High Friction Mechanism of ZDDP Tribofilm Based on in situ AFM Observation of Nano-Friction and Adhesion Properties

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Abstract
Zinc dialkyl dithiophosphate (ZDDP) is a typical anti-wear additive that forms tribofilm on sliding surfaces and prevents adhesion wear but increases the friction force. In this study, the nano-friction and adhesion properties of ZDDP tribofilms were investigated by performing in situ observations by atomic force microscopy to explore the relationship between the formation process and physical properties of ZDDP tribofilm. The results showed that the nano-friction force increased with the formation of the ZDDP tribofilm. In addition, the adhesion force on the ZDDP tribofilm increased with the friction force. It was confirmed that the Young's modulus and nanoindentation hardness of the ZDDP tribofilms were lower than those of steel. However, the contact areas calculated using the Derjaguin–Muller–Toporov (DMT) contact theory were similar. In addition, the shear strengths calculated using the DMT model of the ZDDP tribofilm were substantially higher than those of steel.

Keywords
Tribofilm · Zinc dialkyldithiophosphate · Anti-wear additives · Adhesion property · Atomic force microscopy

1 Introduction
Recent environmental issues have emphasized the importance of improving automobile fuel efficiency [1–3]. The use of lower viscosity oils is one way to improve fuel efficiency, which reduces friction in the form of fluid resistance in automotive engines under hydrodynamic lubrication [2]. However, a lower viscosity results in seizure and increased wear under boundary and mixed lubrication conditions. Therefore, lubricants need to be optimized to improve the lubrication performance of sliding elements [3]. Anti-wear additives play essential roles in improving and expanding the lifespans of engine components. A typical anti-wear additive, zinc dialkyl dithiophosphate (ZDDP), is a multifunctional additive essential for lubricants owing to its anti-oxidation, anti-seizure, and anti-wear properties, has been utilized for approximately 80 years [4–6]. ZDDP forms a tribofilm during rubbing to protect the surface by preventing direct metal/metal contact [7]. ZDDP generally forms a rough and patchy film, a so-called pad-like structure, with a thickness of approximately 50–150 nm [4–6]. It was hypothesized that ZDDP tribofilms consist of a bottom layer of iron/zinc sulfide, middle layer of iron/zinc phosphates and polyphosphate, and top layer of mixed oxide and zinc sulfide [4, 7]. The anti-wear action of phosphates/polyphosphate is to wear self-sacrificingly instead of substrates and protect adhesive wear [8].

On the other hand, ZDDP tribofilms also have the disadvantage of increasing friction, although tribofilms have high anti-wear properties [4, 9, 10, 11–18]. The field targeting high friction of ZDDP tribofilm in the mixed lubrication was studied extensively [4, 9, 10, 17, 19]. Zhang et al. and Miklozic et al. reported that the friction coefficient increased when the ZDDP formed a tribofilm. A rolling contact sliding tester (Mini Traction Machine) was used for the study [10, 19]. They further proposed a high friction mechanism related to the formation of a rough ZDDP tribofilm that resulted in the inhibition of the fluid entrainment into the contact area [10, 19]. In addition, Dawczyk et al. measured the roughness of the tribofilms at each time step and the EHD film thickness using a Mini Traction Machine with Spacer Layer Imaging. The prevailing lambda ratio was also determined [9]. The relationship of all the friction versus lambda ratios...
was studied. Further, they indicated that the change in the surface roughness was responsible for the evolution of the friction. Finally, the inhibition of the fluid entrainment into the contact area was confirmed and an increase in friction was observed as the process condition was changed from mixed to boundary lubrication [9].

Meanwhile, under the boundary lubrication, contradictory reports on the friction properties of ZDDP tribofilms were found. Zhang et al. reported the friction reduction by ZDDPs, which have different alkyl chain types [10]. They used a high-frequency reciprocating rig compared to the base oil between steel/steel pair. In addition, Ueda et al. reported the high anti-scuffing effects and the low friction of ZDDP tribofilm for metal/metal direct contacts [20]. The condition incorporating step load tests using the steel/steel pair was employed. In contrast, there are several reports focused on providing ZDDP solutions for high friction under the boundary lubrication category. Morina et al. reported the ZDDP friction using the reciprocating sliding tests and furnished a comparative study with respect to the base oil [15]. Cai et al. reported that the ZDDP between the Si3N4/steel and steel/steel pair provides superior friction properties as compared to those provided by the base oil, for boundary lubrication [12]. In addition, Coga et al. reported the high friction properties in the ZDDP solution for various types of sliding pairs, namely steel/steel, diamond-like carbon (DLC)/DLC, and steel/DLC. They used the sliding conjunctions of a ball on the disk reciprocating sliding tests [21]. Interestingly, they reported high friction in the ZDDP solution for various types of sliding materials on which the ZDDP forms tribofilms. Further, the friction properties were influenced for different physical and chemical properties [22]. These facts imply that the high friction of ZDDP tribofilm is a characteristic property of the ZDDP-self.

