

**Research Paper** 

# Investigation the Effects of Layer Structure on the Tribological Behaviour of PAI Overlays Containing MoS<sub>2</sub>

Takayuki Doi<sup>1</sup>, Kazuki Enomoto<sup>2\*</sup>, Muhammad Nor Sharudin<sup>3</sup>

<sup>1</sup>Division of Materials Science and Engineering, Graduate School of Meijo University, Aichi, Japan
<sup>2</sup>Department of Materials Science and Engineering, Meijo University, Aichi, Japan
<sup>3</sup>Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia
<sup>\*</sup>Email of Corresponding: enomotok@meijo-u.ac.jp
*Received: September 28, 2021; Accepted: November 25, 2021*

#### Abstract

There is demand for the reduction of friction loss under poor lubricating conditions, for higher contact pressure, and a longer lifetime in internal combustion engines. Overlay technology is one of the effective means for reducing friction loss and improving seizure resistance of journal bearings. The present study describes the fundamental tribological behavior under boundary lubrication of a polyamide-imide (PAI) overlay containing molybdenum disulfide (MoS<sub>2</sub>) powder. Specimens with different layer structures for the overlay were prepared, and the effects of the layer structure of the overlays were investigated experimentally. As result, the MoS<sub>2</sub> in the surface overlay layers became highly aligned through a high-speed spin coating process. In the case of the overlays containing MoS<sub>2</sub>, the coefficient of friction became almost constantly with a gradual increase, and this was in contrast to the case of the overlays without MoS<sub>2</sub>.

#### **Keywords**

Tribology, Overlay, Composite, Solid Lubricant

## 1. Introduction

In order to reduce fuel consumption, the downsizing of the internal combustion engines is progressing. In particular, in sliding equipment, there are also calls for the reduction of friction loss under poor lubricating conditions, for higher contact pressure, and a longer lifetime. For example, in actual journal bearings, texturing technology such as micro-grooving [1] and overlay technology such as foamed soft thin films [2] have been applied to the sliding surface to improve initial running-in and seizure resistance. In previous studies, it has been reported that the creation of a micro-scale texture on a sliding metal surface and the squeezing of a solid lubricant such as molybdenum disulfide (MoS<sub>2</sub>) into the fabricated texture are effective means for reducing the friction coefficient and improving seizure resistance [3,4]. On the other hand, in overlay technology, a polymer overlay containing solid lubricants is an effective method for a moderate initial running-in. In our recent research, the application of a subsurface micro-texture fabricated through micro shot peening and a

Takayuki Doi et al., Investigation the Effects of Layer Structure on the Tribological Behaviour of PAI ..., pp. 5-11

multi-layered structure for the overlay was effective for improving the durability of the overlay. There is other related research that is described in the following lines:

Qin et al. [5] investigated the composition, microstructure, mechanical and tribological behaviors of the  $MoS_2$ -Ti composite coatings using the various analytical techniques (XPS, SEM, XRD, TEM, nano-indentation, scratch, and ball-on-disk test). The results showed that doping Ti using the HIPIMS technique enabled  $MoS_2$  coatings to grow in the form of a dense amorphous structure. The crystallization degree of the  $MoS_2$ -Ti composite coatings decreased with the increase of doped titanium content. Ti reacting with O to form titanium oxides in the surface inhibited the oxidation of  $MoS_2$ . The hardness and adhesion of the composite coatings reached their maximum within a certain range of Ti content. The results showed that doped Ti improved the tribological properties of pure  $MoS_2$  coatings in the atmospheric environment.

Renevier et al [6] reported that MoS<sub>2</sub>/Ti composite coatings have given excellent industrial results for a wide range of cutting and forming applications. Moreover, other metal additions such as Cr, W, Mo, and Zr have been studied with varying compositions and substrates. Laboratory test results using microhardness and nanoindentation testing, scratch adhesion testing, pin on disc, and reciprocating friction and wear tests are presented. In this research, structural analysis was carried out using X-ray diffraction, optical microscopy, scanning electron microscopy, and transmission electron microscopy of cross-sections through the coating. They presented further analysis on the MoS<sub>2</sub>/Ti composite coatings and with other metal additions such as chromium, tungsten, or zirconium.

Bülbül et al [7] determined the effect of working pressure and bias voltage on S/Mo ratio,  $MoS_2$ -Ti composite films were deposited on glass wafers by pulsed-dc magnetron sputtering (PMS). The deposition process was performed for nine different test conditions at various levels of target current, working pressure, and substrate voltage using the Taguchi L9(34) experimental method. They observed that the chemical composition of  $MoS_2$ -Ti composite films was significantly affected by sputtering parameters. It was also observed that the S/Mo ratio decreased as the bias voltage increased at a constant working pressure and the S/Mo ratio increased with increasing working pressure at a constant bias voltage.

