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# The Wear Acceleration of a-C:H coating by Molybdenum-derived Particles

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*Abstract*— **Molybdenum dithiocarbamate (MoDTC) is a prominent friction-modifier in engine oil but has wear accelerating effects on DLC/steel sliding contact. There can be two wear accelerating mechanisms, either MoDTC itself or the Mo-derived compound from MoDTC degradation. However, it has still been unknown. To clarify the effect of MoDTC-degraded materials on DLC, it is necessary to divide which Mo-derived compound has a major role in enhancing wear. Thus, powder-type MoDTC, $MoS_2$, Mo, $MoO_3$, and $Mo_2C$ were dispersed into base oil, and tested on a-C:H DLC against steel ball under boundary lubrication condition at standard engine temperature of 80 ºC. SERS analysis was conducted and proved that $MoO_3$ promotes chemical wear and $Mo_2C$ reacts abrasively to accelerate wear.**

***Keywords— MoDTC; $MoO_3$; $Mo_2C$; a-C:H DLC***

## I. INTRODUCTION

In the recent automotive field in Japan, electric or hybrid type vehicles are the most powerful line-up for customers because of the peoples' awareness toward environmentally friendliness, reduction of harmful chemical waste from an exhaustion gas tubes and low energy consumption. On the other hand, in developing countries still have been continuing to manufacture engine-system included automobiles [1]. Therefore, reducing frictional force and heat at piston rings and liner in an engine cylinder has been still one of the research targets [2]. Several approaches to understand wear acceleration of DLC by lubricant additives [3-15], however, degradation ability of those additives prevents better understanding of wear accelerating ability of itself [4].

Previously, authors reported the effect of degradable materials delivered from MoDTC on wear acceleration of hydrogenated amorphous carbon and silicon doped one [16]. A powder type molybdenum dithiocarbamate (MoDTC) showed higher wear acceleration ability rather than molybdenum trioxide ($MoO_3$) regardless of the hardness of those particles. Of course, $Mo_2C$ which was the highest hardness among pure Mo, $MoO_3$, MoDTC and molybdenum disulphide ($MoS_2$) had a major role to enhance wear because of its hardness such as abrasives in polishing field [17].

MoDTC was reported as an easily degradable compound and has tendency to change it physical and chemical structures. Previous research works presumed that the intermediate products from the degradation of the liquid MoDTC accelerate the DLC wear. Mo-derived compounds such as molybdenum disulphide ($MoS_2$) and molybdenum trioxide ($MoO_3$) are reported to form tribo-layers on hydrogenated DLC and promote chemical wear. The other Mo-derived compound, molybdenum carbide ($Mo_2C$) is revealed to cause an abrasive wear on DLC surface [16, 18-19].

There are a lot of conclusion and assumption being made. However, which Mo compound precisely accelerates the wear; either MoDTC itself or the Mo-derived compounds from the MoDTC degradation has still been unknown. Therefore, it is very essential to identify which Mo-derived compound has a major role to enhance the wear at the real engine condition. Thus, powder-type MoDTC and Mo-derived compounds are used to divide their wear effect on DLC by dispersing each of them into base oil and tested under standard engine temperature of 80 ºC. This paper is focused on the comparison of the wear acceleration mechanism on hydrogenated amorphous carbon (a-C:H DLC).

## II. METHODOLOGY

In this study, Ball-on-disc tribometer as used to analyze the friction and wear behaviour. This type of tribometer simulates the real sliding conditions of many components in automotive engine. It also enables to reach boundary lubrication regime with high contact pressure between the two mating materials. Figure 1 illustrates the whole friction test setup and Fig. 2 shows the Ball-on-disc position during the sliding test.

The upper side mating material was SUJ2 (high-carbon chromium bearing steel) ball with diameter 8.0 mm against a hydrogenated amorphous carbon (a-C:H DLC) disc on the lower side. The DLC was coated on the silicon wafer (Si (100)) substrate by using chemical vapour deposition (CVD) method.

The a-C:H DLC experienced Nano-indentation test (NANOPICS 1000 Elionix ENT-1100a) to determine the coating hardness, which approximately 13.0 GPa. To quantify the roughness, atomic force microscopy, AFM (SPM-9700HT) was used. a-C:H DLC has Ra=1.0 nm roughness, and coating thickness which was approximately 0.5 µm.