Generally, the friction force is influenced by the shear strength and the real area of contact, which are influenced by the sum of the area of each nanoscale junction [23–25]. Therefore, it is important to investigate the nano-friction aspect to propose an accurate friction mechanism. In the case of ZDDP tribofilms, Umer et al. and Ye et al. investigated the nano-friction properties [11, 26]. Ye et al. used the lateral force microscopy for comparing the nano-friction properties of the ZDDP tribofilm with sliding area boundaries [26]. They reported higher friction properties for the ZDDP tribofilm than the steel surface. In addition, Umer et al. reported the friction dependency of the contact pressure, on the steel surface and ZDDP tribofilm, formed by the macro sliding tests [11]. They revealed that the ZDDP tribofilms had high shear strength. Moreover, high shear strength was reported for the ZDDP as compared to the steel surface [11]. These portray the high friction properties (at the nanoscale) of the ZDDP having direct contact. However, the ZDDP tribofilms mechanism developed in Bowden and Taber excludes the consideration of the adhesion properties [24]. At the nanoscale, these properties remarkably influence the shear strength at each contact junction.

The Derjaguin–Muller–Toporov (DMT) model is a theory that describes the contact area generated when the contact surface exerts a high adhesion force [27, 28]. The DMT model is frequently used for materials having hard elastic modulus in the order of GPa. Hence, to explain the friction mechanism of ZDDP, it is necessary to investigate the friction mechanism with a focus on the effects of the adhesion and mechanical properties of ZDDP tribofilms using the DMT model. Therefore, we employed atomic force microscopy (AFM) to observe the friction phenomena dominated by the adhesion properties.

The in situ AFM methods is considered to be one of the most useful techniques for exploring the friction mechanism of the tribofilm formed in lubricants [6, 8, 29–31]. Gogvami et al. succeeded in observing the formation process of ZDDP-derived reaction films in lubricating oil using AFM [6]. They reported that the rate of reaction film formation increased exponentially with increasing temperature and contact pressure [6, 8]. They also made it possible to observe the friction force in the ZDDP solution [31, 32]. In addition, AFM can be used to investigate the physical properties of nanomaterials, such as the adhesion property [32, 33]. Therefore, using AFM, the effects of the adhesion and nano-friction properties of ZDDP tribofilms on nanoscale contacts can be explored and the high friction phenomena of ZDDP on the nanoscale can be explained.

In this study, we investigated the physical properties of ZDDP tribofilm during in situ AFM observation to reveal the friction mechanism of the ZDDP tribofilm. We used the in situ AFM method to measure the physical properties such as the frictional and mechanical properties, as well as the adhesion force between the AFM tip and sliding surface, to analyze the friction mechanism of the ZDDP tribofilm. In addition, we conducted scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) and nanoindentation measurements to investigate the chemical composition, Young’s modulus, and hardness of the ZDDP tribofilm.

2 Experimental

2.1 Lubricants and Materials

Poly-α-olefin 4 (PAO4) and a ZDDP, which has an alkyl structure of secondary C3/C6 mixed, were used as the base oil and lubricant additive, respectively. The viscosity of PAO4 is 2.2 mPa·s at 120 °C [34, 35]. The lubricants were formulated so that the phosphorus content was 0.08 mass%. Bearing steel (AISI 52,100 with a hardness: 700 HV,
arithmetic mean surface roughness $S_a$: 1.4 nm) was used for in situ AFM as the sliding substrate.

### 2.2 In situ AFM Sliding Tests

Fig. 1 shows a schematic of the in situ AFM sliding tests. In situ AFM sliding tests were performed using a commercial AFM system (Nano Navi, Hitachi High-Tech, JP) with a silicon tip (SI-DF20, Hitachi High-Tech, JP) to measure the nano-friction forces in the base oil and ZDDP solution. Subsequently, the tribofilm in the ZDDP solution was formed.

Here, we calculated the normal and torsional spring constants, $k_n$ and $k_t$, using dimensional methods from the following Equations [36, 37]:

\[
k_n = \frac{E_c w T^3}{4 l^3}
\]

\[
k_t = \frac{G_c w T^3}{3 l(h + T/2)^3}
\]

where $E_c$ and $G_c$ are the elastic and shear moduli of the cantilever, respectively; $w$ is the width of the cantilever; $h$ is the height of the cantilever tip; $t$ is the thickness of the cantilever; and $l$ is the length of the cantilever. The cantilever had a tip radius of 140 nm (Fig. S1). Additionally, we obtained the elastic modulus was that of Si (100) [23], and the shear modulus was calculated using the following Equation [23, 38, 39]:

\[
G_c = \frac{E_c}{2(1 + v_c)}
\]