Zhang et al. [8] studied two cold spray coatings, one pure Cu and the other a Cu– MoS<sub>2</sub> composite coating, for their tribology performance in dry air. It was demonstrated that a small amount of MoS<sub>2</sub> (1.8  $\pm$  0.99 wt%) could significantly decrease the coefficient of friction (CoF) from around 0.7 (Cu coating) to 0.14–0.15. MoS<sub>2</sub> patches on the wear track exhibited a lower local CoF, and the main velocity accommodation mechanism was shearing MoS<sub>2</sub>-containing debris. Even though the coating wear rates were high in the early sliding (8.61–12.8 nm/cycle in penetration depth during the first 100 cycles), slow wear (0.12–0.22 nm/cycle) over the subsequent sliding was observed. It was also found that the presence of MoS<sub>2</sub> helped to achieve the high endurance of the first steady-state CoF. They examined the dynamics of the process, material transfer, and phase transformation using scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Raman spectroscopy. They also developed MoS<sub>2</sub> patches on the wear track and the counterface served as reservoirs to replenish MoS<sub>2</sub> in the contact and became depleted with sliding.

Liu et al. [9] prepared nanoscale coral-like molybdenum disulfide  $(MoS_2)$  via a hydrothermal method. It was first used as a lubricating additive for liquid paraffin (LP), and then, it acted as a catalyst for the photoinduced degradation of waste LP after testing. Many influencing factors (modification, concentration, morphology, and temperature) that can influence the tribological properties and photocatalytic degradation level were investigated. Experimental results and related analyses indicated that modification by cetyltrimethylammonium bromide (CTAB) and a proper synthesis temperature are helpful to decrease the friction coefficient, and organic modification, bigger surface area, narrower bandgap and more rim sites with oxidation activity are advantageous to achieve better LP degradation levels. Therefore, coral-like MoS<sub>2</sub> can serve as both lubricating additive and photocatalyst at different working stages in the full life cycle of LP, which exhibits great potential in developing environment-friendly lubricating systems.

Cai et al. [10] investigated the tribological properties of  $MoS_2/C$  coatings with different carbon contents (44.7–84.3 at. %) deposited by magnetron sputtering were systematically under atmospheric environment. During tribological tests, the coating with the least  $MoS_2$  content exhibited the lowest friction coefficient and wear rate, while the coating with the most  $MoS_2$  showed the worst performance. They applied multiple analytical tools such as SEM, EDS, Raman, XPS, and TEM to understand friction and wear mechanism, to investigate the composition and structure. TEM and SEM characteristics proved that the tribofilm with multilayered structure was formed on the tribopair. The C-rich layer adhered to the tribopair and the top layer was well-ordered  $MoS_2$  tribofilm, and the dominated amorphous  $MoS_2$  was found between the two layers. They suggested that the shear plane was mainly made of well-ordered  $MoS_2$  transfer film, while carbon improved the mechanical properties of the coatings, served as a lubricant, and also inhibited the oxidation of  $MoS_2$ .

Chen et al. [11] prepared a novel hybrid material composed of micro-carbon fiber (CF) and hexagonal  $MoS_2$  nanosheets via a one-step hydrothermal method. The hybrid simultaneously had both lubricating and reinforcing effects to improve friction and wear properties of polyimide (PI). More importantly,  $MoS_2$  nanosheets decorated onto the surface of CF increased the interfacial adhesion between CF and the PI matrix. This enhanced the hardness and thermal stability and was also favorable for transferring stress from the matrix to CF during the friction and wear process. Accordingly, the PI/CF-  $MoS_2$  composite exhibited outstanding tribological properties. Also, its friction coefficient and wear rate were only 0.24 and  $2.01 \times 10-6$  mm3/N m, respectively, which were lower than those of PI, PI/CF, and PI/  $MoS_2$ ; this suggested CF-  $MoS_2$  hybrid was a promising additive for enhancing the tribological properties of polymers.

Meng et al. [12] prepared an experimental investigation on a graphite-  $MoS_2$  coated on GCr15 bearing steel through air spraying and its tribological performances. Its coefficient of friction (COF) and wear scar width (WSW) were also investigated through the MFT-5000 multifunction tribometer and other test equipment. The experimental results showed that the addition of graphite can effectively decrease the COF and narrow the WSW of the  $MoS_2$ . There exists a critical applied load for wearing out the surface with the graphite-  $MoS_2$  coating. Moreover, there exists an optimal rotational speed of 500 rpm to decrease the COF and WSW of the GCr15 steel.