The a-C:H DLC was submerged in the mixture of base oil and 5 different particles inside a rotary steel holder fitted with a thermocouple. Base oil Poly-alpha-olefin (PAO) with viscosity 19.0 mm2/s was used in this study. The mixture was heated until 80 °C which imitates the standard engine temperature, in order to identify the oil temperature effect on the DLC wear.

The 5 different particles; MoDTC, $MoS_2$, Mo, $MoO_3$, and $Mo_2C$ have size between 2.0 to 5.0 µm were dispersed into the base oil with 0.1% volume percentage, respectively. Fig. 3 (a) to (e) shows the FESEM images of the particles, following the particles hardness respectively. The particles hardness was as follows; MoDTC (1.0 GPa), $MoS_2$ (1.0 GPa), Mo (1.5 GPa), $MoO_3$ (2.5 GPa), and $Mo_2C$ (15 GPa). All particles were procured from the material supplier, except $MoO_3$. The $MoO_3$ was experimentally synthesized from $MoS_2$ in the laboratory.

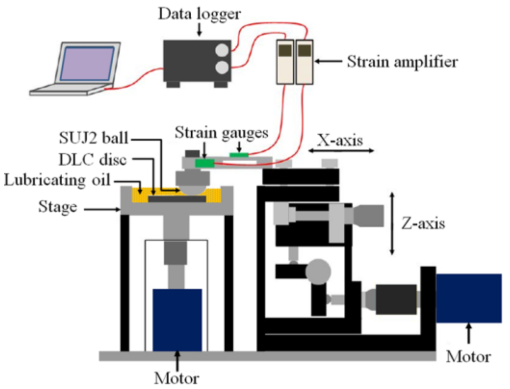


Fig.1 The schematic image of Ball-on-disc tibometer

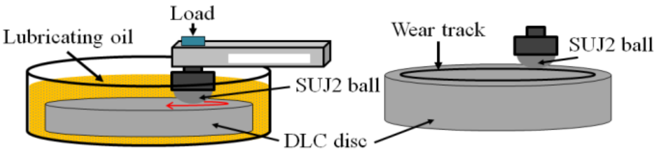


Fig.2 The schematic image of Ball-on-disc tribometer

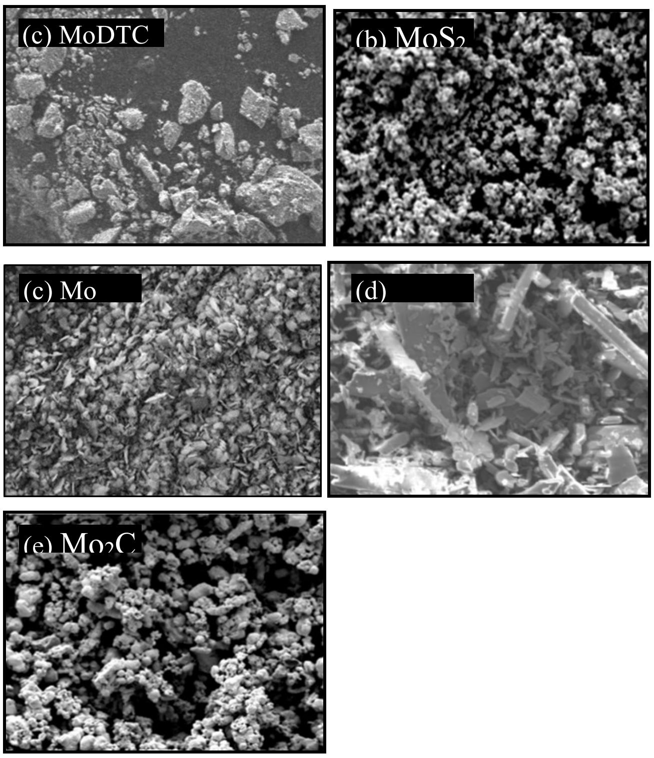


Fig.3 Additive particles images by FESEM

Before starting the friction test, the mixtures of base oil with the 5 different particles were stirred in the ultrasonic bath for one hour to refrain particles settlement and uneven mixture. The test was conducted under an applied load of 1.0 N which corresponds to the maximum initial Hertzian contact pressure of 455 MPa for 1500 cycles in 10 minutes with 0.5 m/s speed at 80°C.