where $v_c$ is Poisson’s ratio of the cantilever. In addition, we set the normal and lateral forces by detecting the normal deflection of the position-sensitive photodetector (PSPD). Therefore, it was necessary to determine the sensitivities of the AFM optical system for normal and lateral deflection, $S_n$ and $S_l$, respectively [37, 40, 41]. The sensitivity of the AFM optical system for the normal deflection was calculated from the gradient of the force–displacement curve (FD curve), and that for lateral deflection was calculated using the following Equations [41]:

\[
S_i = \alpha \frac{h + T}{l} S_n
\]

where $\alpha$ is a unique correction constant used to correct the output ratio between the normal and lateral voltage signals. In this experiment, we calculated the normal and lateral forces, $F_n$ and $F_l$, as follows:

\[
F_n = k_n S_n V_n
\]

\[
F_l = k_l S_l V_l
\]

where $V_n$ and $V_l$ are the photo potentials of the PSPD in the normal and lateral directions, respectively [40–42].

Using Eqs. (2) and (4), Eq. (6) can then be rewritten as
Table 1 shows the normal and torsional spring constants, normal and lateral sensitivity, unique correction constant ($\alpha$), elastic and shear modulus, Poisson’s ratio, and each measurement parameter of the cantilever. To measure the shape of each cantilever, we used 3D laser scanning microscopy (VK-X150, KEYENCE, Japan) and SEM (TM4000, Hitachi High-Tech, Japan).

In situ AFM sliding tests were conducted by imaging of the contact mode until 600 cycles with a normal force of 2000 nN, sliding frequency of 20.0 Hz (sliding velocity: 80.0 µm/s), oil temperature of 120 °C, and an image range of 2.0 µm × 2.0 µm (128 pixels × 128 pixels) by acquiring the lateral voltage signal at an operating angle of 90°. Subsequently, we acquired a height image in a range of 4.0 µm × 4.0 µm (256 pixels × 256 pixels) to confirm the tribofilm growth on a sliding area. A normal force of 800 nN and a sliding frequency of 2.0 Hz (sliding velocity: 8.0 µm/s) were used to acquire the images. The AFM tip started the scanning process from the top left region. It traced and retraced the same line and later moved to the next line. The same procedure was followed for all the lines up to 128-pixel. Finally, the tip returned to the start point as shown in Fig. 1 (b). One AFM image was counted as one cycle. The friction forces of one cycle were averaged using the frictional signals of 16,384 points (128 pixels × 128 pixels). The AFM tip continuously touches the sliding surface. Therefore, the lubrication regime is considered as the boundary lubrication. In addition, the FD curves were obtained for every 50 cycles with an indentation depth of approximately 60 nm and an indentation frequency of 10 Hz using identical cantilevers with in situ AFM sliding tests.

### 2.3 Surface Analysis

An analysis of the surface was conducted on the AFM sliding area using a SEM/EDS (SUPRA40, ZEISS, DE) and nanoindentation system (iMicro, Nanomechanics, US). After performing the in situ AFM sliding tests, all test specimens were cleaned by slowly shaking them in 30 ml of n-hexane for 30 s.

#### 2.3.1 SEM/EDS Analysis

SEM/EDS was conducted to investigate the chemical composition of the rubbed surface at 0 (outside), 200, 400, and 600 cycles by in situ AFM sliding tests under an accelerating voltage of 5 keV. Additionally, the rubbed samples obtained following 0, 200, 400, and 600 cycles were prepared using an identical cantilever at different locations on the same steel substrates in 2.0 µm × 2.0 µm regions while maintaining the exact conditions existing during the in situ AFM sliding tests. The 0-cycle sample was not rubbed by the AFM cantilever. In addition, EDS spectra of the 2.0 µm × 2.0 µm regions were recorded to obtain the EDS spectrum of the entire sliding surface. The atomic concentrations in the sliding areas from each EDS spectrum were calculated using the ZAF correction method [43].

#### 2.3.2 Nanoindentation Measurement

Continuous stiffness measurements (CSMs) were performed to measure the Young’s modulus and nanoindentation hardness of the tribofilm at an indentation depth of 100 nm with constant strain rate of 0.2 s⁻¹ [44]. The CSM method has the advantage of continuously determining the Young's modulus and hardness to the indentation depth. The principle of the CSM method is to determine the stiffness from the

\[
F_i = \alpha \frac{G_w T^3}{3h^2} \left( h + \frac{T}{2} \right) S_n V_i
\]  

(7)

