エステル系基油中における Cr 添加 DLC 膜の摩擦特性

Friction Properties of Cr-DLC Films under the Ester Oil Lubrication

東大・工（院）*裵　水旼　　都市大・工（正）**崔　埈豪

Su-Min Bae*, Junho Choi**

*The University of Tokyo, **Tokyo City University

1. Introduction

Lubricants play a crucial role in maintaining mechanical systems by acting as a lubricating layer, minimizing asperity-asperity interactions between contacting bodies. Careful selection and application of lubricants can significantly prolong the lifespan of mechanical systems, ensuring smooth and efficient operation. In particular, low-viscosity oils have the potential for substantial energy savings within mechanical systems under electrohydrodynamic and hydrodynamic lubrication. For example, in the automotive sector, the adoption of low-viscosity oils is considered a proactive measure to address concerns related to fuel consumption and greenhouse gas emissions. Relevant reports suggest that a 25% reduction in oil viscosity leads to fuel savings of 0.6-5.5% [1]. However, low-viscosity oils come with conspicuous disadvantages that require careful consideration for practical applications. A primary drawback is the formation of a thin barrier on surfaces, which becomes problematic, especially under boundary lubrication. The thin oil film is susceptible to surface degradation under high temperature and pressure, conditions commonly encountered in general mechanical components, resulting in increased friction, accelerated wear, and potential damage to machine components.

To address this issue, the research applied diamond-like carbon (DLC) coatings, considering their benefits such as high hardness, superior durability, corrosion resistance, and low-frictional nature under boundary lubrication. With the aim of modifying the coating's surface chemistry and eliciting tribologically favorable products from the MoDTC decomposition, Cr was appropriately adopted as a dopant into DLC due to its chemical affinity to organic matter [2]. Further, the tribological properties of Cr-DLC coatings were evaluated under low-viscosity oil lubrication, and the tribochemical role of Cr doping on MoDTC decomposition was investigated.

2. Experiments

DLC and Cr-DLC coatings were fabricated using a hybridized plasma deposition technique that combined bipolar plasma-based ion implantation and deposition (PBII&D) with RF magnetron sputtering. A reciprocating tribometer was utilized to assess the tribological properties of the coatings. All sliding tests were conducted under boundary lubrication conditions, with a sliding frequency of 1 Hz and a stroke of 8 mm. The normal load, temperature, and duration were set at 3 N, 80°C, and 15 minutes, respectively. Ester-based synthetic oil (referred to LO hereafter) served as a low-viscosity oil, and a binary lubricant additive package of molybdenum dithiocarbamates (MoDTC) and zinc dialkyl dithiophosphates (ZDDP) was blended. Raman spectroscopy was employed to analyze the tribofilm formed through the tribochemical reactions of the additives. For tribofilm analysis, the specimens were rinsed with heptane before measurement to eliminate any residual lubricant on the surface.

3. Results and discussion

The averaged coefficients of friction (COF) values and wear rates for all coatings are presented in Fig. 1(a,b). Cr-DLC 1 demonstrated the lowest averaged COF (~0.07) and wear rate (3.3×10^{-11} $mm^3/N\cdot mm$) in LO lubrication, surpassing DLC and Cr-DLC 2 with wear rates of 1.2×10^{-10} and 2.5×10^{-10} $mm^3/N\cdot mm$, respectively. Cr-DLC 3 exhibited the highest wear rate, suggesting a potential deficiency in adhesion. The inclusion of MoDTC into LO resulted in COFs for all coatings recorded at ~0.13. Although the averaged COFs decreased with Cr doping, the values generally remained higher than those observed with LO alone. Cr-DLC 2 recorded a lower value of ~0.09 compared to other coatings; nevertheless, it was relatively higher than the typical COF range of 0.04–0.08 observed in MoDTC-containing lubrication. While MoDTC is known for producing molybdenum disulfide (MoS_2), a low-frictional material, the obtained COFs did not support the presence of MoS_2 in the tribofilm. The tribochemical products of the tribofilm generated under LO + MoDTC lubrication were strongly affected by competitive adsorption between LO and MoDTC. The cause of competitive adsorption is attributed to the ester functional group within the LO molecule, resulting in polarity. Since the polarity hinders the access of lubricant additives to the surface and interferes with their lubricating ability.