To eliminate oil stains and contaminants, all samples were cleaned with benzene, then acetone in an ultrasonic bath before and after the friction test. The wear of DLC discs was observed by using optical microscope and FE-SEM (JEOL, JSM-7000FK). Then DLC discs were analyzed by Raman spectroscopy (RENISHAW) under 488 nm wavelengths and 0.5 mW output beam within the range of 800-1800 cm-1 to obtain the surface-enhanced Raman scattering (SERS) results.

Since the normal Raman wavelength can penetrate several micrometer depth into the coating surface, the final result could be affected. Therefore, SERS procedure was introduced in order to obtain the topmost surface information only. Experimentally, certain part of the wear track on a-C:H disc were covered by a droplet of gold nanoparticles (AuNP) mixture. The AuNP was then let to dry before underwent the Raman analysis.

## III. Results

### *A. Friction coefficient of a-C:H DLC disc at 80°C*

Figure 4 shows the average friction coefficient results of a-C:H disc against SUJ2 ball with 0.1 vol.% dispersion of the 5 different Mo-derived particles (MoDTC, $MoO_3$, $Mo_2C$, $MoS_2$, and Mo) and one mixed-particles ($MoO_3$, $Mo_2C$, Mo) into PAO base oil, respectively. The average friction coefficient was taken at a steady-state after the running-in period.

From the results, Mo and the mixed-particles showed the most effective particle to increase the friction coefficient to approximately 0.12. $MoO_3$ and $MoS_2$ shared almost the same lowest value at 0.07, approximately. Meanwhile, MoDTC and $Mo_2C$ gave a friction coefficient of nearly 0.09 and 0.11, respectively. However, MoDTC as a well-known friction-modifier was not functioned effectively to maintain the friction coefficient at the lowest level at 80°C.

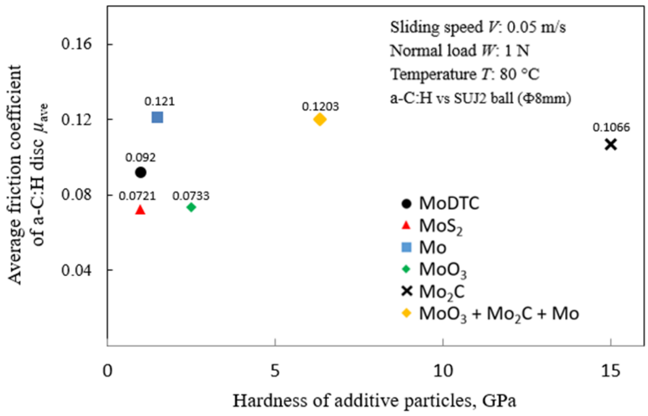


Fig.4 The average friction coefficient of a-C:H DLC

### *B. Optical Microscope and Field Emission Scanning Electron Microscope (FESEM) observation of wear track on a-C:H DLC disc*

After the friction test, the a-C:H discs went through optical microscopic tests and FESEM observations to study the effect of the 5 different particles on wear track, respectively. Mainly, $Mo_2C$ and mixed particles gave severe