Table 1 Each parameter of AFM system and the cantilevers using the AFM measurement in PAO4 and ZDDP solution

| Parameter                          | PAO4   | ZDDP   |
|-----------------------------------|--------|--------|
| Length, $l$                       | 231.6 µm | 232.1 µm |
| Width, $w$                        | 30.1 µm | 31.1 µm |
| Thickness, $t$                    | 4.6 µm  | 4.5 µm  |
| Height of the tip, $h$             | 10.5 µm | 12.5 µm |
| Elastic modulus, $E_c$            | 130 GPa | 130 GPa |
| Shear modulus, $G_c$              | 50 GPa  | 50 GPa  |
| Poisson’s ratio, $\nu$            | 0.28    | 0.28    |
| Normal spring constant, $k_n$     | 7.5 N/m | 7.4 N/m |
| Torsional spring constant, $k_t$  | 1293.6 N/m | 942.5 N/m |
| Sensitivity of AFM optical system (normal), $S_n$ | 77.8 nm/V | 82.7 nm/V |
| Sensitivity of AFM optical system (lateral), $S_l$ | 1.72 nm/V | 2.10 nm/V |
| Unique correction constant of AFM, $\alpha$ | 0.4 | 0.4 |
oscillatory component of the displacement and the phase difference between the load and displacement, which is done by applying a small AC load to the DC component of the indentation load change with a constant strain rate [44]. The stiffness $S$, which for an elastic contact is given by the ratio of the load amplitude to the depth amplitude can therefore be calculated continuously during the loading cycle by the following Equation:

$$S = \frac{\Delta P}{\Delta h}$$  \hspace{1cm} (8)

where $\Delta P$ is the ratio of peak-to-peak load amplitude on the indenter and $\Delta h$ is the peak-to-peak depth amplitude of the indenter. The nanoindentation hardness was obtained by the following Equation:

$$H = \frac{P}{A_c}$$  \hspace{1cm} (9)

where $A_c$ is the projected contact area. $A_c$ is investigated by tip corrections, which were performed to prevent errors due to the geometry of the contact area by making the area function of the nanoindentation [45]. Preliminary indents were performed 25 times on fused silica (Young’s modulus: 72.5 GPa, hardness: 9.5 GPa) to characterize the tip defect of the Berkovich.

The Young’s modulus was calculated using following Equations:

$$E^* = \frac{S}{2} \sqrt{\frac{\pi}{A_c}}$$  \hspace{1cm} (10)

$$\frac{1}{E^*} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i}$$  \hspace{1cm} (11)

where $E^*$ is the apparent reduced modulus, and $E_s$, $\nu_s$, $E_i$ and $\nu_i$ are the Young’s modulus and the Poisson’s ratio for the sample (s) and indenter (i). The Young’s modulus was calculated assuming that the mechanical properties on the surface were uniform, and the Poisson’s ratio for each sample ($\nu_s$) was assumed to be 0.3. A diamond Berkovich tip (Young’s modulus of diamond $E_i = 1140$ GPa, Poisson’s ratio of diamond $\nu_i = 0.07$, nominal tip radius $\leq 20$ nm) was used for the nanoindentation measurements. The small superimposed displacement had an amplitude of 2.0 nm at a frequency of 110 Hz. AFM observations were used to obtain topographic information regarding the existence of pile-up around the indents. Five indents have been performed for each sample at different locations on the steel and tribofilm.

3 Results

3.1 In situ AFM Sliding Tests

Fig. 2 shows the friction behavior acquired using the in situ AFM sliding tests. The friction force for each cycle is averaged from 16,384 points (128 × 128) situated on a sliding area of 2 µm × 2 µm. As shown in Fig. 2(a), the base oil exhibited a constant friction force of approximately 70 nN up to 350 cycles, whereafter the friction force decreased gradually to 55 nN at 600 cycles. However, as shown in Fig. 2(b), the friction force in the ZDDP solution gradually increased with sliding until 300 cycles. After 300 cycles, the friction force became stable with a high friction force. The friction force was measured to be 116 nN at 600 cycles. From these results, we found that ZDDP also increased the friction force on nanoscale contacts.

![Fig. 2](image-url) Friction behavior lubricated in a base oil and b ZDDP solution by in situ AFM sliding tests
where $h_0$ and $h$ are the tribofilm heights at the 0 cycle and at any time $t$ of the in situ AFM sliding test, respectively. $n$ is the reaction order, while $K$ is the reaction constant. At the 0 cycle, the tribofilm height can be taken as zero. Later, the tribofilm growth ($1/h^{n-1}$) was linearly fitted as the function of sliding cycles as shown in Fig. S8. Eventually, we can obtain $n = 0.26$ and $K = 0.081$ nm/cycle. This reaction order and the reaction constant are similar to other previous reports [6, 8].

Figure 3 shows AFM images of the sliding area rubbed in base oil at 0 and 600 cycles. These results show that there was no wear on the sliding steel surface. Figure 4 shows AFM images from 0 to 600 cycles in ZDDP solution. These images reveal that tribofilm was formed on the sliding area in ZDDP solution. Figure 5 shows the thickness of the tribofilm formed in ZDDP solution as the number of sliding cycles increased. The thickness of the tribofilm increased rapidly up to 500 cycles. Subsequently, constant thickness of approximately 100 nm was reported for next 600 cycles. Evidently, the tribofilm formed in ZDDP solution grew by sliding between AFM tip and steel.

