The Effect of Carbon Structure of DLC Coatings on Friction Characteristics of MoDTC-derived Tribofilm by Using an in situ reflectance spectroscopy

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Abstract

In this paper, we prepared 6 types of DLC coatings with varying carbon structures (amorphous ta-C coating and GNC coatings that include nano graphite crystals) and different doped Ta amounts to study friction characteristics. Results from the friction test with MoDTC-added lubricant revealed that DLC coatings with a higher $I_D/I_G$ ratio exhibited a lower friction coefficient. Furthermore, in situ observations using a reflectance spectroscopy showed that the tribofilm formed on the DLC coatings with a higher $I_D/I_G$ ratio maintained a higher MoS$_2$ / (MoS$_2$ + MoO$_3$) ratio. This ratio strongly correlated with its friction coefficient. From the measurement of a work function of each DLC coating, the DLC coatings with a higher $I_D/I_G$ ratio had a higher work function, which indicated to include larger amount of the defect of graphite structure. This active defect of graphite structure was considered to enhance the friction reduction effect of MoDTC. The findings of this paper suggest a material design concept for a DLC coating that amplifies the effects of lubricant additives in reducing friction.

1. Introduction

Recently, saving energy consumption and reducing carbon dioxide emissions have become significant issues worldwide. In order to develop eco-friendly machinery, it is necessary to reduce friction and wear on sliding surfaces. In the context of automobiles, Holmberg et al. reported that friction losses in mechanical parts such as engines and transmissions account for approximately 16.5% of input energy[1]. Especially, at a higher contact pressure situation and a lower sliding speed condition, lubrication regime transfers to a boundary lubrication regime, which causes a higher friction and wear. To reduce a friction and wear of boundary lubrication regime, DLC (diamond-like carbon) coatings are applied to the sliding parts. DLC coatings possess an amorphous structure that includes sp$_2$ and sp$_3$ bonding of carbon atoms. Consequently, DLC coatings exhibit ideal tribological properties such as low friction, high hardness, and high wear resistance in a dry condition[2–5] and in presence of lubricant[6–10].

In addition to the original friction performance of DLC coatings, the interaction with lubricant additives plays a crucial role in improving their tribological properties[11, 12]. One significant lubricant additive for friction reduction is MoDTC (molybdenum dithiocarbamate). MoDTC reacts chemically and forms a thin layer of products call tribofilm on the sliding surface. Its tribofilm includes sheet-like MoS$_2$, which acts as a solid lubricant and reduce friction[13–15].

The friction characteristics of DLC coatings with MoDTC-added lubricant was analyzed by some researchers[16–18]. Miyake et.al. reported that doping Ti to DLC coating enhanced the friction reduction effect of MoDTC, and its friction coefficient decreased to 0.03[19]. Furthermore, de Barros'Bouchet et al. evaluated the tribological properties of a-C, a-C:H, and Ti-C:H coatings in lubricants containing MoDTC and ZDDP (zinc dialkyldithiophosphate)[20]. As a result, the a-C:H coating generated MoS$_2$-rich tribofilm, and then exhibited the lower friction. Nakashima et al. reported successful reduction of silica scale adhesion from geothermal steam by using DLC coatings[21, 22]. According to their research, reducing
defects in graphite bindings was crucial in suppressing silica adhesion since defects were active and had higher adhesion energy. From these previous researches, the carbon structure and doped material is considered to be significant to the effect of lubricant additives, but the suitable coating properties which enhances friction reduction effect of MoDTC is unclear at this stage.

In this paper, we aimed to investigate the influence of the carbon structure in DLC coatings on the formation of MoDTC-derived tribofilm and its friction characteristics. To achieve this goal, DLC coatings with different carbon structures were utilized: ta-C (tetrahedral amorphous carbon) coatings[23–25] and GNC (graphene nanocrystallites) coatings[26–28]. Additionally, the effect of metal doping was evaluated by depositing Tantalum-doped ta-C and GNC coatings, studying their friction properties in a lubricant containing MoDTC[29, 30]. The characteristics of the tribofilm fluctuates during friction, which has effect on the friction coefficient[31–35]. Hence, conducting in situ analysis of the tribofilm is deemed effective. In this study, we employed in situ reflectance spectroscopy to measure the tribofilm thickness and estimate its composition based on optical properties. In situ reflectance spectroscopy has proven effective in elucidating the friction mechanism of nm-scaled transformed layers of DLC coatings[36–40], oil film structure of two-phase lubricants[41], he adsorption of ester in boundary lubrication regimes[42], and MoDTC-derived tribofilm[43]. By combining the in situ observations of tribofilm characteristics with coating properties, we aimed to identify the factors in DLC coatings that influence the friction reduction of MoDTC.