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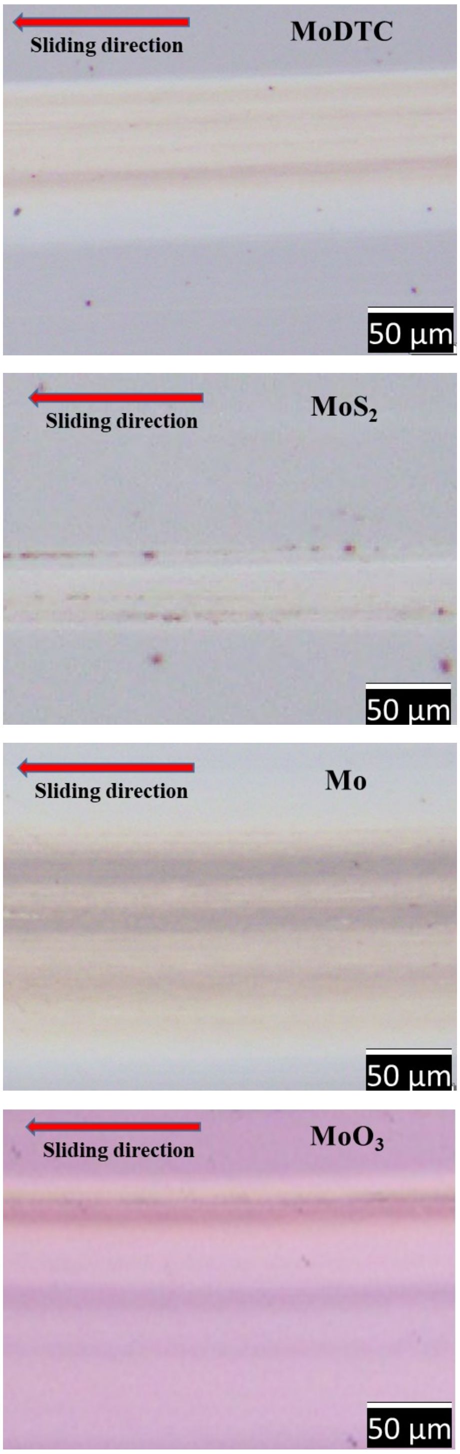
wear effect onto the a-C:H disc. Referring to Fig. 5, $MoO_3$ showed a very smooth surface. This is probably due to the softened surface by graphitization.

Meanwhile, there are severe scratches that took place on the image of $Mo_2C$ caused by the rubbing repetition of hard particles. There are also several coating flakes peeled off from the surface. Meanwhile, a kind of graphitic layer and spalling occurs at the center of the wear track on the image for the mixed particles. Kind of coating flakes and wear debris also visible. MoDTC, $MoS_2$, and Mo shows smooth wear track and no sign of peeling-off take place on the original a-C:H coating.



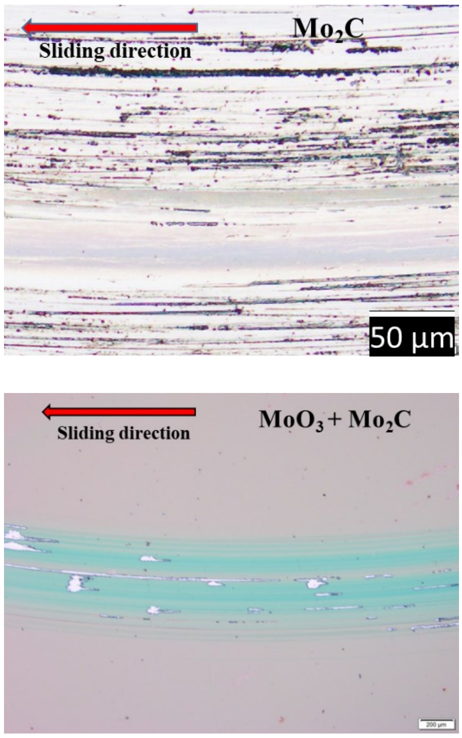




Fig.5 The optical and its enlargement FESEM images of wear track on a-C:H disc

### C. *The specific wear rate of a-C:H DLC disc at 80°C*

Figure 6 shows the specific wear rate of a-C:H discs against the hardness of the additive particles, respectively at 80°C. At first, $MoS_2$, which is prominent as solid lubricant showed the lowest specific wear rate at 2.92 x $10^{-6}$ $mm^3$/N.m. Meanwhile, MoDTC and Mo also showed almost the same low specific wear rate, approximately around 7.86 x $10^{-6}$ $mm^3$/N.m and 8.07 x $10^{-6}$ $mm^3$/N.m respectively. It was probably related to the hardness since their hardness was around 1.0-1.5 GPa. Low hardness did not give significant effect to speed up the specific wear rate, chemically or mechanically at high temperature.

However, the specific wear rate of $MoO_3$ at 25.67 x $10^{-6}$ $mm^3$/N.m was very surprised since it also had a low hardness (2.5 GPa). Therefore, the specific wear rate 3.05 x $10^{-6}$ $mm^3$/N.m at 23°C done by authors in [16] was added for comparison. It revealed that the specific wear rate rose almost 9 times. This increment showed that temperature did give affection to escalate the specific wear rate of $MoO_3$, regardless of the hardness.