The COFs were significantly reduced by adding ZDDP in LO + MoDTC, as shown in Fig. 1(a). The primary reason for the reduced friction was the formation of a MoS_2-rich tribofilm; since ZDDP is known to preferentially adsorb to the surface and form a phosphate tribofilm, which facilitates the effective diffusion of MoDTC. As a result, a MoS_2-rich tribofilm is effectively generated. Raman analysis provided evidence of the abundant production of MoS_2 in the tribofilm. As shown in Fig. 2, the spectra of DLC, Cr-DLC 1, and Cr-DLC 2 exhibited three 1st-order Raman peaks of MoS_2 at wavelengths of 230, 383, and 408 cm^{-1}, corresponding to in-plane longitudinal acoustic mode (LA(M)), in-plane (E^1_{2g}), and out-of-plane (A_{1g}) vibrational modes within Mo-S-Mo, respectively, as reported in [3]. Additionally, the spectra featured additional 2nd-order Raman peaks of MoS_2 at wavelengths of 455, 545, 596, and 641 cm^{-1}, corresponding to 2LA(M), E_{1g}+LA(M), E^1_{2g}+LA(M), and A_{1g}+LA(M), respectively [4]. According to De Barros Bouchet et al. [5], the simultaneous use of MoDTC and ZDDP has a synergistic effect in promoting the production of MoS_2 in the tribofilm, because ZDDP acts to sulfurize the intermediate molybdenum oxysulfide species of decomposed MoDTC by supplying sulfur atoms. This was evidenced by the rise of 2nd-order peaks resulting from increased production of MoS_2 [6]. The synergistic effect also contributed to the improvement in durability, as indicated by lower wear rates observed in coatings under LO + MoDTC + ZDDP lubrication compared to those observed with LO + MoDTC lubrication.

The tribochemical reactions in DLC and Cr-DLC coatings were distinguished by the decreased MoO_3 ratio. Oxygen is crucial in forming MoO_3 in the chemical pathway $MoO_2 \rightarrow MoO_3$. However, oxygen is also important for the oxidation of CrC_x wear particles. This leads to a competition between the chemical pathway $MoO_2 \rightarrow MoO_3$ and the oxidation of CrC_x. As a result, MoO_2, being chemically unstable, oxidizes with a lower chance, making it more susceptible to sulfurization by ZDDP.

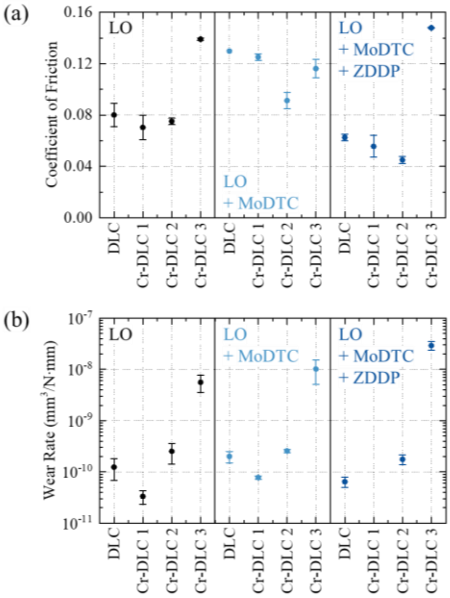

Fig. 1 (a) The averaged coefficients of friction and (b) wear rates under LO, LO + MoDTC, and LO + MoDTC + ZDDP lubrication.

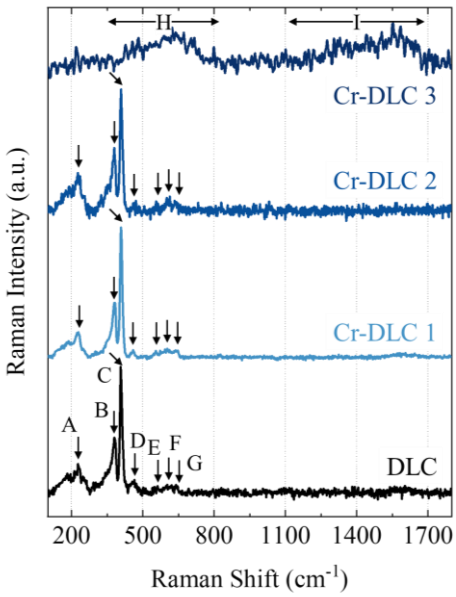

Fig. 2 Raman spectra of the tribofilm formed under LO + MoDTC + ZDDP lubrication. The label A-I were based on [3,4].

4. Conclusion

The tribological characteristics of Cr-DLC coatings were investigated under low-viscosity oil lubrication. The impact of Cr doping on tribochemical processes was examined in LO lubrication with a binary additive package of MoDTC and ZDDP. Elevated COFs were observed under LO + MoDTC lubrication because the adsorption of MoDTC was interrupted by the polarity of LO, resulting in the absence of MoS_2 in the tribofilm. The inclusion of ZDDP into LO + MoDTC lubrication facilitated the formation of a MoS_2-rich tribofilm. The highly polar ZDDP is preferentially adsorbed, enabling the effective diffusion of the intermediate Mo oxysulfide. A gradual reduction in COF was achieved through Cr doping under LO + MoDTC + ZDDP. CrC_x played a role in capturing oxygen dissolved in the lubricant, hindering the oxidation of MoO_2.

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