2. Experiment

2.1. Preparation of ta-C and ta-C:Ta coatings

ta-C and Tantalum-doped ta-C (ta-C:Ta) coatings were deposited using the FCVA (filtered cathode vacuum arc) method, as illustrated in Fig. 1. A SUJ2 steel disk was used as the substrate for ta-C coating, while a Si wafer was used for ta-C:Ta coatings. Prior to deposition, the substrate underwent a 20-minute pre-sputtering process with Ar ions to remove surface contaminants. During the deposition process, carbon ions were generated through arc discharge from a graphite target (with a purity of 99.99%). The current used for ta-C deposition was 50 A, while for ta-C:Ta deposition, it was 80 A. The generated carbon ions were accelerated by a bias voltage of -100 V applied to the substrate. The substrate was placed on a rotation table, rotating at 10 rpm for ta-C deposition and 4 rpm for ta-C:Ta deposition. The FCVA system also featured a magnetron sputtering source used to introduce tantalum into the ta-C coating by sputtering a tantalum target (with a purity of 99.99%) using argon ions. The amount of doped tantalum was adjusted by varying the discharge current. Table 1 presents the properties of the ta-C and ta-C:Ta coatings. In this paper, the ta-C and ta-C:Ta coatings are referred to as ta-C, ta-C:Ta_{0.024}, and ta-C:Ta_{0.103}, based on their tantalum-to-carbon ratios measured by XPS (X-ray photoelectron spectroscopy) using the PHI Quantera III instrument from ULVAC-PHI Inc., Japan.
<table>
<thead>
<tr>
<th></th>
<th>ta-C</th>
<th>ta-C:Ta$_{0.024}$</th>
<th>ta-C:Ta$_{0.103}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness $H$, GPa</td>
<td>22.9</td>
<td>12.3</td>
<td>9.5</td>
</tr>
<tr>
<td>Young's modulus $E$, GPa</td>
<td>253.2</td>
<td>162.0</td>
<td>159.3</td>
</tr>
<tr>
<td>Arithmetical mean roughness $R_a$, nm</td>
<td>5.2</td>
<td>2.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Root mean square roughness $R_q$, nm</td>
<td>11.3</td>
<td>5.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Film thickness $t$, nm</td>
<td>127</td>
<td>87</td>
<td>115</td>
</tr>
<tr>
<td>Ta/C ratio</td>
<td>0</td>
<td>0.024</td>
<td>0.103</td>
</tr>
</tbody>
</table>

2.2. Preparation of GNC and GNC:Ta coatings

Pure and tantalum-doped graphene nanocrystalline carbon (GNC) films were deposited on p-type < 100 > silicon substrates using a multifunctional ECR (electron cyclotron resonance) plasma sputtering system, as schematically shown in Fig. 2[27]. This system combines ECR plasma sputtering and magnetron sputtering to achieve its unique hybrid sputtering function. The ECR plasma sputtering method was employed to deposit the GNC film with low-energy electron irradiation, while the magnetron sputtering allowed for independent control of the doping parameters during film deposition. The vacuum chamber maintained a background pressure of $8 \times 10^{-5}$ Pa, with argon gas used to maintain a working pressure of $1 \times 10^{-1}$ Pa. A mirror-confinement magnetic field was created using magnetic coils, and the ECR plasma was generated by introducing microwave (2.45 GHz, 500 W) through a quartz window. Before deposition, the silicon substrate underwent cleaning by argon ion sputtering for 3 minutes. Then, the ECR carbon target was sputtered by argon ions with a bias voltage of -500 V to provide carbon atoms for film growth. During film deposition, low-energy electron irradiation onto the film was achieved by applying a positive bias voltage of +80 V to the substrate. The electron irradiation energy was approximately 80 eV, and the electron irradiation density was 66.2 mA/cm$^2$. Magnetron target currents were set at 100 mA and 300 mA to achieve different tantalum doping concentrations. The deposition time was 30 minutes, and the film thickness was approximately 150 nm.
Table 2
Properties of GNC and GNC:Ta coatings

<table>
<thead>
<tr>
<th></th>
<th>GNC</th>
<th>GNC:Ta_{0.030}</th>
<th>GNC:Ta_{0.113}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness $H$, GPa</td>
<td>1.1</td>
<td>5.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Young’s modulus $E$, GPa</td>
<td>56.5</td>
<td>87.2</td>
<td>91.5</td>
</tr>
<tr>
<td>Arithmetical mean roughness $R_a$, nm</td>
<td>18.3</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Root mean square roughness $R_q$, nm</td>
<td>22.3</td>
<td>5.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Film thickness $t$, nm</td>
<td>166</td>
<td>147</td>
<td>170</td>
</tr>
<tr>
<td>Ta/C ratio</td>
<td>0</td>
<td>0.030</td>
<td>0.113</td>
</tr>
</tbody>
</table>

