ta-C/Steel 接触面での MoDTC 由来トライボ被膜の形成に及ぼす TiO2 ナノ粒子の摩擦触媒的影響

Tribocatalytic Reaction Enabled by TiO_2 Nanoparticle for MoDTC-Derived Tribofilm Formation at ta-C/Steel Contact

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1. Introduction

Tribochemically generated tribofilms play a pivotal role in enhancing lubrication and preventing surface damage in tribological systems [1]. These films, derived from friction by-products, are crucial for the efficiency of tribosystems. Oil-soluble additives like molybdenum dithiocarbamate (MoDTC) and zinc dialkyl dithiophosphates (ZnDTPs) are commonly employed in transportation machinery to form low-shear, wear-protecting tribofilms. Specifically, MoDTC is esteemed for its ability to produce MoS2-containing tribofilms, serving as an effective friction modifier and extreme pressure additive [2].

Concurrently, there's a surge in research on surface treatments for engine components to bolster long-term durability. Environmental concerns and the push for miniaturization of engine parts have shifted lubrication regimes towards mixed and boundary lubrication [3]. Tetrahedral amorphous carbon (ta-C) coatings, a variant of diamond-like carbon (DLC) known for high hardness and chemical stability, have emerged as suitable hard coatings [4]. However, their chemical stability can impede tribofilm formation, leading to explorations into metal-doped DLCs (Me-DLCs) to enhance reactivity with additives.

Tribocatalysts, particularly nanoparticles (NPs), have garnered attention for their mechanochemical promotion of material reactions. While TiC coatings and Ti-doped DLCs exhibit favorable triboreaction characteristics, they compromise hardness of DLC. Introducing titanium-based NPs into lubricants offers potential friction improvements without degrading ta-C. Titanium's minimal d-orbital count and high reactivity make it ideal for tribological applications. Among its oxides, rutile-phase TiO_2 is notable for its high dielectric constant, beneficial for triboelectric applications.

This study incorporates anatase-phase and rutile-phase titanium dioxide NPs (a-TDONPs and r-TDONPs) into poly alpha-olefin (PAO4) with 700 ppm of MoDTC. The aim is to harness titanium's valence bonding and TiO2's catalytic properties to enhance lubricity in ta-C/steel tribopairs. Optimal TDONP concentrations for friction performance were determined, acknowledging that long-term dispersion and precipitation were beyond this study's scope.

2. Experimental procedure

a-TDONPs and r-TDONPs (EM Japan Co., LTD., Tokyo, Japan; purity = >3 N; φ = 30 nm) were prepared to confirm their friction properties at similar sizes and purity. Since anatase (H = 12.5 GPa) is chemically more unstable and has a lower hardness than rutile (H = 15.5 GPa), two types of TDONPs were used to compare the difference as tribocatalysts. Anatase is used in the photocatalyst field, and rutile is used as an excellent triboelectric material, so its usefulness in tribocatalysis was evaluated. On the other hand, inorganic TiO_2 has poor surface compatibility with oil, so its dispersing performance is extremely poor. In order to disperse even during the tribotest, we proceeded with the following surface treatment. A technique to improve dispersibility has been reported to react with oleic acid (OA), an organic alteration agent, in n-hexane as oil-based suspensions. Through this, inorganic nanoparticles chemically absorb alkyl canes, increasing the oil affinity of inorganic nanoparticles. First, TDONPs, OA, and n-hexane were ultrasonically mixed at a ratio of 1 g:1 g:100 mL, respectively. After that, the mixed solution was stirred with a magnetic stirrer (AS ONE CHPS-170DF, Osaka, Japan) to evenly treat the surface. For sufficient reaction, the temperature of the solution was set to 60 °C, and the reaction was elicited by stirring for 5 h. After the reaction was complete, the TDONPs were collected on a PTFE membrane filter (Merck Omnipore, Bellerica, MA, USA, pore size: 0.2 μm) by vacuum filtration and washed with isopropyl alcohol and de-ionized water to remove unbound OA and n-hexane. Finally, the OA-modified TDONPs were heated in a furnace at 100 °C for 1 day to evaporate residual moisture and contaminants. Hereinafter, 'TDONPs' refer to 'OA-modified TDONPs'.

The friction performance of TDONPs was evaluated using a ball-on-disk-type tribometer and tribotests were repeated at least 3 times to assure reliability. A ta-C-coated disk and a SUJ2 ball (diameter 8 mm) were utilized as a DLC/steel tribopair. PAO4 mixed with 700 ppm MoDTC and 0–2.5 wt.% TDONPs were heated in an oil bath and functioned as a lubricant. A load of ~10 N was applied using a weight of 1 kg, and the ta-C coated disk rotated at a sliding speed of 34 mm/s for 3 h, corresponding to ~250 m of sliding distance. The maximum contact pressure was ~1.3 GPa, and the coefficient of friction (CoF) was collected in an initial boundary lubrication regime with a Lambda ratio less than 1.