Next, for investigating the order of the ZDDP reaction to form tribofilms on the sliding surfaces, a power law was fitted as described by the following equation:

$$\frac{1}{h^{n-1}} = \frac{1}{h_0^{n-1}} - (n - 1)Kt$$

(12)

where $h_0$ and $h$ are the tribofilm heights at the 0 cycle and at any time $t$ of the in situ AFM sliding test, respectively. $n$ is the reaction order, while $K$ is the reaction constant. At the 0 cycle, the tribofilm height can be taken as zero. Later, the tribofilm growth ($1/h^{n-1}$) was linearly fitted as the function of sliding cycles as shown in Fig. S8. Eventually, we can obtain $n = 0.26$ and $K = 0.081$ nm/cycle. This reaction order and the reaction constant are similar to other previous reports [6, 8].
3.2 Measurement of Adhesion Property

Figure 6 shows the FD curves obtained using base oil and ZDDP solution at 0 and 600 cycles. From Fig. 6, we confirmed the adhesion forces generated in base oil and ZDDP solution. Therefore, we found that it is possible to evaluate the adhesion properties in lubricants at high temperatures. The magnitudes of the adhesion forces in base oil at 0 and 600 cycles were 2.5 and 3.1 nN, while those in the ZDDP solution were 1.7 and 14.0 nN, respectively. In other words, the adhesion force in base oil remained similar throughout 600 cycles. In contrast, the adhesive force in the ZDDP solution during the 600 cycles was approximately eight times higher than that at 0 cycles.

Figure 7 shows the adhesion force on the sliding area in base oil and ZDDP solution as a function of the number of sliding cycles. In the case of base oil, the adhesion force remained constant until 600 cycles. In contrast, the adhesion force in ZDDP solution increased with the number of sliding cycles. Therefore, from Fig. 4 and Fig. 7, we found that the adhesion force increased with the growth of the tribofilm formed in the ZDDP solution.

3.3 SEM/EDS Analysis

To analyze the chemical composition of the tribofilm formed by ZDDP, we conducted SEM/EDS analysis the surfaces on the steel sample rubbed at 0 (outside), 200, 400, and 600 cycles present. Figure 8 shows the SEM images and EDS profiles obtained after 0, 200, and 600 cycles (see Fig. S4 for the SEM image and EDS profile at 400 cycles). The SEM images show that a tribofilm was formed on each sliding area at 200 and 600 cycles and that the amount of the tribofilm increased with the number of sliding cycles, similar to the AFM results. Additionally, from the EDS profile, we confirmed the peaks of Zn, P, and S at 200 and 600 cycles. These findings demonstrate that the tribofilm was composed of ZDDP-derived elements. In contrast, the peaks of Zn, P, and S at 0 cycles, which is on no sliding area, were relatively low.
Figure 9 shows the atomic concentrations of Zn, P, and S at 0–600 cycles. EDS spectra are known to contain information on elements situated deeper the surface for substrates (approximately 1 μm) [6]. It is difficult to describe the atomic concentration simply. However, these results indicate that the atomic concentrations of Zn, P, and S increased monotonically up to 600 cycles. Evidently, the tribofilm grew monotonically due to the reaction of ZDDP, which was also observed by in situ AFM.

### 3.4 Nanoindentation Measurement

Nanoindentation tests were conducted to examine the Young’s modulus and hardness of the ZDDP tribofilm...
formed by performing in situ AFM sliding tests. The pile-up of the indents on the ZDDP tribofilm was not confirmed shown in Fig. S5. Figure 10 shows the results of the nanoindentation tests on the steel and ZDDP tribofilm. The results show that the Young’s modulus and nanoindentation hardness of the ZDDP tribofilm was lower than those of the steel surface, regardless of the indentation depth. The Young’s modulus and the nanoindentation hardness of steel/ZDDP tribofilm were measured to be 183 GPa/159 GPa, and 8.11 GPa/6.46 GPa, respectively, at an indentation depth of 10 nm.

4 Discussion

4.1 Nature of the ZDDP Tribofilm Formed by in situ AFM

We confirmed that the shape of the tribofilm was rough (Figs. 4 and 8). In addition, the ZDDP thickness was approximately 100 nm. Later, a ZDDP tribofilm with a constant thickness was obtained (Fig. 5). The ZDDP forms a tribofilm of specific shape which is known as the pad-like structure at the thickness of 50–150 nm, on a macroscale sliding test [4, 6, 8]. Gosvami et al. reported that the ZDDP forms a rough tribofilm of 30–40 nm thickness, using the in situ AFM [6]. Dorgham et al. also demonstrated that the ZDDP formed rough tribofilm. Here, the tribofilm thickness was changed from 30–300 nm using the contact pressure [8]. Therefore, the topography of the ZDDP tribofilm and its thickness are consistent with our results.