2.2. Pin-on-disk friction tests with *in situ* reflectance spectroscopy

In this study, a pin-on-disk type friction tester, as depicted in Fig. 3, was utilized to evaluate the friction properties of each DLC coating in a lubricant containing MoDTC. The friction tester was equipped with reflectance spectroscopy (OPTM-H2, Otsuka Electronics Co., Ltd.) to enable *in situ* analysis of the contact point, which was positioned above the contact area. A sapphire hemisphere (diameter of $\varphi$ 8 mm) was used as the mating material for the DLC coatings due to its high transmittance of over 85% in the visible light range. The specific friction test conditions are detailed in Table 3. The measurement spot of the reflectance spectroscopy had a diameter of approximately $\varphi$ 10 µm, which was smaller than the Hertzian contact diameter of approximately $\varphi$ 40 µm under the given friction test conditions.

The friction tests were conducted with a normal load of 0.3 N, a lubricant test temperature of 80°C, and a sliding speed of 18.8 mm/s. The average Hertzian contact pressure, calculated based on the test conditions, ranged from 149 MPa (GNC pure) to 326 MPa (ta-C pure). Furthermore, the film thickness ratio $\lambda$ for the friction tests was less than 0.29, indicating that all the tests were performed under boundary lubrication conditions.
### Table 3
Friction test condition

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Pure PAO4 / PAO4 + MoDTC 700 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sliding cycles $N$</td>
<td>300</td>
</tr>
<tr>
<td>Sliding speed $v$</td>
<td>18.8 mm/s</td>
</tr>
<tr>
<td>Normal load $L$</td>
<td>0.3 N</td>
</tr>
<tr>
<td>Temperature $T$</td>
<td>80 °C</td>
</tr>
<tr>
<td>Average Hertzian contact pressure $p$</td>
<td>149 to 326 MPa</td>
</tr>
<tr>
<td>Initial film thickness ratio $\Lambda$</td>
<td>Less than 0.29 (Boundary lubrication)</td>
</tr>
</tbody>
</table>

#### 2.3 Reflectance fitting

The thickness and optical properties were calculated using the OPTM post-analysis software (Otsuka Electronics Co., Ltd., Japan) based on the *in situ* observed reflectance $R$. Reflectance $R$ was determined using Eq. (1):

$$ R = \frac{\text{Intensity of reflected light}}{\text{Intensity of incident light}} $$

1

For the calculation, the optical model shown in Fig. 4 was utilized. The substrate and atmosphere were represented by Si (Si wafer) and sapphire (sapphire hemisphere), respectively. The DLC coating was also included in the model with fixed optical properties representing the as-deposited state. In the analysis, the tribofilm derived from MoDTC was defined as the analysis layer, with its thickness and optical properties set as variable values. Additionally, each DLC coating had a different surface roughness, so a roughness layer was also considered in the optical model. The roughness in the optical model was treated as a mixture state of two materials (with a ratio of 0.5 and 0.5) according to Eq. (2)[44].

$$ 0.5 \frac{\epsilon_{\text{DLC}} - \epsilon_{rl}}{\epsilon_{\text{DLC}} + 2\epsilon_{rl}} + 0.5 \frac{\epsilon_{\text{tribofilm}} - \epsilon_{rl}}{\epsilon_{\text{tribofilm}} + 2\epsilon_{rl}} = 0 $$

2

Here, $\epsilon$ represents the complex dielectric constant, which is calculated using the refractive index $n$ and the extinction coefficient $k$ with Eq. (3):

$$ \epsilon = \epsilon_1 - i \epsilon_2 = (n^2 - k^2) - i(2nk) $$

3
The reflectance of the optical model $R_{01234}$ was calculated using Eqs. (4)-(10):

$$R_{01234} = |r_{01234}|^2$$

$$r_{01234} = \frac{r_{01} + r_{1234} \exp(-i2\beta_1)}{1 + r_{01} r_{1234} \exp(-i2\beta_1)}$$

$$r_{1234} = \frac{r_{12} + r_{234} \exp(-i2\beta_2)}{1 + r_{12} r_{234} \exp(-i2\beta_2)}$$

$$r_{234} = \frac{r_{23} + r_{34} \exp(-i2\beta_3)}{1 + r_{23} r_{34} \exp(-i2\beta_3)}$$

$$N_m = n_m - i k_m (m = 0,1,2,3,4, N_m, n_m, k_m)$$

$$r_{ij} = \frac{N_i \cos \theta_i - N_j \cos \theta_j}{N_i \cos \theta_i + N_j \cos \theta_j} (i = 0,1,23, j = 1,2,3,4)$$