3. Results and discussion

First, 0.0, 1.0, 1.5, 2.0, and 2.5 wt.% of a-TDONPs and r-TDONPs were mixed with lubricating oil in which 700 ppm of MoDTC was added to PAO4 (Figure 1). Tribotest was conducted at a temperature of 80 °C, which is similar to the environment of a vehicle engine and where MoDTC can be activated. At this time, the initial Lambda ratio was very low, ~0.05, meaning that friction was dominated by solid lubrication. The friction performance of the ta-C/steel tribopair was evaluated at a load of 10 N and a speed of 34 mm/s. As a result, the friction tended to decrease as the addition of TDONPs increased. The oil without a-TDONPs showed a friction of 0.074, and the oil with 2 wt.% of a-TDONPs and r-TDONPs showed a friction improvement effect of approximately 57% and 100% at 0.047 and 0.037 of friction coefficient, respectively. However, with an addition amount of 2.5 wt.%, the friction increased to 0.063 and fluctuated unstably. Similar wear rate was observed even when the amount of a-TDONPs was increased to 2 wt.% compared to the case where TDONPs were not added. On the other hand, in the case of r-TDONPs, the wear rate slightly decreased as the addition amount increased up to 2 wt.%. However, as the concentration exceeded 2 wt.%, the wear increased in both the anatase and the rutile. At the amount of 2.5 wt.% TDONPs in PAO4, the TDONPs no longer kept their dispersibility and precipitated on the surface and outside of ta-C, which is believed to be the cause of the increase in friction. In addition, a noticeable increase in wear was observed in rutile, which has relatively higher hardness compared to anatase, and it is believed that this caused three-body wear in ta-C, causing a rapid increase in wear.

Representatively, the composition of the tribofilm formed under the addition of 0.0 wt.% and 2.0 wt.% of a-TDONPs or r-TDONPs was investigated by using EDS (Figure 2). Since the EDS energy levels of Mo *L* and S *K* are similar, it is difficult to distinguish them, so they were not divided. As a result, when TDONPs were not added, Mo or S signals were mainly detected outside the wear track on ta-C. In contrast, when 2.0 wt.% of a-TDONPs was added, Mo or S signals were also strongly detected in the center of the wear track on ta-C. Moreover, in r-TDONPs, Mo or S intensity was obtained extensively inside the wear track of ta-C. The friction coefficient gradually decreased as the formation area of the tribofilm containing Mo or S increased on the ta-C disk. The addition of TDONPs could form MoDTC-derived tribofilms on the ta-C disk, and their effects were different for each phase of TiO_2. On the other hand, a Ti interlayer was deposited to increase ta-C adhesion; therefore, no significant difference could be obtained in the Ti mapping result. On the surface of the steel ball, the Mo or S intensity was detected weakly and narrowly under lubrication without TDONPs addition. On the other hand, under the lubricant added with 2.0 wt.% of a-TDONPs or r-TDONPs, the intensity of Mo or S inside the worn surface was higher than that outside the worn surface on the steel ball. At the same time, Ti was detected at the same location as Mo or S. This might suggest that Ti, which we intended, played a role as the adhesive layer of tribofilm. Based on the results so far, it was deduced that Ti increased the adhesion of Mo-or S-containing tribofilms.

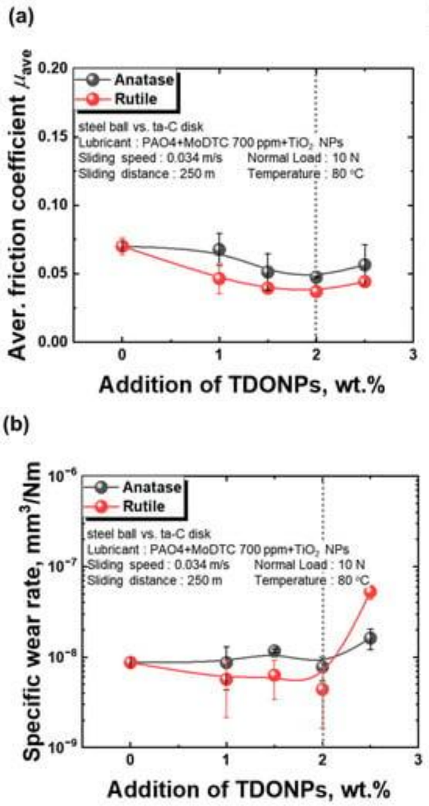

Fig. 1 (a) Friction coefficient for steady-state and (b) specific wear rate of ta-C disk under PAO4 mixed with MoDTC 700 ppm and various addition amounts of TDONPs.

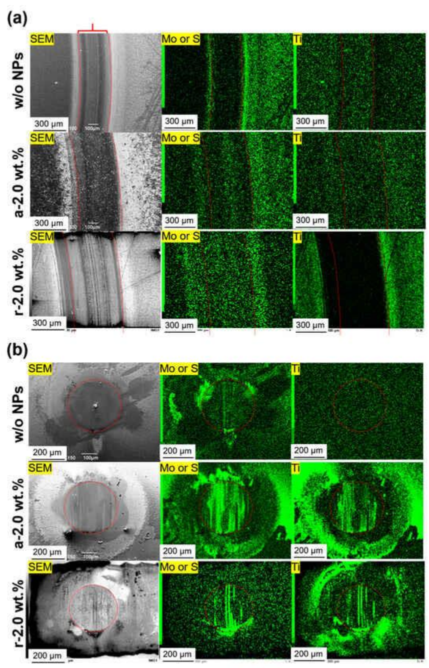

Fig. 2 Images of SEM and EDS mapping on (a) ta-C disk and (b) steel ball.

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