Additionally, Dorgham et al. confirmed a drastic change in the topography due to the increasing thickness of the ZDDP tribofilm. They conducted novel creep and squeeze flow measurements also. The study was conducted by considering the cause of the topography changes in the ZDDP tribofilm to be its viscoelastic property [46]. However, in our experiments, the drastic change in the topography was not reported. In our experiments, we chose a high vertical load as compared to Dorgham et al. In contrast, Gosvami et al. also reported that the mechanical properties of the ZDDP tribofilm were influenced by the contact pressure. Using the macroscale sliding tests, numerous studies reported the nanoindentation hardness of the ZDDP tribofilms (formed by the macrofriction tests) to be within the range of 1 to 10 GPa. Moreover, significant variations were observed for various sliding conditions [47–51]. In addition, Nehme et al. measured the nanoindentation hardnesses of tribofilms formed at higher and lower contact loads and showed that a higher contact pressure causes the formation of harder and thicker tribofilms in fully formulated oil containing ZDDP [49]. Therefore, we considered that the variation in mechanical properties of the ZDDP tribofilm was caused by the differences in contact load during the sliding test. Meanwhile, most of these studies showed that the Young’s modulus and nanoindentation hardness of the ZDDP tribofilms are softer than those of steel surfaces [47, 48]. This tendency was confirmed on our experiments.

Subsequently, from Fig. 8, the ZDDP tribofilm was composed of Zn, P, and S as well as many previous studies [4]. ZDDP is also known to form Fe/Zn sulfide and phosphates during sliding [4, 6, 8]. These reports suggests that ZDDP also formed a tribofilm composed of sulfide and phosphates during the sliding cycles using in situ AFM. The growth behavior of the ZDDP tribofilm can be fitted using a power law equation from 50 to 500 cycles, and the reaction $n$ was calculated as 0.26. Gosvami et al. reported that the ZDDP growth behavior of the FeO sputter film on the Si wafer had low and fast growth steps. In addition, the reaction order on the faster formation step was approximately 0.2. Dorghela

![Fig. 10](image-url) Young’s modulus and nano indentation hardness of steel and sliding surface lubricated in ZDDP solution
et al. reported that the reaction order was approximately 0.07 to 0.22. The reaction order relates to different aspects. For example, a dependency on the ZDDP concentration, the change of the reactants, and the reactivity of ZDDP can be associated to the reaction order. Gosvami et al. and Dorgal et al. reported that the fraction order of the reaction relates to the multi-reaction phase because the growth rates were changing with the sliding cycles. Generally, the ZDDP has a gradation structure for various types of tribo-layers [6, 8]. This reaction order (as the fraction values) suggests the formation of the ZDDP tribofilm as the gradational structure, including the nano and macro sliding ZDDP tribofilm formation [4, 6, 8].

### 4.2 High Friction Mechanism of the ZDDP Tribofilm Using in situ AFM

The friction force and adhesion properties of the initial sliding cycle was lower than that at 600 cycles according to Figs. 2, 6 and 7. Therefore, it is considered that the adhesion property of ZDDP tribofilm is responsible for the increase in the friction force. Figure 11 confirms the correlation between the adhesion force and nano-friction force. Oblak and Kalin investigated the macroscopic friction and adhesion properties of tribofilms formed on steel and diamond-like carbon coatings and suggested that the adhesion property was directly correlated with the macroscopic friction on each tribofilm [36]. Therefore, we have hypothesis that the friction force in ZDDP solution dominated by the adhesion. Therefore, we have conducted the identification of influence of adhesion.

#### 4.2.1 Assumption of Contact Area on ZDDP Tribofilm

To calculate the contact area of the sliding AFM tip, we first calculated the maximum contact pressure from the nanoindentation results at an indentation depth of 10 nm. The DMT model was used because of the high adhesion exhibited by the ZDDP tribofilm [27, 28]. Here, we assumed that the AFM tip is a spherical, the contact area is circular, and the ZDDP tribofilm is a uniform single layer. The DMT model enables to calculate the surface energy using the following Equations [27, 28]:

$$ W_{ad} = -2\pi \gamma R $$  \hfill (13)

$$ p_{max} = \frac{3W}{2\pi a^2} $$  \hfill (14)

$$ a^3 = \frac{R}{K}(W + 2\pi R') $$  \hfill (15)

$$ \frac{1}{K} = \frac{4}{3} \left( \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_c^2}{E_c} \right) $$  \hfill (16)

$$ \frac{1}{R'} = \frac{1}{R_s} + \frac{1}{R_c} $$  \hfill (17)

where $W$ is the normal load (2000 nN); $K$, and $R$ are the combined Young’s modulus and reduced radius of curvature between the AFM tip and sample, and $R_s$ and $R_c$ are the radii of the sample and the cantilever, respectively. The sample was assumed to be flat ($R_s = \infty$) and the Poisson’s ratio of steel and the ZDDP tribofilm $\nu_s$ was assumed to be 0.3 [47].