$$\beta_m = \frac{2\pi t_m N_m \cos \theta_m}{\lambda}$$

Here, $r_{ij}$ represents the amplitude reflectivity between the interfaces of $i$ and $j$. $\beta_m$ is the interference phase angle, $N_m$, $n_m$, and $k_m$ are the complex refractive index, the refractive index, and the extinction coefficient of each layer, respectively, and $t_m$ is the thickness of each layer. The suffixes 0, 1, 2, 3, and 4 indicate sapphire, the tribofilm derived from MoDTC, the roughness layer of the DLC coatings, the DLC coatings, and the Si substrate, respectively. The calculated reflectance $R_{01234}$ (Equations (4)-(10)) was fitted to the in situ measured reflectance $R$ (Eq. (1)) using the nonlinear least-squares method, resulting in the determination of the thickness $t$, the spectrum of refractive index $n$, and the extinction coefficient $k$ of the tribofilm.
3. Material characteristics of each coating and its friction property

3.1. Characteristics of DLC coatings evaluated by Raman spectroscopy X ray photoelectron spectroscopy and Kelvin force microscope

A Raman spectroscopy (RENSHAW, in Via Reflex) equipment with a laser wavelength of 532 nm was used to evaluate coating properties. The measured Raman spectrum was deconvoluted to two typical DLC peaks, G band located between 1500–1600 cm\(^{-1}\) and D band located around 1350 cm\(^{-1}\) by using Gaussian function. The measured Raman spectra and deconvolution were indicated in Fig. 5. The ta-C and ta-C:Ta coatings showed broad Raman spectra, while the GNC and GNC:Ta coatings exhibited relatively sharp G and D peaks. The ratio of intensity of G and D peaks were shown as \(I_D/I_G\) ratio in Fig. 6. The \(I_D/I_G\) ratio of ta-C:Ta coatings increased from 0.19 to 1.00 with an increasing Ta/C ratio. On the other hand, the \(I_D/I_G\) ratio of GNC:Ta coatings remained around 1.2 regardless of the Ta/C ratio. G peak derives from a vibration of graphite, and D peak derives from defects of sp\(^2\) structure\[45, 46\]. Therefore, it was considered that the specimens with higher \(I_D/I_G\) ratio such as GNC:Ta coatings and ta-C:Ta\_0.103 coating included large number of defects of graphite.

Furthermore, the ratio of C-C sp\(^2\) bonding and C-C sp\(^3\) bonding of each coating was investigated by using XPS equipment. The C1s narrow peak (280 eV – 295 eV) was obtained, and its background was calculated by using Shirley method as shown in Fig. 7\[48\]. In the case of the ta-C pure and GNC pure coatings, the C 1s narrow peak was deconvoluted into C-C sp\(^2\) (284.4 eV), C-C sp\(^3\) (285.4 eV) and C-O (287.6 eV)\[49\]. In the case of Ta doped DLC coatings, C-Ta (283.6 eV) was considered in addition to C-C sp\(^2\), C-C sp\(^3\), and C-O\[50\]. The results of peak deconvolution are indicated in Fig. 8, and calculated \(\text{sp}^2/\left(\text{sp}^2 + \text{sp}^3\right)\) ratio from Fig. 8 were shown in Fig. 9. The ta-C pure coating had the smallest \(\text{sp}^2/\left(\text{sp}^2 + \text{sp}^3\right)\) ratio of 0.33, which indicated the sp\(^3\) rich structure. For both ta-C:Ta and GNC:Ta coatings, \(\text{sp}^2/\left(\text{sp}^2 + \text{sp}^3\right)\) ratio increased with a larger Ta/C ratio. Thus, the doping Ta contributed to make the sp\(^2\) bonding in the DLC coatings.

In addition, we measured a work function of DLC coatings used in the friction tests. A work function of DLC surface was evaluated by Kelvin method, and Kelvin force microscopy (KFM) mode of an atomic force microscopy (SPA-400, Hitachi High-Tech) was utilized. In a KFM measurement, a contact potential difference \(\Delta V\) between specimen (DLC coatings) and probe (Rh coated cantilever, Si-DF3-R, Hitachi High-Tech). A work function of the DLC coatings were calculated from measured \(\Delta V\) by using Eq. (14) below;

\[
\Delta V = \frac{\varphi_{\text{specimen}} - \varphi_{\text{probe}}}{e}
\]

\(e\) indicates elementary charge, \(\varphi_{\text{specimen}}\) and \(\varphi_{\text{probe}}\) indicates a work function of a specimen and a probe, respectively. In the experiment, \(\varphi_{\text{probe}}\) was the work function of Rh, 4.98 eV\[51\]. The measured work
function of 6 type DLC coatings was indicated in Fig. 10. The work function of ta-C pure coating was 4.93 eV, which value was typical to ta-C coating[52]. The work function of GNC coatings decreased from 5.14 eV to 5.00 eV with increasing Ta/C ratio. In the case of ta-C:Ta coating, the work function of ta-C:Ta$_{0.024}$ coating and ta-C:Ta$_{0.103}$ was 4.83 eV and 5.01 eV.

