC-steel and the steel-steel contacts that were lubricated with PAO, PPG, and TMP ester are shown in Fig. 6. Lubrication with TMP ester yielded the lowest wear volume on the uncoated steel disk and the steel cylinder when it was in contact with the uncoated steel disk; lubrication with PPG and PAO yielded higher wear volumes on the uncoated steel disk and steel cylinder. On the other hand, lubrication with PPG resulted in the lowest wear volume on the DLC-coated disks and steel cylinder, followed by lubrication with TMP ester and PAO. In particular, the a-C:H-steel tribopair exhibited low wear volume for all lubricants. This indicates that the
type of DLC film played an important role in the wear properties when lubricated with based oils. Moreover, although lubrication with TMP ester resulted in lower friction than lubrication with PPG at the a-C:H-steel and ta-C-steel contacts (Fig. 3), the TMP-lubricated specimens exhibited higher wear volume those lubricated with PPG. It was estimated that the repeated adsorption and desorption of TMP molecules led to corrosion and an eventual increase in the wear volume on the DLC-coated surfaces. On the other hand, although the ta-C-steel tribopair lubricated with PPG and TMP exhibited much lower friction than the cases of the a-C:H film [Fig. 3(a-c)], the wear volumes for the ta-C film lubricated with PPG and TMP were higher than the cases of the a-C:H film. It was estimated that the chemical interaction between the lubricant additives and the ta-C surface caused the higher chemical wear compared to the cases of the a-C:H film.

3.2. QCM-D results
To reveal the adsorption properties of based oils on ferrous and carbon surfaces, QCM-D measurements were performed using iron and carbon sensors.

Figure 7(a-f) shows the frequency change and the dissipation change as functions of the measurement time. Figure 8 shows the average frequency change (during the last 600 s of the test period) of the carbon sensor and the iron sensor before and after rinsing. The changes in frequency indicate the amount of non-polar lubricant (PAO) adsorbed on the QCM sensor; however, it cannot be assumed that the non-polar lubricant was adsorbed on the sensor surfaces. Therefore, the frequency change resulting from the adsorption of PAO was dominated by the effect of its viscosity [14]. On the other hand, it should be noted that there was a difference between the adsorption of lubricants on the iron and carbon sensors. For the carbon sensor, the adsorption of TMP ester and PPG exhibited larger frequency change than the adsorption of PAO before and after rinsing. On the other hand, there was no difference between the frequency change resulting from the adsorption of PPG and PAO on the iron sensor, indicating that it was more difficult
Ultralow Friction of a Tetrahedral Amorphous Carbon Film Lubricated with an Environmentally Friendly Ester-Based Oil

Therefore, it can be inferred that PPG did not reduce friction at the steel-steel contact (Fig. 3).

To take into account the effects of the viscoelastic properties of the adsorbed layer, $\Delta D$ is plotted against $\Delta f$ in Fig. 9 to eliminate time as an explicit parameter and to obtain additional information on the adsorption processes through an analysis of the slope, $\partial \Delta D / \partial \Delta f$, which indicates that an increase in the viscosity or thickness of the adsorbed layers [15]. In the initial phase, the $\Delta D-\Delta f$ plots for all based oils show the same linear slope. This indicates that there was no difference between an increase in the viscosity or thickness of the adsorbed layers of PAO, PPG, and TMP ester. In the second phase, however, the slopes of the $\Delta D-\Delta f$ plots for PAO and PPG are small and almost constant, whereas the $\Delta D-\Delta f$ plot for TMP ester is linear with a small slope. This indicates that additional TMP molecules were inserted in the space of the initial layer with steric effects after the initial phases. This adsorption behavior is discussed below. These results show that the adsorption behavior of based oils depended on the type of based oil.

3.3. FT-IR results

It is well known that thermal effects, hydrolysis, and tribo-mechanical stress decompose ester-based oils on sliding surfaces. To clarify the decomposition process of TMP ester, TMP ester was analyzed after the friction test by FT-IR in the ATR mode. We expected TMP ester to decompose during sliding; however, as shown in Fig. 10,
there was no difference between the FT-IR spectra of TMP ester before and after the friction tests at the DLC-steel contacts. This indicates that TMP ester was directly adsorbed on the sliding surface and formed low-friction tribofilms without going through decomposition.