On the other hand, the specific wear rate of $Mo_2C$ showed the highest at 58.34 x $10^{-6}$ $mm^3$/N.m. Authors also compared the result at 23°C from [16] which was around 50.03 x $10^{-6}$ $mm^3$/N.m. The increment rate was not so much and initially proved that the abrasive $Mo_2C$ particles had less affection by temperature. For mixed-particles of $MoO_3$, $Mo_2C$, Mo, it displayed a high specific wear rate at 50.12 x $10^{-6}$ $mm^3$/N.m. It was less than $Mo_2C$ but higher than $MoO_3$. This was very interesting to figure-out whether $MoO_3$ or $Mo_2C$ did give a significant effect on this mixture.

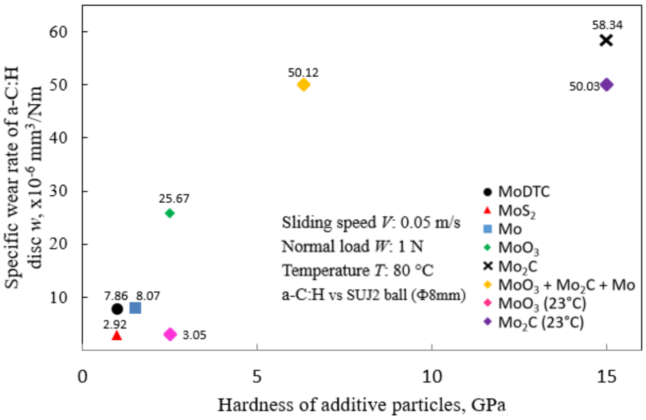



Fig.6 The specific wear rate of a-C:H disc against SUJ2 ball

*D. The surface-enhanced Raman scattering (SERS) analysis of a-C:H DLC disc*

The purpose of conducting surface-enhanced Raman scattering (SERS) instead of normal Raman analysis was to collect the topmost surface data on the a-C:H discs. Since the normal Raman wavelength can penetrate several micrometre depths into the coating surface, it was very critical to precisely measure the graphitization and the structural changes took place on the DLC surfaces.

The fundamental characterization of graphitization is the ID/IG ratio increment and the G-peak position shift. To identify the defect density of DLC surface, the rise of intensity ratio (ID/IG) of the maximum disordered D-peak (ID) intensity to the maximum graphite G-peak (IG) intensity in the Raman spectra was needed [21]. SERS measurement was the best option to give more accurate result. Figure 7 compared the ID/IG ratio of $MoO_3$ for normal Raman analysis and SERS analysis. It showed that SERS analysis had a more significant ID/IG ratio value since it measured at a very shallow area inside the wear track of the a-C:H discs.

Figure 8 shows the $I_D/I_G$ ratio of SERS analysis for all additive particles, respectively. $MoS_2$ and Mo showed a decrement from outside to inside of the wear track. This implied the fact that no graphitization and significant structural changes occurred for both additive particles. Meanwhile, there are a slight increment of $I_D/I_G$ ratio for MoDTC and $Mo_2C$. However, it was too small. It was assumed that no presence of graphitization and the structural changes was mainly caused by the polishing effect from the abrasive $Mo_2C$ particles on the topmost surface of a-C:H disc [16]. The abrasive effect was also proved on the FESEM image in Fig. 5.

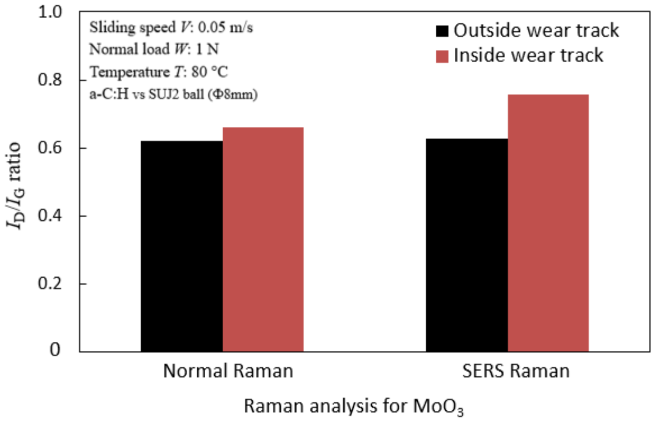



Fig.7 The comparison of $I_D/I_G$ ratio between normal Raman and SERS Raman

The $I_D/I_G$ ratio of $MoO_3$ and mixed-particles was quite attractive as the ratio increased from outside to inside almost at the same trend. A structural defect probably occured due to graphitization according to this phenomenon. Theoretically, graphitization happened when the friction coefficient decreases and lead to the increment of the specific wear rate [22].