3.2 Friction test results of ta-C:Ta and GNC:Ta coatings with MoDTC-added lubricant

Friction characteristics of DLC coatings in a MoDTC-added lubricant were indicated in Fig. 11. As illustrated in Fig. 11(a), the ta-C:Ta$_{0.113}$ coating exhibited the lowest friction coefficient among all DLC specimens, which value was reduced to around 0.07 in the end of the friction test. Conversely, ta-C:Ta$_{0.024}$ coating exhibited the highest friction among all DLC coatings. The friction characteristics of GNC coatings in MoDTC-added lubricant were compared in Fig. 11(b). All GNC coatings exhibited similar friction coefficients and fluctuated around 0.10 regardless of Ta/C ratio (Ta concentration). From the results of GNC:Ta coatings, Ta concentration was not considered to be significant to friction reduction effect of MoDTC. As an important coating property, the relation between average friction coefficient (average of 3 times friction tests for each DLC coating) and $I_{D}/I_{G}$ ratio were shown in Fig. 12. In Fig. 12, coatings with a higher $I_{D}/I_{G}$ ratio (such as ta-C:Ta$_{0.103}$ and all GNC:Ta coatings) tended to exhibit a lower friction, approximately 0.10 or less, with the MoDTC-added lubricant. These results suggested that the DLC coatings with higher $I_{D}/I_{G}$ ratio was effective to reduce friction with MoDTC-added lubricant. Considering the case of the ta-C pure coating, its $I_{D}/I_{G}$ ratio was lower than that of the ta-C:Ta$_{0.024}$ coating. However, its average friction coefficient was 0.124, which was lower than that of ta-C:Ta$_{0.024}$.

The ta-C pure coating had the highest hardness of 22.9 GPa of all the coatings. Due to its high hardness, the mating sapphire hemisphere had a larger wear. Measured diameter of the wear track was 305.7 µm, which value was larger than the initial Hertzian contact diameter of 34.2 µm. Therefore, it was considered that reducing contact pressure and transferring to the mild lubrication condition caused by wear contributed to reducing friction, which was also verified from Raman spectroscopy in the next chapter.

3.3 Raman spectroscopy of the tribofilm formed on each coating

Raman spectroscopy is a useful technique to evaluate MoDTC-derived tribofilm. This is because a major product of MoS$_2$ has two unique peaks of $A_{1g}$ peak at 409 cm$^{-1}$ and $E_{2g}$ peak at 383 cm$^{-1}$. [32, 53] In the present paper, Raman analysis of tribofilm formed on four specimens, ta-C pure, ta-C:Ta$_{0.024}$, ta-C:Ta$_{0.103}$ and GNC:Ta$_{0.030}$, was conducted. The Raman spectra of four specimens was indicated in Fig. 13. The peaks of $A_{1g}$ and $E_{2g}$ were observed from the tribofilm on the ta-C:Ta$_{0.024}$, GNC:Ta$_{0.030}$ and ta-C:Ta$_{0.103}$ coatings, and especially higher intensity of GNC:Ta$_{0.030}$ and ta-C:Ta$_{0.103}$ coatings. On the other hand, the peaks of $A_{1g}$ and $E_{2g}$ were hardly observed from the tribofilm on the ta-C pure coating, which indicated a weak generation of MoS$_2$. The intensities of $A_{1g}$ and $E_{2g}$ peaks correlate with the amount of MoS$_2$ on the
tribofilm. Therefore, the relation between the intensity of $A_{1g}$ peak and friction coefficient was indicated in Fig. 14. The specimen with higher $A_{1g}$ peak intensity such as the GNC:Ta$_{0.030}$ and ta-C:Ta$_{0.103}$ coatings tended to be lower friction of around 0.10. From the result, friction reduction of the GNC:Ta$_{0.030}$ and ta-C:Ta$_{0.103}$ coatings was caused by rich generation of MoS$_2$. In addition, the tribofilm with higher intensity of MoS$_2$-derived $A_{1g}$ peak was formed on the specimen with higher $I_D/I_G$ ratio such as GNC:Ta$_{0.030}$ ($I_D/I_G = 1.16$) and ta-C:Ta$_{0.103}$ ($I_D/I_G = 1.00$). From the result, it was considered that the characteristics of DLC coatings had an effect on a generation of low-shear material of MoS$_2$.