3.4. XPS results

XPS depth analysis were performed on the DLC-coated steel disks after the friction tests by using Ar-ion etching (etching time: 10 s; etched-film thickness according to the sputter etch rate of SiO₂: 1 nm). A binding energy of 284.8 eV for adventitious C was used as the reference for charge correction. Figure 11 shows that the XPS peaks of the C1s spectra originated from worn surfaces of both DLC films that were lubricated with PAO, PPG, and TMP ester, with and without Ar etching. When the films were lubricated with TMP ester, the C1s peak at a binding energy at 288-289 eV

![Graph of FT-IR spectra showing the difference between TMP ester before and after friction test at DLC-steel contacts.](image-url)
corresponding to the carbonyl group was observed for both DLC films. In particular, the peak is clearly visible in the spectrum of the ta-C film, demonstrating that TMP ester was strongly adsorbed on the ta-C surface. Moreover, the disappearance of the peak at 288-289 eV after etching indicates that TMP ester formed a thin tribofilm with a thickness of a few nanometers. On the other hand, for lubrication with PPG and PAO, there were no differences between the C1s spectra before and after etching for both DLC films. Thus, PAO and PPG might be weakly adsorbed on the DLC surface and their tribofilms were rinsed by n-hexane.

3.5. AFM results

Based on the results of the friction tests and surface analyses, it was estimated that tribofilms strongly affected the tribological properties of the DLC films. To reveal the mechanisms of the ultralow friction of the ta-C film that was lubricated with TMP ester, AFM measurements were performed on both DLC surfaces after the friction tests. Figure 12 shows the topography and the lateral force mapping of both DLC surfaces before and after the friction tests. The darker regions in the lateral force maps indicate low lateral force, and the brighter regions indicate high lateral force. Force-displacement curves of the low-friction regions in the lateral force map (Fig. 12) of the wear tracks of DLC surfaces before and after the friction tests were obtained using a silicon cantilever. When the cantilever approached from a few nanometers above the surface, the cantilever snapped upon contact owing to the long-range attractive interactions. When the cantilever was retracted from the surface, it deflected downward and remained in contact with the surface past the z = 0 position until the cantilever deflection force was equal to the adhesive force and the cantilever was suddenly pulled off the surface [16]. This pull-off force was measured in the low-friction region on the DLC surfaces, and one example of the force curve is shown in Fig. 13. The pull-off force was measured on the DLC surfaces before and after the friction tests, as shown in Fig. 14. For both DLC surfaces, lubrication with TMP ester gave the highest adhesive force followed by lubrication with PPG and PAO and the as-deposited surface. In particular, the adhesive forces of the ta-C surfaces lubricated with TMP ester were much higher than that of the other cases. These results indicate the formation of the high viscous film on ta-C surfaces that is lubricated with TMP ester and that the properties of the tribofilm on sliding surfaces are dependent on the type of
DLC coating.

Figure 15 shows the nanoscale frictional properties of low-friction regions on DLC surfaces after friction tests at different normal loads of 100, 200, 300, 500, 700, and 1000 nN. For the a-C:H surface, the frictional force of all based oils dramatically increased as the applied load was increased. On the other hand, even though the frictional force on the ta-C surface lubricated with PAO was much higher than the forces on other lubricated DLC surfaces, the frictional forces for ta-C surfaces lubricated with PPG and TMP ester were much lower than those of other lubricated DLC surfaces at a wide range of normal loads. In particular, lubrication with TMP ester yielded the lowest frictional force at high loads (500-1000 nN). It can thus be concluded that TMP ester formed tribofilms with excellent low-friction properties on ta-C surfaces. On the other hand, the friction force for ta-C surfaces lubricated with PPG dramatically increased at relatively

- Adhesive force

Fig. 13 One example of the force curve on DLC surfaces
3.6. Discussion

The tribological properties of the DLC films that were lubricated with based oils were revealed by the friction tests and surface analyses.