Figure 12 shows each calculated surface energy and contact area on steel and the ZDDP tribofilm. From Fig. 12(a), we confirmed that the surface energy on the tribofilm was higher than that on steel. The calculated maximum contact pressures on the steel and ZDDP tribofilm with the AFM tip were 3.50 GPa and 3.37 GPa, respectively. These values are much lower than the measured nanoindentation hardnesses, which were 8.11 GPa and 6.46 GPa for the steel and ZDDP tribofilm, respectively. These calculated results suggest that the deformation between the AFM tip and the sliding surface is elastic. Consequently, we calculated the contact area $\pi a^2$ solely from the DMT model.

Figure 12(b) shows the contact areas of the steel and ZDDP tribofilm using the DMT model. From these results, we confirmed that the values of the contact area were
remarkably similar between the steel and ZDDP tribofilm. Therefore, we assumed that the main cause of the high friction of the ZDDP tribofilm was not the increase in the contact area.

4.2.2 Assumption of Shear Strength on ZDDP Tribofilm

The friction force consisted of adhesin, plowing, hysteresis and viscous contribution on sliding area. Therefore, friction force \( F_l \) is expressed using the following Equation [52]:

\[
F_l = F_a + F_p + F_h + F_v
\]

(18)

where \( F_a, F_p, F_h, \) and \( F_v \) are friction forces from adhesion, plowing, hysteresis and viscous contributions, respectively. From the previous reports, it is known that the ZDDP tribofilms have a viscous top layer composed of the alkyl chains of ZDDP molecules [4, 46]. In addition, Dorgham et al. investigated the viscoelastic properties of the ZDDP tribofilm using two novel measurements considering creep and squeeze flow, against the ZDDP tribofilm formed by the in situ AFM. Their investigation helped addressing the viscoelastic behavior of the ZDDP tribofilm as a new triboreactive phenomenon. Therefore, it is important to consider the contribution of the viscous and viscoelastic properties. These properties are estimated by hysteresis and viscous friction on the ZDDP friction properties of our in situ AFM results. We confirmed no velocity-dependence of the friction force on the ZDDP tribofilms. On the contrary, the viscous or viscoelastic properties depended on the sliding velocities (see Fig. S6). In addition, plowing friction occurs during the plastic deformation. However, the deformation was found to be within the elastic region as per our friction measurements, when using the in situ AFM.

Moreover, Oblak and Kalin investigated the macroscopic friction and adhesion properties of tribofilms formed on steel and diamond-like carbon coatings and suggested that the adhesion property was directly correlated with the macroscopic friction on each tribofilm [36]. In our experiment, the scale of the sliding tests is not similar. However, the tendency of the adhesion properties is found to be identical. Therefore, the adhesion properties of the ZDDP tribofilm is considered to be contributing to the friction force. In addition, Tomala et al. also reported that the formation of ZDDP increases the adhesion force to approximately 20 nN [53]. In contrast, Gosvami et al. reported that the adhesion is relatively low in ZDDP solution. The DLC-coated cantilever was used as it offers low surface energy [54]. These reports support our results that the high adhesion property of ZDDP tribofilms cause the increased friction in our experiments. Therefore, we ignored the plowing, hysteresis and viscous friction and considered that the friction force was dominated by adhesive friction.

\[
F_l = F_a = \tau A_r
\]

(19)

where \( \tau \) and \( A_r \) are the shear strength and contact area, respectively. Therefore, to identify the effects of high friction by the ZDDP tribofilm, we examined the shear strength of the ZDDP tribofilm.

Figure 13 shows the shear strength of the steel and ZDDP tribofilm after 600 cycles. We confirmed that there was a significant difference in shear strength between the steel and ZDDP tribofilm. Therefore, we assumed that the increase in friction force by the ZDDP tribofilm was caused by the
increase in shear strength on nanoscale contacts by the increase in adhesion on the ZDDP tribofilms.

Using the macroscale sliding tests, Zhang et al. reported the friction reduction by the ZDDPs, which have different alkyl chain types. The results were obtained using a high-frequency reciprocating rig compared to the base oil for steel/steel pair under the boundary lubrication category. In contrast, Morina et al., Cai et al., and Coga et al. reported high friction properties for the ZDDP, despite the protection of surface wear by limiting the metal/metal direct contacts [12, 15, 21]. Generally, the metal/metal friction is much higher, as reported by Bowden and Tayber [24]. Therefore, we consider that the existence of iron oxide, whose reactivity is lower than that of the nascent steel surface, decreases the friction.