### 3.4 EDS analysis of the tribofilm

Components of tribofilm was analyzed by energy dispersive X-ray spectroscopy (EDS). The EDS spectra of the tribofilm were compared in Fig. 15. For the tribofilms formed on the ta-C:Ta$_{0.024}$, GNC:Ta$_{0.030}$, and ta-C:Ta$_{0.103}$ coatings, the existence of C and O were confirmed. In simple peaks of C(Kα) at 0.277 keV and O(Kα) at 0.525 keV, and convolutions of Ta (M) at 1.71 keV with Si (Kα) at 1.74 keV and Mo (Lα) at 2.29 keV with S (Kα) at 2.31 keV were observed. Specifically, a peak corresponding to Al (Kα) was identified from the tribofilm on the ta-C:Ta$_{0.024}$ coating. Aluminum was considered to be derived from the wear particles of sapphire hemisphere (Al$_2$O$_3$). The ta-C:Ta$_{0.024}$ coating was relatively hard material of 12.3 GPa compared with the GNC:Ta$_{0.030}$ and ta-C:Ta$_{0.103}$ coatings of 5.2 GPa and 9.5 GPa, respectively. Thus the mating sapphire of the ta-C:Ta$_{0.024}$ generated the wear particles, which was included in the tribofilm.

### 4. In situ observation of the tribofilm by using a reflectance spectroscopy

4. **In situ** observation of the tribofilm by using a reflectance spectroscopy

#### 4.1 Transition of tribofilm thickness

A thickness $t$ and optical properties including refractive index $n$ and extinction coefficient $k$ of the tribofilm was calculated by using a formula of optical interference indicated in Eq. (4)-(10). The analysis and consideration was conducted to the tribofilm formed on the ta-C:Ta$_{0.024}$, ta-C:Ta$_{0.103}$, GNC pure, GNC:Ta$_{0.030}$ and GNC:Ta$_{0.113}$ coatings with every 60 cycles. The calculated tribofilm thickness was shown in Fig. 16. In the case of tribofilm on the GNC pure coating, the reflectance at 60 cycles was noisy and less than minimum resolution of 0.01 of the equipment, so the analysis was conducted after 120 cycles. The tribofilm on the ta-C:Ta$_{0.103}$ coating consistently exhibited a thickness of around 6 nm, which value was less than half of the other tribofilm thickness. In Fig. 17, the relation between tribofilm thickness and friction coefficient was indicated. 3 types of GNC:Ta coating had the similar friction characteristics of around 0.10. However, the tribofilm thickness on the GNC:Ta$_{0.113}$ was mostly over 25 nm, which value was larger than the tribofilm on the GNC pure and GNC:Ta$_{0.030}$ coatings by 10 nm.
Therefore, we considered that the other characteristics of the tribofilm had more significant effect on a friction property, so we also considered the transition of the tribofilm composition.

4.2 Estimation of tribofilm composition from its optical properties

From the calculation of optical interference, optical properties were also calculated in addition to the thickness. As an example, the transition of refractive index \( n \) and extinction coefficient \( k \) of the tribofilm formed on the ta-C:Ta\(_{0.103}\) coating were shown in Fig. 18. The specimen experienced a gradual friction reduction with a friction progress in MoDTC-added lubricant. In terms of the optical properties, both refractive index and extinction coefficient increased with friction progress. This result indicated that \textit{in situ} reflectance spectroscopy was effective to observe the evolution of tribofilm and its friction property simultaneously. The optical properties of the tribofilm was considered to be determined by its components such as MoDTC-derived products and wear particle of DLC coating. Thus, we tried to estimate the composition of the tribofilm from its optical properties by using effective medium approximation (EMA)[44].

In EMA method, the complex dielectric constant of the mixture (tribofilm in this case) was determined by complex dielectric constant and volume fraction of each component as described in Eqs. (11) and (12)

\[
\sum_{i=1}^{n} f_i \frac{\epsilon_i - \epsilon_{tribofilm}}{\epsilon_i + 2\epsilon_{tribofilm}} = 0
\]

\[
\sum_{i=1}^{n} f_i = 1
\]

\( \epsilon_{tribofilm} \) means a complex dielectric constant of the tribofilm, which value was calculated by using a refractive index and extinction coefficient of \textit{in situ} reflectance spectroscopy. \( \epsilon_i \) means a complex dielectric constant of each component, which value was calculated by using a pre-measured refractive index and extinction coefficient. Complex dielectric constant was calculated by using a refractive index \( n \) and extinction coefficient \( k \) as shown in Eq. (13).

\[
\epsilon_i = \left( n_i^2 - k_i^2 \right) - i \left( 2n_i k_i \right)
\]

In the case of the tribofilm formed on the ta-C:Ta\(_{0.103}\), GNC pure, GNC:Ta\(_{0.030}\) and GNC:Ta\(_{0.113}\) coatings, the tribofilm was assumed 3 components of MoS\(_2\), MoO\(_3\) and wear particles from DLC coatings. MoS\(_2\) and MoO\(_3\) are the major products from MoDTC, which optical properties were measured by using the pure
specimen of MoS$_2$ and MoO$_3$. The optical properties of wear particles from DLC coatings were used the value of as-deposited state of each coating. Furthermore, the tribofilm on the ta-C:Ta$_{0.024}$ coating also considered the existence of sapphire in addition to MoS$_2$, MoO$_3$ and DLC particles because it included wear particles of the mating sapphire as described in the chapter 3.4. 