However, the effects of detailed structure, such as film thickness, the volume fraction of  $MoS_2$ , and the alignment of  $MoS_2$ , have yet to be explained.

The present study describes the fundamental tribological behavior under boundary lubrication conditions of a polyamide-imide (PAI) overlay containing molybdenum disulfide ( $MoS_2$ ) powder. Specimens with different layer structures for the overlay were prepared, and the effects of the layer structure of the overlays were investigated experimentally.

Takayuki Doi et al., Investigation the Effects of Layer Structure on the Tribological Behaviour of PAI ..., pp. 5-11

# 2. Methodology

An aluminum cast alloy (AC8A) disc was employed as the metal substrate. The surface texture of the substrate was mainly fabricated using micro shot peening, to improve the adhesion strength between the overlay and the substrate. PAI was employed as the overlay material. PAI overlay and a composite overlay dispersed solid lubricant such as  $MoS_2$  were coated onto the micro-textured surface using a spin coating technique. First, the intermediate layer of PAI was coated onto the textured substrate then the surface layer of PAI or PAI+  $MoS_2$  was coated onto the intermediate layer. It was possible to control the thickness of the overlay layers through the revolution speed of the spin coating. The specimens were baked in an electric furnace after vaporizing the solvent had been vaporized on a hot plate.

The film thickness and surface profile of the surface layer were controlled by polishing using diamond slurry. The total film thickness was 10  $\mu$ m. Figure 1 shows the surface morphology of the non-treated surfaces (NT, Figure 1(a)), textured surfaces (SP, Figure1 (b)), overlay surfaces (OL, Figure 1(c)), and polished surfaces (P, Figure.1 (d)). Four types of specimens with different layer structures were prepared, as shown in Figure 2. The alignment of MoS<sub>2</sub> in the overlay layers was evaluated using wide-angle X-ray diffraction.



Figure.1 Optical microscope images and profiles of the surfaces of the specimens before friction test

Tribological properties were evaluated using a three-ball-on-disc type testing apparatus under lubricating conditions. The mating specimens were balls made of chromium alloy steel (SUJ2). The testing surfaces were flat, 1.5 mm in diameter, and with a mirror finish, and the balls were placed at equal intervals (=120 degrees) on the same circumference. The testing conditions were a sliding speed of 0.25 m/s, an applied load of 200 N (an apparent contact pressure of 40 MPa), a sliding time of 3600 sec. 40 µl of PAO (5 cSt at 313 K) was employed as a lubricant.



Figure 2. Schematics of the prepared overlay structures that were coated onto the micro-textured substrates. (M: Middle layer, S: Surface layer) (a) 2 μm PAI surface layer on 8 μm PAI middle layer (b) 2 μm PAI+ MoS<sub>2</sub> surface layer on 8 μm PAI middle layer (c) 8 μm PAI surface layer on 2 μm PAI middle layer (d) 8 μm PAI+ MoS<sub>2</sub> surface layer on 2 μm PAI middle layer

### 3. Results and discussion

In the case of  $MoS_2$  powder, the strongest diffraction peak that was observed derived from the (002) of  $MoS_2$  at 14.30. Diffraction peaks deriving from the (004) and the (006) were also observed. On the other hand, in the case of the overlay containing  $MoS_2$ , the strongest peak that was observed derived from the (002) of  $MoS_2$ , and another peak was observed at 390. This peak was derived from the (103) of  $MoS_2$ , perpendicular to the (002) of  $MoS_2$ .

In order to compare the alignments of  $MoS_2$ , an intensity ratio  $((I_{(002)})/I_{(103)})$  was calculated. In the case of the thin top PAI+  $MoS_2$  layer, the value of  $(I_{(002)})/I_{(103)}$  was 57.1, which was higher than the value of the thick top PAI+  $MoS_2$  layer (39.1). This result indicates that the  $MoS_2$  in the surface overlay layer became highly aligned through the high-speed spin coating process.