Figure 4 and Fig. 6 proved the theory for $MoO_3$ whereby the low friction coefficient resulted to a higher specific wear rate. For mixed-particles, although the friction coefficient and the specific wear rate were quite high, the increment of $I_D/I_G$ ratio and the FESEM image indicated that both $MoO_3$ and $Mo_2C$ particles react thoroughly on the a-C:H disc surface. The particular effect of $MoO_3$ and $Mo_2C$ on the surface were further elaborate in the discussion part.

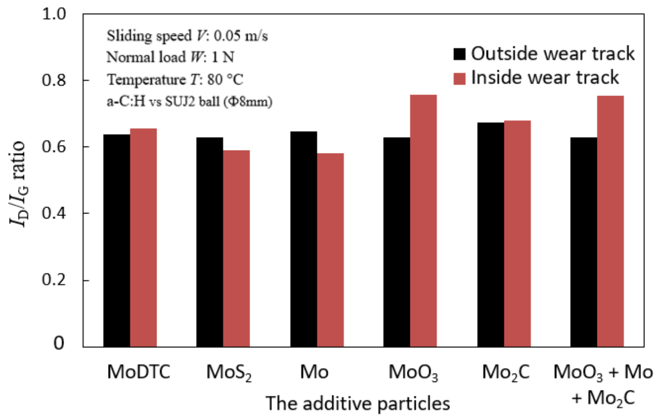



Fig.8 The $I_D/I_G$ ratio inside and outside the wear track of a-C:H disc

## IV. Discussion

The simulation of using 5 different particles at standard engine condition was very important to understand the behaviour of each Mo-derived compound and to identify which compound mainly accelerates the DLC wear. The FESEM images and the SERS analysis result suggests that the structural changes effected by several Mo-derived compounds due to graphitization. Apparently, graphitization was presumed to be occurred due to the evolution of sp2 from sp3 bonding or the development of dangling bonds by the dismantling of C-C or C=C bonds on the contact surface [16]. In general, carbon atoms have a tendency of making π-bond to be thermally stable. Therefore, if carbonaceous coating surface experienced some sort of chemical or mechanical reaction by additives or counterpart material, the topmost surface tend to be graphitic

Based on the SERS results, the ID/IG ratio of $MoO_3$ and mixed-particles had a consequential increment, and thus the graphitization and structural changes occurred. For $MoO_3$, it was assumed the dismantled carbon bonds made a new covalent bonds with oxygen and cause an oxidation wear. Due to the oxidation wear, the DLC surface became soften and cause the specific wear rate to be increased.

For the mixed-particles, the duration of particles entering the contact area was very important to identify the particles effect. The $Mo_2C$ particles entered the contact point and attack the surface statistically. Then, the wear debris dispersed throughout the surface area. Meanwhile $MoO_3$ particles continued to making up covalent bond on the surface area and also on the dispersed debris.

On the other hand, although $Mo_2C$ showed a slight increment of the ID/IG ratio, it was difficult to justify the graphitization. From the FESEM image, the high specific wear rate primarily occurred due to the rubbing repetition of high hardness $Mo_2C$ particles which gradually scratched the DLC surface.

Last but not least, $MoS_2$ which is well-known as a solid lubricant were assumed to form a protective layer on the DLC surface, covering the asperity tips and reducing the wear rate. This statement is also supported by the finding in [23-30], which stated that $MoS_2$ promotes tribofilm formation to give excellent wear resistant ability. Since the research aim is to identify the wear acceleration material from the MoDTC degradation, Mo and $MoS_2$ has not played a role to enhance wear.

## CONCLUSION

In this study, the friction and wear of the hydrogenated DLC against SUJ2 ball under lubrication of Mo-derived particles into base oil under boundary lubrication at high temperature were investigated. It is often presumed that MoDTC degraded into other materials and led to the wear acceleration. Therefore, the usage of 5 different particles; MoDTC, $MoS_2$, $MoO_3$, $Mo_2C$, and, Mo were significant to divide which Mo-derived compound has a significant role in enhancing wear. a-C: were used to analyze the tribological effects.

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