A transition of the volume fraction of the tribofilm estimated from optical properties were indicated in Fig. 19. As shown in Fig. 19(a), the tribofilm on the ta-C:Ta$_{0.024}$ coating contained approximately 34% of sapphire. In terms of MoDTC-derived products, the tribofilm contained almost same volume fraction of MoS$_2$ and MoO$_3$. In the case of the tribofilm on the ta-C:Ta$_{0.103}$ coating, which experienced a friction reduction to 0.07, the volume fraction of MoS$_2$ in the tribofilm on ta-C:Ta$_{0.103}$ increased from 40.6 vol.% to 50.2 vol. % with friction. Instead of MoS$_2$ fraction increasing, the volume fraction of MoO$_3$ of the tribofilm decreased from 32.5 vol. % to 15.9 vol. %. To evaluate the effect of MoDTC-derived products on friction characteristics, MoS$_2$/ (MoS$_2$ + MoO$_3$) ratio was calculated from the volume fraction shown in Fig. 19, and the relation between MoS$_2$/ (MoS$_2$ + MoO$_3$) ratio and friction coefficient was indicated in Fig. 20. MoS$_2$/ (MoS$_2$ + MoO$_3$) ratio of the tribofilm on the ta-C:Ta$_{0.103}$ coatings increased to 0.75, and friction decreased to 0.07. On the other hand, MoS$_2$/ (MoS$_2$ + MoO$_3$) ratio of the tribofilm on the ta-C:Ta$_{0.024}$ coatings was around 0.50, and friction coefficient was over 0.12. The plots of the tribofilm formed on GNC:Ta coatings concentrated at MoS$_2$/ (MoS$_2$ + MoO$_3$) ratio of around 0.65 and friction coefficient of around 0.10. The correlation coefficient $R$ between MoS$_2$/ (MoS$_2$ + MoO$_3$) ratio and friction coefficient was $R = -0.85$, which indicated the strong correlation.

Thus, it was considered that the friction coefficient was strongly affected by the generation of low-shear material of MoS$_2$ of MoDTC-derived materials, and the DLC coatings with higher $I_D/I_G$ ratio enhanced the generation of MoS$_2$. 

5. Discussion

5.1 Consideration of the measured work function and $I_D/I_G$ ratio

The relation between $I_D/I_G$ ratio and work function was indicated in Fig. 21. Generally, the DLC coatings with higher $I_D/I_G$ ratio had a higher work function except the ta-C pure coating. Akada et. al. reported that the work function of highly oriented pyrolytic graphite (HOPG, defect-free graphite) increased with damage caused by Ar plasma[54]. Thus, it was considered that the DLC coating with higher work function included large amount of defect of graphite structure (graphite edge), which increased the intensity of D peak in a Raman analysis. Furthermore, the of ta-C pure coating had a smaller $sp^2/ (sp^2 + sp^3)$ ratio of 0.33, which indicated $sp^3$-rich amorphous structure. Thus, the work function of the ta-C pure coating is considered to be determined by another factor such as dangling bonds except graphite edge.
5.2 Consideration of friction reduction effect of tribofilm formed on each DLC coating

Nakashima et.al. reported that adhered of silica occurred on the graphite edge with a higher work function[22]. In addition, Murashima et. al. reported that ZnDTP-derived tribofilm was richly generated on the DLC coating with a higher sp²/sp³ ratio and including graphite edge[55]. From these previous reports, defects of graphite are considered to be active and have effect on lubricant additives. In addition, Murabayashi proposed the decomposition process of MoDTC on a DLC coating by molecular dynamics simulation[56]. In their report, MoDTC adheres to a DLC surface and give an electron to DLC, which process enhances the decomposition of MoDTC. Thus, graphite edge was considered to be significant as the site that MoDTC adhered and react with DLC surface, which was the reason why the specimen with higher \( \frac{I_D}{I_G} \) ratio showed a lower friction with MoDTC.

In addition, the ta-C:ta_{0.103} coating exhibited the lowest friction coefficient of 0.07 and kept the tribofilm with large MoS₂ concentration in all DLC specimens. In previous reports by Komori, a hard and rough DLC coating encouraged MoS₂-rich tribofilm due to higher contact pressure at asperities and larger frictional heat. In the present paper, 3 types of GNC:Ta coatings had a higher \( \frac{I_D}{I_G} \) ratio of around 1.2, but hardness was ranged from 1.1 GPa (GNC pure) to 6.0 GPa (GNC:Ta_{0.113}), which was softer than the ta-C:Ta_{0.103} coating of 9.5 GPa. Thus, the ta-C:Ta_{0.103} coating was considered to be the suitable state in the perspective of including active site of graphite edge and enough hardness to encourage the generation of MoS₂ and friction reduction.