The difference between the friction coefficients of the a-C:H-steel and the ta-C-steel contacts can be attributed to the different surface terminations of the a-C:H and ta-C films. In the hydrogenated DLC film (a-C:H film), the dangling bonds of carbon atoms were terminated by hydrogen atoms and there were hardly active sites on the sliding surfaces as shown in Fig 16 (a). In contrast, the hydrogen-free ta-C film contained a number of chemical reaction sites owing to the dangling bonding of carbon atoms, allowing the functional groups of TMP ester and PPG to easily connect with carbon atoms on the sliding surfaces through O atoms to form a low-friction monomolecular layer as shown in Fig 16 (b). Therefore, the ta-C films that were lubricated with PPG and TMP ester showed the low friction.

On the other hand, the difference between the friction coefficients of DLC films lubricated with PPG and TMP ester can be attributed to the different number of functional groups and adsorption behavior. A TMP molecule has three ester groups, whereas a PPG molecule has only one hydroxyl group, in which means that it was easier for TMP ester to connect with C atoms and then form a low-friction tribofilms between sliding surfaces. Moreover, there was a difference between the adsorption behavior of PPG and TMP ester on carbon surfaces. The ΔD-Δf plots (Fig. 9) indicate that PPG formed a monomolecular layer on the carbon surfaces, whereas TMP ester may have formed an adsorbed film with steric effects on the carbon surfaces. Thus, the initial phase can be associated with the formation of a non-dense layer (low coverage layer). The second phase can be seen as characterized by rearrangement of TMP molecules and the transition to a more stable conformation with increment in the coverage of adsorbed molecular. Therefore, it can be inferred that the properties of TMP-derived tribofilms were different from those of PPG-derived tribofilms (see AFM results). Moreover, Fig. 17 shows the relationship between the frequency change of the iron sensor and the average friction coefficients of the steel-steel tribopair (black points); it also shows the relationship between the frequency change of the carbon sensor and the average friction coefficients of the DLC-steel tribopairs (blue and red points). The frequency change of ester-based oils increased with decreases in the average frictional
Hikaru Okubo, Seiya Watanabe, Chiharu Tadokoro and Shinya Sasaki


coefficient of the steel-steel tribopair and the DLC-steel tribopairs. This indicates that the adsorption behavior of based oils play an important role in the low-friction properties of DLC films.

From all these results, the combination of the ta-C film and TMP ester is the new ultra-low-friction and environmentally friendly sliding system. However, additional detailed analysis is necessary to identify the mechanism of the ultralow friction phenomena of the ta-C film lubricated with ester-based oils.

4. Conclusions

The tribological properties of DLC films lubricated with based oils were investigated. The main conclusions are summarized as follows:

1. When lubricated with TMP ester, the frictional coefficient of the ta-C-steel tribopair was reduced to 0.015, which represents a 90% reduction from that (0.105) of the steel-steel tribopair. However, this excellent reduction in frictional coefficient was not observed for the a-C:H-steel tribopair. The type of DLC coating played an important role in the ultralow-friction phenomenon when it was lubricated with ester-based oils.

2. From the QCM-D and FT-IR results, it was determined that the frequency change of based oils increased with decreases in the average friction coefficient of the steel-steel tribopair and the DLC-steel tribopair. The $\Delta D-\Delta f$ plots of adsorption of all based oils showed that the adsorption behavior of TMP ester was different from that of PAO and PPG on the carbon surfaces. Moreover, TMP ester was directly adsorbed on the sliding surface and formed a low-friction tribofilm without going through the decomposition process. Therefore, the adsorption properties of ester-based oils were key factors of the frictional properties of the DLC films.

3. There were no differences between the C1s spectra before and after etching for both DLC films lubricated with PPG or PAO. However, a peak corresponding to carbonyl groups or carboxyl groups is observed for both DLC films lubricated with TMP ester. In particular, the peak was clearly observed in the spectrum of the ta-C film, demonstrating that TMP ester was strongly adsorbed on the ta-C surface. Moreover, the disappearance of the peak after Ar-ion etching indicates that TMP ester formed a thin tribofilm with a thickness of a few nanometers.

4. The AFM results indicate the formation of a high-viscosity and the low-friction film on DLC surfaces that were lubricated with TMP ester. In particular, TMP ester formed tribofilms with much higher viscosity and much lower friction on the ta-C surface than the a-C:H surface.

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References