The steel surface was mainly covered by iron oxides measuring approximately 20 nm thick [24, 55]. The wear was not confirmed with our in situ AFM sliding tests. In previous research, Umer et al. also reported that the nano-friction of the ZDDP tribofilm formed by the macro sliding test is higher than the no-worn steel surface [11]. Their nano-friction measurements on steel were conducted between silicon tip and iron oxides. Their findings are consistent with our experimental results. In addition, high friction of the ZDDP tribofilms is confirmed at the macroscale [12, 21], regardless of the sliding pair. For example, the DLC/DLC and Si3N4/steel pairs. The DLC is known to be possessing chemically inert properties [54]. In addition, the Si3N4 is known to be chemically stable as compared to steel [56]. Therefore, in the case of low reactive sliding material, the ZDDP is considered to increase friction by the influence of the high surface energy of the ZDDP tribofilm. In contrast, Gosvami et al. reported that the formation of the ZDDP tribofilm leads to low friction for the steel/steel pair using a multi-contact in situ AFM [31]. In their study, the nascent steel surface was exposed. Moreover, there was high friction between the metal/metal contacts because of the worn steel AFM tip.

4.3 Difference Between Macro- and Nano-friction Property

In our experiments, the friction coefficient after 600 cycles for the base oil and the ZDDP solution were approximately 0.03 and 0.06, respectively. These coefficients are significantly lower than those observed at the macroscale (approximately 0.10 to 0.20), corresponding to the boundary-to-mixed lubrication conditions [4, 10–17]. The diplomacy with the macroscale sliding tests is also related to the differences in the contact pressure. Umer et al. reported that the shear strength of the ZDDP tribofilm formed by fully formulated oil, changed with the increase in contact pressure. Their relationship described in [11] is as follows:

$$\tau = \tau_0 + \zeta p$$  \hspace{1cm} (20)

where $\zeta$ is the pressure coefficient of the boundary shear strength of the surface asperities, $\tau_0$ and $p$ are the shear strength at zero contact pressure, and the contact pressure, respectively. In addition, they reported that the pressure coefficient $\zeta$ of steel and ZDDP tribofilm are 0.23 and 0.29 in each lubricant, respectively [11]. From these results, high dependency of the shear strength on the pressure is observed. Further, during the macroscale sliding tests, the contact pressure at single asperity reaches the plastic flow pressure. Moreover, high contact pressures as compared to our results are reported. In other words, at the real contact areas, wear of the sliding surface proceeds with the sliding cycles. Moreover, the neat surfaces are exposed, while the metal and metal direct contact causes high friction because of high adhesion. Therefore, we considered that the dependency of shear strength on the contact pressure increases friction at the macroscale. In addition, it is considered that the steel surface offers low friction when the nascent steel surfaces are not covered with iron oxide.

Finally, based on the difference between macro- and nano-friction, it would be difficult to conclude that our nano-friction results have no relationship with macrofriction. The sliding surface experiences surface wear. Subsequently, less wear is observed as compared to the initial cycle. Further, the sliding surfaces are known to react with the dissolved oxygen and form an iron oxide layer on the sliding surfaces [55, 57]. In these cases, we considered that the ZDDP tribofilm could increase friction compared to the steel surface because of the high surface energy of the ZDDP tribofilm. On the basis...
of the above discussion, we conclude that the high friction of the ZDDP tribofilms is highly influenced by the adhesion properties.

5 Conclusions

We conducted an in situ AFM sliding test, SEM/EDS analysis, and nanoindentation measurements to explain the friction mechanism of ZDDP. The following conclusions were drawn:

- From the in situ AFM sliding test, we confirmed that the friction in the ZDDP solution increased with increasing tribofilm growth. The SEM/EDS analysis confirmed that the chemical composition of the tribofilm formed by in situ AFM sliding tests included Zn, P, and S. These results indicate that the formation of the ZDDP tribofilm caused high friction in the ZDDP solution on nanoscale contacts.
- We confirmed that the adhesion force increased with the ZDDP tribofilm growth from the FD curves in the ZDDP solution. This result indicates that the ZDDP tribofilm has a high adhesion property.
- We confirmed from the nanoindentation results that the Young’s modulus and nanoindentation hardness of the ZDDP tribofilm were lower than those of the steel surface. However, the contact areas calculated using the Hertz contact theory were similar. We therefore assumed that the influence of the contact area on the friction property was low in our experiments.
- We confirmed the relationship between the adhesion and nano-friction force and found a correlation. In addition, the shear strength of the ZDDP tribofilm calculated using the Hertz model was substantially higher than that of steel. These results suggest that the high adhesion force of the ZDDP tribofilm contributes to the high friction.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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