6. Conclusion

In the present paper, the effect of carbon structure of DLC coatings on friction reduction with MoDTC-added lubricant was investigated. To reach the objective, ta-C coatings (amorphous structure) and GNC coatings (including nano-graphite crystal) were prepared with different deposition methods. In addition, to investigate the effect of doping metal to DLC coatings, Ta doped ta-C coating with different Ta amount (ta-C pure, ta-C:Ta_{0.024} and ta-C:Ta_{0.103} coatings) and Ta doped GNC coating with different Ta amount (GNC pure, GNC:Ta_{0.030} and GNC:Ta_{0.113} coatings) were prepared. In the friction test, \textit{in situ} observation of thickness and composition of the tribofilm by using a reflectance spectroscopy was conducted to evaluate the relation between the characteristics of tribofilm and friction properties. The important results are described below;

- 3 types of GNC:Ta coatings had a larger \( \frac{I_D}{I_G} \) ratio of around 1.2 regardless of Ta amount. On the other hand, \( \frac{I_D}{I_G} \) ratio of ta-C:Ta coatings increased from 0.19 to 1.00 with increasing Ta amount.
- The friction coefficient of ta-C:Ta_{0.103} coatings decreased to the least value of 0.07 with friction progress in MoDTC-added lubricant. The friction coefficient of the GNC:Ta coatings fluctuated around 0.10. Conversely, the ta-C:Ta_{0.024} coatings showed the relatively larger friction coefficient of
0.17, which suggested the weak contribution of MoDTC. Generally, friction coefficient decreased with higher $I_D/I_G$ ratio coatings.

- From the *in situ* analysis of tribofilm, there was a strong relation between the $\text{MoS}_2/\left(\text{MoS}_2 + \text{MoO}_3\right)$ ratio and friction coefficient with correlation coefficient of $-0.85$, which indicated that the concentration of $\text{MoS}_2$ in the tribofilm determined the friction characteristics.

- The DLC coatings with higher $I_D/I_G$ ratio had a larger work function, which indicated the existence of large amount of graphite edge as an active site. Thus, it was considered that the DLC coatings with higher $I_D/I_G$ enhanced the generation of $\text{MoS}_2$ from MoDTC and enhanced friction reduction.

**Declarations**

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationship that could appeared to influence the work reported in this paper.

**CRediT authorship contribution statement**

**Naoya Hashizume**: Methodology, Investigation, Writing – original draft. **Yusei Yamamoto**: Methodology, Investigation, Writing – review & editing. **Cheng Chen**: Methodology, Investigation, Writing – review & editing. **Takayuki Tokoroyama**: Methodology, Investigation, Writing – review & editing. **Ruixi Zhang**: Methodology, Writing – review & editing. **Dongfeng Diao**: Conceptualization, Project administration, Resources, Supervision, Writing – review & editing. **Noritsugu Umehara**: Conceptualization, Project administration, Resources, Supervision, Writing – review & editing.

**Data availability statement**

The data used in this research is available upon request.

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**References**


Figures

![Diagram](image-url)
Schematics of FCVA deposition system for ta-C and ta-C:Ta coatings

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_ta-C:Ta coatings vs. Sapphire hemisphere
Lubricant: PAO4 + MoDTC 700 ppm
Sliding cycles $N$: 300, Sliding speed $v$: 18.8 mm/s
Normal load $F$: 0.3 N, Temperature $T$: 80 °C

(a) ta-C:Ta 

(b) GNC:Ta coatings vs. Sapphire hemisphere
Lubricant: PAO4 + MoDTC 700 ppm
Sliding cycles $N$: 300, Sliding speed $v$: 18.8 mm/s
Normal load $F$: 0.3 N, Temperature $T$: 80 °C

GNC pure

GNC:Ta$_{0.113}$

GNC:Ta$_{0.030}$
Friction characteristics with MoDTC-added lubricant (a)ta-C:Ta coatings (b)GNC:Ta coatings

Relation between $I_D/I_G$ ratio and friction coefficient with MoDTC-added lubricant

Figure 12

- ta-C:Ta / GNC:Ta coatings vs. Sapphire hemisphere
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Transition of the composition of the tribofilm formed on each DLC coating
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Relation between MoS$_2$ / (MoS$_2$ + MoO$_3$) ratio and friction coefficient
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Relation between work function and $I_D/I_G$ ratio of each DLC coating