Figure 3 shows the initial friction behavior of the various overlays. In the case of the overlays without  $MoS_2$ , the coefficient of friction increased in the early stages, then became almost constantly with a gradual decrease. However, in the case of the overlays containing  $MoS_2$ , the coefficient of friction became almost constant with a gradual increase. These results indicate that aligned  $MoS_2$  in the surface layers was effective for a moderate running-in. Figure 4 shows optical micrographs of the overlay surfaces without or with  $MoS_2$  after the friction test. In the case of the overlay surface without  $MoS_2$ , some grooves were observed at the center of the friction track in Figure 4(a) and (c). Almost no differences resulting from the thickness of the surface layers were observed. On the other hand, in the case of the overlay surface with  $MoS_2$ , friction tracks were observed on the right side. In Figures 4(b) and (d), the red dots indicate  $MoS_2$  particles on the surface. Before the friction test, many agglomerates of  $MoS_2$  were observed on the surface. After the friction test, however, few agglomerates were observed on the wear track



Figure 3. Friction behavior of the various overlays in the initial running-in



Figure 4. Overlay surfaces without MoS<sub>2</sub> and with MoS<sub>2</sub> after friction test. (a) Thin surface layer without MoS<sub>2</sub> MoS<sub>2</sub> (b) Thin surface layer with MoS<sub>2</sub> (c) Thick surface layer without MoS<sub>2</sub> (d) Thick surface layer with MoS<sub>2</sub> Red dots indicate MoS<sub>2</sub> particles on the surface

## 4. Conclusion

The present study describes the tribological behavior of PAI overlays containing  $MoS_2$  powder. The  $MoS_2$  in the surface overlay layers became highly aligned through a high-speed spin coating process.

In the case of the overlays containing  $MoS_2$ , the coefficient of friction became almost constant with a gradual increase, and this was in contrast to the case of the overlays without  $MoS_2$ .

## 5. References

- [1] Kumada, Y., Hashizume, K. and Kimura, Y. 1998. Performance of Plain Bearings with Circumferential Microgrooves. Japanese Society of Tribologists. 43: 456-461.
- [2] Sonobe, H. 2011. Trend of Plain Bearing Overlays for Diesel Engines, Journal of Japan Institute of Marine Engineering. 46(16):1-10.
- [3] Horiba, Y., Kobayashi, S., Akita, H. and Usami, H. 2013. Friction properties of MoS<sub>2</sub> penetrated aluminum alloy. Proceedings of JAST Tribology Conference.
- [4] Ishihara, J. Enomoto, K. and Usami, H. 2015. Tribological properties of polymer overlay coated on the microtextured metal substrate. Proceedings of Malaysian International Tribology Conference.
- [5] Qin, X., Ke, P., Wang, A., and Kim, K. H. 2013. Microstructure, Mechanical and Tribological Behaviors of MoS<sub>2</sub>-Ti Composite Coatings Deposited by a Hybrid HIPIMS Method. Surface and Coatings Technology. 228 (9):275-281.
- [6] Renevier, N. M., Fox, V. C., Teer, D. G., and Hampshire, J. 2000. Coating Characteristics and Tribological Properties of Sputter-Deposited MoS<sub>2</sub>/Metal Composite Coatings Deposited by Closed Field Unbalanced Magnetron Sputter Ion Plating. Surface and Coatings Technology. 127(1): 24-37.
- [7] Bülbül, F., Efeoğlu, İ., and Arslan, E., 2007. The Effect of Bias Voltage and Working Pressure on S/Mo Ratio at MoS<sub>2</sub>-Ti Composite Films. Applied Surface Science. 253(9): 4415-4419.
- [8] Zhang, Y., Shockley, J. M., Vo, P. and Chromik, R. R. 2016. Tribological Behavior of a Cold-Sprayed Cu- MoS<sub>2</sub> Composite Coating During Dry Sliding Wear. Tribology Letters. 62(1): Article number: 9.
- [9] Liu, L., Huang, Z. B., Peng, Y. T. and Huang, P. 2017. Enhanced Lubrication and Photo-Catalytic Degradation of Liquid Paraffin by Coral-like MoS<sub>2</sub>. New Journal of Chemistry. 41(15): 7674-7680.
- [10] Cai, S., Guo, P., Liu, J. Z., Zhang, D., Ke, P. L., Wang, A. Y., and Zhu, Y. J. 2017. Friction and Wear Mechanism of MoS<sub>2</sub>/C Composite Coatings Under Atmospheric Environment. Tribology Letters. 65(3). Article number: 79.
- [11] Chen, B. Li, X., Jia, Y., Li, X. Yang, J., Yan, F. and Li, C. 2018. MoS<sub>2</sub> nanosheets-decorated carbon fiber hybrid for improving the friction and wear properties of polyimide composite. Composites Part A: Applied Science and Manufacturing. 109: 232-238.
- [12] Meng, F. M., Cui, Z. T., Cheng, Z. T., and Han, H. L. 2018. Experimental Study on Tribological Properties of Graphite-MoS<sub>2</sub> Coating on GCr15. Journal of Tribology. 140(5): 051303.